

RECEIVED MAY 21 1963

MASTER

MATERIALS REQUIREMENTS FOR THERMIONIC ENERGY CONVERSION

by

R.C. Allen  
C.H. Skeen

Atomics International

A Division of North American Aviation, Inc.  
P.O. Box 309 Canoga Park, California

Conf - 59-2

CONF - 5

WITHDRAWN

I. INTRODUCTION

Thermionic energy conversion is the conversion of thermal energy directly to electrical energy by the emission of electrons from a heated surface, the subsequent collection on a cooler surface and the return of the electrons to the emitting surface through an external load. This form of direct energy conversion is now being developed for both military and civilian applications. Thermionic converters for use with solar energy are planned as small power sources for some space missions. Radioisotope heat sources are also being developed for use with thermionic converters for small power requirements. The real potential of nuclear energy in conjunction with thermionics, however, lies in the nuclear thermionic reactor system. Here the lack of moving parts, the high heat rejection temperature and the potential high power density result in a power-to-weight ratio that is significantly greater than other power sources and thus is very attractive for the space program. Compactness and silence are also important features of this system. A considerable amount of research is currently being directed toward this goal. Another important heat source is fossil fuel. Flame-fired thermionic converters are being developed for small, silent, light weight and portable power sources for special military applications. Eventually thermionic converters fueled with

ORINS LIBRARY  
DADDER AVENUE  
WITHDRAWN

## **DISCLAIMER**

**This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.**

## **DISCLAIMER**

**Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.**

natural or bottled gas may be significant for certain civilian power requirements.

In order to make thermionic energy conversion attractive as a practical source of electricity, the materials involved in both the converter and heat source must operate at extremely high temperature, up to the range of 1200-1800°C (2200-3300°F). Furthermore, and this is the main cause for the difficult and pressing materials problems, in most cases the materials must operate and remain stable at these temperatures for several thousand hours. There are, therefore, many materials problems associated with the development of thermionic energy conversion. These involve the basic components of thermionic converters, the heat sources, and the coupling of the converter to the heat source. It is the purpose of this paper to review in a broad sense these materials problems. Their significance, however, can be appreciated only with a knowledge of some of the fundamentals of thermionic energy conversion and its potential applications. The next two sections of this paper are concerned with these areas. The specific materials problems are then discussed.

## II. FUNDAMENTALS OF THERMIONIC ENERGY CONVERSION

A thermionic converter is a system in which thermal energy is converted directly into electrical energy. In Figure 1 the essential features of a thermionic converter are shown. The components important to the processes of thermionic energy conversion are the emitter, collector, interelectrode gas, the insulators, the electrical leads and support structures. An emitter is heated to a temperature high enough to cause emission (boiling off) of electrons. These electrons cross an interelectrode space to a collector where their electron potential energy is higher. An external load provides a path

by which these electrons can do useful work while returning to the emitter.

The potential energy diagram for an idealized converter is shown in Figure 2. The quantities are negative electrical potentials or electron potentials. The emitter and collector work functions are  $\phi_e$  and  $\phi_c$  respectively.  $V_o$  is the output voltage across both the leads,  $V_w$ , and the load,  $V$ , and  $e$  is the electronic charge. The work function is the difference in energy of an electron inside and outside of the metal. The lower the work function, the higher the emitted current is for a given emitter temperature. Also, the difference between the emitter and collector work function is related to the output voltage.

By definition the thermionic energy conversion efficiency is the ratio of the useful power delivered to the external load to the power input to the emitter. An expression for this efficiency has been worked out in varying degrees of completeness by several authors<sup>1-11</sup> under the basic assumption that space charge effects can be ignored. The expressions made by Richardson<sup>10</sup> and Stanatham<sup>11</sup> are the most complete in that explicit account is taken of Joulean heating losses in the plasma, thermal conductivity losses through the plasma and back-emission of electrons from the collector. However, the review presented here follows those of Rasor<sup>8</sup> and Schock<sup>9</sup> more closely.

The efficiency is given by the expression

$$\eta = \frac{J V}{Q_e + Q_r + Q_c} \quad \dots (1)$$

where

$J$  is the output current density

$V$  is the corresponding output voltage

$Q_e$  is the electron cooling of the emitter

$Q_r$  is radiant heat lost by the system

$Q_c$  is the conductive heat losses through

local lead wires and the supports

By considering the ideal converter, that is one which is limited by the emission processes and in which transport losses in the inter-electrode spaces are neglected, the various factors in Equation 1 can be computed and an upper limit on performance for all types of thermionic converters can be determined. The maximum obtainable efficiency for a given emitter is determined by a few parameters which include the emitter temperature, the collector work function and the emissivity. These independent variables specify optimum values for  $V_o$ , the output voltage,  $J$ , the output current, the collector temperature and the lead dimensions. It is only necessary that the emitter work function be equal to or less than a critical value given by  $\phi_{crit} = eV_o + \phi_c$  in order to achieve maximum efficiency. Using reasonable values for the independent variables including a collector work function of 1.7 ev the computations yield the results given in Figure 3. The significant features are:

- a. the maximum efficiency increases with increasing temperature
- b. the optimum power density increases with temperature but at high temperatures and high emissivities very high current densities are required for optimum performance
- c. at the lowest temperatures, the output density is also low, of the order of a few watts per square centimeter.

As stated above, the calculations are for an ideal converter in which transport losses and space charge effects are ignored. In a practical case, the density of electrons in the interelectrode space is so large that additional flow of electrons from the emitter is impeded unless precautions are taken to reduce or eliminate the space

charge. Overcoming these space charge effects turns out to be a major problem in general. The interelectrode spacing can be made so small that the space charge has a minor effect on the output power and the efficiencies approach their optimum values. In this case, however, the machining and assembly tolerances are so stringent (the spacing between the emitter and collector is less than  $\sim 0.001$  inch) that this design is impractical. Additionally, the close spacing tends to allow the collector to be more easily contaminated with materials evaporated from the emitter causing a decrease in the output power. The space charge can be reduced or eliminated by the addition of a gas such as cesium which becomes ionized either by volume or surface ionization mechanisms. With this method of overcoming the space charge, useful power densities can be obtained with interelectrode spacings of several thousandths of an inch. The use of cesium, however, introduces other effects which tend to lower performance. For spacings of the order of tens of thousandths of an inch the Joulean heating losses of the plasma become excessive; and for very close spacings, the conductive heat losses of the plasma become excessive.

The theoretical power densities and efficiencies shown in Figure 3 have not been obtained in practice. With an emitter temperature of  $2000^{\circ}\text{K}$ , several companies have built cesiated converters with outputs of  $7\text{--}9 \text{ watts/cm}^2$  at output voltages of  $0.7 - 0.8$  volts. There have also been exceptional performances with power densities up to  $20 \text{ watts/cm}^2$  at these temperatures. In general, these latter are considered to be anomalies which are not as yet understood, but the results show that high outputs can be obtained and a considerable amount of research is currently underway in areas which definitely will bring about significant improvements. One recent type of converter, however, has performed reliably at outputs of  $20 \text{ watts/cm}^2$ .

### III. APPLICATIONS OF THERMIONIC ENERGY CONVERSION

#### A. Solar Thermionic Systems

The requirements for power in space vehicles have caused the interest in solar-thermionic power systems. Basically, the solar flux is reflected from a mirror and focused into a cavity absorber composed of the emitters of an array of thermionic diodes. This system utilizes the energy of the sun relatively efficiently, has a high heat rejection temperature, thereby reducing radiator size, and converts heat to electricity with no moving parts. To date no such system has been flight tested but a generator consisting of five diodes has been assembled and operated with solar energy. The generator, when tested with electrical heat, produced 62 watts at 4.8 volts and 75 watts at 3.5 volts. In the next few years, systems capable of several hundred watts will be available.

Since the heat source is radiant energy, and the thermionic diodes operate in vacuum, the thermionic materials problems associated with solar-thermionic power systems are mainly those of the diode itself.

#### B. Flame-Fired Thermionic Systems

The combustion of gases such as methane, propane and gasoline provides an adequate heat source for thermionic conversion. The adiabatic flame temperatures are near 1900°C. Thus, these fossil fuels can be utilized to heat thermionic emitters to thermionic temperatures with sufficient heat fluxes. Burners have been designed and operated to maintain an emitter at 1500°C with a heat flux of 40-50 watts/cm<sup>2</sup>.

Currently, the main interest in such a development is a lightweight portable source for military applications. Research and development currently is being undertaken to develop the required burners, materials and thermionic converters for gasoline powered



generators in the 5-200 watt power range. Thermionic conversion for these applications potentially offers the advantages of high power-to-weight-ratio, operation with logistically available fuel, portability, silent operation, expeditious startup in arctic conditions, and simplicity of operation and maintenance.

The burner development is proceeding satisfactorily in terms of attainable temperatures and heat fluxes. The extremely corrosive nature of the flame and combustion products as well as permeation of combustion gases into the converter are at present the crucial materials problems.

### C. Isotopic Thermionic System

Small radioisotope-powered electrical generating units have recognized advantages for specialized military applications. The energy or heat source is self-contained and thus the fuel supply problem for remote, unmanned stations is eliminated. Coupled with direct conversion methods, power supplies in the range of a few hundred watts can be designed with no moving parts for operation at predetermined power levels for substantial periods of time ranging from months to years depending on the decay rate of the radioisotope. Disadvantages include the very high costs and the hazards associated with radioisotopes and the fact that the energy release is not constant with time, which means that excess heat must be dissipated during the initial phase of operation. Furthermore, alpha emitting isotope sources cause considerable pressure rises which further complicate the radioisotope containment problem.

At present, a low-power thermionic converter utilizing curium-242 as the heat source is being developed for the Atomic Energy Commission. With the availability of the longer-lived isotopes now being produced, however, power supplies of several hundred watts

capable of operating for periods greater than a year will become feasible.

#### D. Nuclear Reactor Thermionic Systems

There are three concepts for nuclear reactor thermionic power systems. One concept is the out-of-core conduction heat source in which the heat is conducted from the core to the thermionic converters mounted externally to the core. This concept has the advantage of completely static operation but requires very high core temperatures and is limited in size to the tens of kilowatts of power. A second design concept uses a high temperature reactor with a liquid metal loop for heating thermionic converters mounted in the radiator. This has the great advantage of separating the reactor from the converter. However, the reactor coolant loop must operate at temperatures slightly above the thermionic emitter temperature. In order to achieve power densities of a few watts per square centimeter required for compact systems of 10 lbs/kwe or less, the coolant loop must operate at temperatures considerably above present day technology. Another problem is that the converter array in the radiator must be insulated electrically from the coolant loop and the insulating material must be at the emitter temperature. The third concept is the incore design in which the thermionic converters are an integral part of the fuel element. This system has the advantage that the coolant loop operates at the heat rejection temperature--1100°K or less. The out-of-core components that could be used in this system are currently being developed in other space power programs, and thus the problems with this concept lie in the reactor core. Here the basic concept is that the fuel or the fuel with its cladding is the emitter. This fuel-emitter structure is cylindrical in shape and is mounted inside the collector assembly, which consists of the collector, an electrical insulating layer and

another metal sheath in contact with the liquid metal coolant. This fuel element must operate at temperatures much higher than present day fuel element technology permits.

All of these concepts have difficult materials problems in that each must be coupled to a very high temperature reactor, either directly or by means of a very high temperature coolant loop.

#### IV. MATERIALS PROBLEMS

In any of these converter systems it is necessary, as mentioned in the previous sections, that a solar, radioisotopic, fossil-fueled or nuclear heat source be available. The emitter material must be mated to the heat source in some manner. A spectrum of possible problems that must be investigated and solved so that the design objectives of the systems can be met are introduced by the following circumstances: the high-temperature emitter is in contact with a high-temperature heat source, an interelectrode plasma, and through insulators and support structures with other parts of the converter which are at lower temperatures; and, the system must remain stable for periods up to 15,000 hours. The majority of the materials problems are associated with the emitter structure. These emitter problems, as well as those of the other components, are discussed in the following sections.

##### A. The Emitter

##### 1. Work Function

In the discussion of efficiency, it was made clear that for a given emitter temperature and other fixed conditions such as the work function of the collector, an emitter work function equal to or less than the critical value was necessary for optimum results. If the assumptions made for determining the efficiencies in Section II are used, the value of this work function varies from approximately 2.7 ev at 1800°K to 3.5 ev at 2400°K. Emitters can then be discussed in terms of

ways in which this critical work function can be obtained. One way to obtain this, in principle, is to use a material which may be a pure metal or an alloy which has the desired work function. Such materials are called elemental emitters. Another approach is to use a metal (the refractory metals) or some metal alloys or compounds on which cesium vapor will be adsorbed. The adsorbed cesium affects the work function of the surface and the pressure of the cesium vapor can be changed to alter the work function to the critical value. Such electrodes are referred to as cesium refluxed emitters. Another way is to dispense a material to the surface through pores or by bulk diffusion and thereby obtain a composite work function which is equal to the critical value. Such materials are the so-called dispenser-type emitters. A summary of these emitters is given in Figure 4.<sup>12</sup>

It turns out that the dispenser emitters available today are unsatisfactory because of the rather low temperatures at which they must be operated and the poor chemical, mechanical and thermal stabilities they possess. For example, they cannot be relied upon to remain chemically stable because the dispensate may run out. Integrity of the alkaline earth oxides cannot be assured because of sputtering at the electrodes. Further, these oxides are usually characterized by a high temperature coefficient for the composite work function which could cause patch effects in the oxides when they are used in systems which have non-uniform heat sources. These patch effects could cause the performance to degrade rapidly. However, it should be mentioned that matrix-type emitters<sup>13</sup> are being developed which show promise of overcoming these various instabilities.

The cesiated refractory metals meet the requirements as emitters in most of the applications. In addition to the problems summarized in the table, however, there is another problem. These metals are characterized by a patchy surface. This probably limits the

area that is effective in electron emission to about one-quarter of the surface under normal operating conditions. Ignoring the contribution of the non-emitting areas to surface ionization of cesium, it is clear that this effect leads to poor performance. Research is now underway<sup>14</sup> to obtain refractory metal emitters with uniform work function. This then offers promise of overcoming any degrading effects due to the "patch effect."

There is now evidence<sup>15</sup> that refractory metal surfaces activated with fluorine (this may also apply to other adsorbed gases) should greatly enhance the performance from the emitter standpoint in that the critical work function can be obtained with much lower cesium vapor pressure than with a cesiated pure refractory metal. It could well be that the combination of controlling crystal orientation and special activation techniques could lead to the emitters of the future. The problem is one of ascertaining the effects of these changes and how they can be maintained. A special problem due to gas additives in diodes can arise. Tests must be made to show these additives do not attack seals or act as mass transfer agent for the electrode materials.

## 2. Emissivity

In Equation 1 the net total emissivity of the emitter-collector system enters through the radiation heat term  $Q_r$ . The smaller the net emissivity, the larger the efficiency. That is, for low emitter emissivity, more heat goes into evaporating electrons than into radiation losses and for low collector emissivity more radiant heat is reflected back to the emitter. It turns out that oxide and metallic electrodes have emissivities which are functions of temperature; that of the oxides increasing with temperature (and usually with time) and that of the metals and some of their alloys decreasing with tem-

perature. The cesiated refractory metal converters have emissivities of 0.1-0.2, whereas in the carbide system, the emitters<sup>16</sup> have emissivities of 0.7-0.9. The important problem, however, is the variation of the emissivities with time. The emitters may be affected by fission products or other contaminants from the heat source, phase changes in alloys, and radiation damage. The collector may be affected by deposition of species evaporated from the emitter. This has been observed for systems with carbide emitters.<sup>16</sup> In general, however, these effects, particularly those related to the diffusion of constituents or by-products of the heat source, have not been properly evaluated.

### 3. Vaporization

Several authors<sup>17-20</sup> have discussed the manner in which vaporization limits the choice of the emitter material. An expression for the vaporization rate of the emitter surface into a vacuum is given by the equation

$$q_o = Q \exp \left( \frac{-\Delta F}{kT_e} \right) \quad \dots (2)$$

where  $\Delta F$  is the free energy change per atom for the vaporization process

$k$  is the Boltzmann constant

$T_e$  is the absolute temperature

$$Q = 44.4 \left( \frac{M}{T} \right)^{1/2} / d$$

( $M$  is the molecular weight of the emitter and  
 $d$  its density in grams/cm<sup>3</sup>)

In conjunction with the vaporization rate of the emitter, several criteria for acceptable emitters have been adopted. As an example Rasor<sup>17</sup> and Hansen and Rasor<sup>18</sup> adopted the criterion that for typical values of  $Q$  and  $T_e$  and for an output current density of 10 amps/cm<sup>2</sup> the surface should not recede at the rate of more than 6 mils/year. This enabled

them to use the ratio of  $\Delta F/\phi_e$  as figure of merit for the selection of an emitter. Values of  $\Delta F/\phi_e$  of less than about 1.2 are unacceptable. The figures of merit for several emitters operating at  $10 \text{ amp/cm}^2$  are listed in Table I. The bare metals (without adsorbed cesium) are poor emitter materials and the carbides listed are only marginal. An adsorbed film on the surface, however, considerably improves the figure of merit so that these emitters are acceptable as measured by this criterion. The evaporation rate is more rapid the higher the surface temperature and thus it is clear that the requirements of high efficiency and long lifetime cause severe high temperature materials problems.

TABLE I

Figure of Merit of Elementary Emitter Materials

<u>Material</u>	<u><math>\phi(\text{ev})</math></u>	<u><math>\Delta F/\phi</math></u>
Mo	4.3	0.6
C	4.3	0.7
Re	4.7	0.8
W	4.6	1.0
Ta	4.2	1.0
ZrC	3.8	1.0
UC	3.3	1.1
80-20 mol % ZrC-UC	3.3	1.2

It has been mentioned numerous times in the literature that materials evaporated from the emitter can condense onto and poison the collector and cause the efficiency of the converter to be reduced drastically. Statements have been made that there was really no need to try to reduce the work function of the collector much below the lowest obtainable at the emitter because the materials that condense on the collector after evaporation from the emitter would predominate. At first glance this seems plausible and is undoubtedly the case for

vacuum converters where a very close spacing is required to overcome space charge effects. Other considerations such as machining and spacing tolerances rule against such closed spaced converters and some plasma such as a cesium vapor is necessary in the interelectrode space. With the cesium vapor present the emitter will continue to evaporate and perhaps some of this evaporated material will reach the collector and condense thereon. It should be recognized, however, that the cesium could greatly impede both of these processes. The problem that exists today for cesium vapor converters in this regard is to determine: 1) the effect of cesium adsorbed on the emitter surface on the evaporation of the substrate, 2) the effect of the interelectrode cesium vapor on the mass transfer of the evaporated emitter to the collector and, 3) the effect of the cesium adsorbed on the collector on the deposition of the emitter material on the collector.

To date two experiments have been performed to determine the effect of an adsorbed cesium layer on the vaporization and condensation of a metal substrate. Richardson et al.<sup>21</sup> measured the transport of molybdenum from a hot filament at 2100°K to a nickel collector in a 1.0 mm Hg cesium atmosphere. They found that the ratio of the transported amount in vacuum to that in cesium varied from 7 to 24 as the spacing increased from 0.004 to 0.016 inch. Hansen<sup>22</sup> performed an experiment at low cesium pressures where the scattering in the gas was minimized. He concluded that at cesium coverages, cesium pressures, and electrode temperatures of interest in thermionic energy conversion, the vaporized refractory emitter material has only a 0.0005 to 0.0013 probability of sticking to the collector, and that a low condensation coefficient is the dominating factor determining material transport in converters. The actual effects on vaporization itself, however, have yet to be determined. These short time experiments are not conclusive,



and long lifetime experiments must be performed.

#### 4. Thermal, Mechanical and Electrical Properties

The thermal, mechanical and electrical properties of the materials in a converter are of direct importance in both the efficiency of the conversion of thermal to electrical energy and the lifetime of the converter. This is especially true of the emitter which must operate at very high temperatures and also, in many applications, undergo large temperature cycles.

The important thermal properties of emitters which are not discussed elsewhere in this paper are the thermal expansion coefficients and the thermal conductivity. The first of these must be known to mate the emitter with the heat source, the insulators and the external electrical leads. The thermal conductivity must be such that severe temperature gradients do not exist between the heat source and the emitting surface; and, heat must be conducted efficiently to the emitter surface. The important electrical property is the resistivity. This must be sufficiently small that the emitter will not have a large voltage drop across it. The mechanical properties include: elastic moduli, the ultimate tensile strength and creep strength. These properties must be known in order that a converter may be designed so that important dimensions, such as interelectrode spacing, will be preserved throughout its use.

With the exception of niobium and iridium the electrical conductivities of the refractory metals (Ir, Nb, Mo, Re, Ta and W) have been measured<sup>23</sup> from room temperatures to temperatures in excess of 2000°C. A similar statement can be made about these metals with regard to thermal expansion coefficients and thermal conductivities. It appears that the electrical and thermal properties of refractory metals are satisfactory for thermionic energy conversion. A survey of the mechanical properties reveals that very little information is available

for the refractory metals, particularly at the high temperatures of emitter operation.

It is conceivable that alloys of the refractory metals or their compounds could be better materials for thermionic converters. Some alloys are definitely more ductile than the refractory metals. However, the overall knowledge of their thermal, mechanical and electrical properties is insufficient at this time to permit their evaluation for use in thermionic converters.

Another area that needs investigation is the change with time of the thermal, mechanical and electrical properties at emitter temperatures. These properties could be affected by recrystallization of the material if it is initially in the cold worked state or by excessive grain growth if it is originally in the crystalline state. These properties must thus be studied as a function of time and temperature. In addition, the effects of nuclear radiation have not been determined.

#### 5. Chemical Stability

The emitter, which operates at a very high temperature must not deteriorate because of chemical reactions with other components of the converter or the heat source. The compatibility of the emitter with fuel in the nuclear application and the protection of the emitter from oxidation in a flame-fired converter are two of the most pressing problems in thermionics today.

In a nuclear reactor thermionic application, the cesium vapor refractory metal incore concept requires that the refractory metal emitter be in contact with the nuclear fuel at, of course, the very high emitter temperatures. The uranium bearing carbides are one of the most promising fuel types and thus the interaction between this fuel, and its constituents, and the refractory metal emitter-cladding

must be known. Only in the last year or so have these interactions been studied at temperatures of interest to thermionic systems. Some of the results have been reported. General Atomic<sup>24</sup> has studied combinations of  $\text{UO}_2$ , UC,  $\text{UC}_2$ , and UC-ZrC (90/10 and 10/90 mol-%) with tungsten, molybdenum, niobium and tantalum by the diffusion couple method. In the temperature range 2073° to 2273°K they find that the only combinations suitable for long life operation are UC, UC-ZrC (10/90 mol-%), UC-ZrC (90/10 mol-%),  $\text{UO}_2$  with W, and UC-ZrC(10/90 mol-%) with Mo. Considerable effort is now underway to extend this type of measurement to other fuel-emitter combinations and it is generally felt that the compatibility problem can be solved. Another related problem of equal importance is that of radiation swelling of the fuel-emitter structure. Recent theoretical and experimental studies<sup>25</sup> have shown that the stability of metallic fuel materials can be significantly improved by suitable alloying additions and heat treatments. This improvement in the ability of uranium fuel to retain its fission products without swelling is thought to be due to the trapping of the fission gas atoms in small groups such that their mobility is greatly decreased and therefore the collection of gas atoms into large, damaging bubbles is prevented. The continued development of these techniques and their applications to high temperature fuels of interest to thermionic reactors will, if successful, greatly enhance the possibility of nuclear thermionic reactors.

In flame-fired converters, protection of the emitter from erosion by the fuel constituents, flame by-products and flame impingement presents a major problem. Refractory metals without exception have very poor oxidation resistance at the temperatures of interest, 1200-1400°C, and would last for minutes only without a protective coating.

Many types of protective coatings have, and are being

investigated. Among these are refractory oxide glasses, platinum based coatings, silicon carbides, and for molybdenum, molybdenum disilicide. W.R. Martini<sup>26</sup> has compared several commercially available coatings including tin-aluminum, molybdenum disilicide and silicon carbide. He used two types of tests. One was the heating of coated wires 1/16" in diameter by 6" in length by the passage of an electric current. Table II shows the results of these tests. Durak-B, T-61, and AI-coat are basically molybdenum disilicides. R-505C, TI-Kote and Pyro SiC are basically silicon carbides. Al-Sn is an aluminum-tin coating and KS is a "modified disilicide" coating which is considered obsolete\* and is being replaced by K-A, which is "a further modified disilicide," and is being developed for niobium. The manufacturer of these coatings are listed at the bottom of the table. Since thermal cycling is important in flame-fired applications the resistance of the coating to thermal cycling is necessary. Table II shows some results of thermal cycling tests on coated refractory metal wires. Durak-B has excellent thermal cycling characteristics and T-61, which is nearly the same coating, is also expected to be good.

The second type of test performed by Martini<sup>26</sup> was the actual flame heating of the inside of a coated thimble 1" in diameter and 3" in depth. In these experiments, with the flame inside the thimble, these "hot shells" are subjected to flame conditions of a complete thermionic converter of the type being developed by Atomics International. The results as of this writing are shown in Table III.

It is quite clear from these data that the coatings are not as yet developed sufficiently for use in practical thermionic converters.

---

\*Information from the Chromizing Corporation

TABLE II

Results of Tests of Coatings to Protect Refractory Metals  
from Oxidation when Electrically Heated in Air

<u>Metal</u>	<u>Source</u>	<u>Coating</u>	<u>Longest Time to Failure at 1350°C in air</u>
Mo	Fansteel	Durak-B	629 hrs
Ta	Fansteel	KS	26
Mo	Fansteel	Al-Sn	196
Mo	Fansteel	Al-Coat	710 (one only)
Mo	Fansteel	T-61	120
Mo	Fansteel	mod. T-61	887
Ta	Fansteel	R-505C	192+
Mo	Fansteel	TI-Kote	5
Mo	Fansteel	Raytheon Pyro SiC	15

TABLE III

Results of Tests of Coatings to Protect Refractory Metals  
from Oxidation and Flame-Impingement

<u>Metal</u>	<u>Method of Fabrication</u>	<u>Shape</u>	<u>Coating</u>	<u>Temp. °C</u>	<u>Longest Time to Failure</u>
Mo	deep drawn	Flat Bot.	Durak-B	1000-1365	236
Mo	deep drawn	Flat Bot.	Durak-B	1300	76
Mo	deep drawn	Flat Bot.	TI-Kote	1350	42
Mo	vapor deposited	Flat Bot.	TI-Kote	1000-1350	78
Mo	deep drawn	Flat Bot.	Al-Sn	1130 max.	4

These results, however, represent considerable improvement in the last few months and it is expected that the refinement of present techniques and the incorporation of better engineering practices in the use of presently available coatings will lead to further improvements and possibly the solution of the problem for some applications.

In a cesium vapor thermionic converter, cesium comes in contact with the electrodes, insulators and some bonding agents. These components must, of course, be stable in the presence of cesium throughout the appropriate temperature ranges. Tests have been and are now being performed to examine the compatibility of various materials with cesium. Test conditions have ranged from exposures of two hours<sup>27</sup> to 1000 hours<sup>28</sup> in cesium from liquid to vapor at 1-10 torr, and material temperatures up to 2000°C. These tests have conclusively proven that the noble metals such as silver, gold, platinum and some of their alloys such as BT silver solder are readily and severely attacked by cesium and hence should not be used in cesium vapor conversion systems. It should also be pointed out that quartz reacts with cesium. Tests<sup>28</sup> on oxygen-free-high-purity-copper (OFHC) at 370°C in a cesium vapor of 10 torr showed no effect for a thousand hour test. However, with the cesium vapor pressure the same and the OFHC at 750°C, investigation of the surface revealed the presence of what appeared to be a Cs-Cu alloy. Tantalum at 1300°C reacts with cesium at these pressures in less than 1000 hours. The same experimenters found that nickel at temperatures of 750°C does not react with cesium nor does a nickel-titanium alloy (28% Ni - 72% Ti). Also Kovar does not react with cesium according to these tests at the lower temperatures. Zirconium at 1300°C does react with cesium.

At the present time the various physiochemical properties of some intermetallic compounds such as the zirconium and niobium beryllides are being determined.<sup>29</sup> These experiments will include some

tests for their compatibility with cesium. It is planned to hold the samples at fixed temperatures up to 1000°C for periods ranging from one to two days.

Also at the present time some physiochemical properties of some of the refractory compounds are being measured<sup>30,31</sup> for several refractory materials such as ZrC, UC and ThC. These latter will include cesium compatibility tests with the substances at temperatures to about 2000°C and cesium vapor pressure up to 1 torr. It is interesting to note in addition that the latter set of experiments will include thermal cycling tests (up to 50 cycles from room temperature to 2000°C) as well as the effects of recrystallization and grain growth upon the various physiochemical properties.

Chandler and Hoffman<sup>32</sup> have carried out some very worthwhile tests to define and understand better the basic mechanisms affecting the compatibility of various structural metals with cesium. It was not their goal to decide whether or not these materials would be good for specific uses. They performed static capsule tests at 870°C and boiling refluxing capsule tests at 980° and 1340°C. The container materials tested were Inconel-X, 310 stainless steel, zirconium, hafnium, niobium, and niobium plus 1% zirconium, molybdenum, tantalum and tungsten. Their goal was to have a continuous test for 30 days and this was achieved for the 870° and 980°C runs whereas only 54-1/2 hours was attained in the 1340°C test before some of the capsules failed forcing termination of the measurements.

It was concluded that all of the materials tested at 870°C with the exception of zirconium which has a phase change near this temperature are adequate for structural application in stagnant cesium liquid or vapor at this temperature. Niobium, niobium-1% zirconium alloy, molybdenum and tantalum do not appear corrosion resistant to boiling,

splashing, and refluxing cesium at 980°C. Of these, molybdenum is the least compatible. Niobium-1% zirconium alloy suffers grain boundary attacks which are associated with preferential corrosion of zirconium from this alloy at 980°C. At 1340°C the niobium-1% zirconium alloy was the best material tested. The grain boundary attack evident at 980°C did not appear at 1340°C. Molybdenum was found to dissolve rapidly in boiling cesium at 1350°C leaving the molybdenum surface with a smooth mirror finish.

It was further concluded in this experiment<sup>32</sup> that the interstitials enter the compatibility problem. Both the 310 stainless steel and Inconel-X are decarburized by cesium of the purity used in these tests. Additionally it was concluded that oxygen may be one of the most important variables in compatibility tests. The mode of corrosion included intergranular attack and general dissolution but it was not certain which of these modes would be operative as a function of the chemical composition of the material used; and, the mode of attack can change with different exposure conditions. It was felt that fluxing of oxides may contribute to dissolution.

For the future Chandler and Hoffman have suggested that their studies be extended to include:

- a. Stress corrosion studies in which stress, temperature and composition of vapor phase would be used as variables
- b. Study of cesium compatibility factors in refluxing. The detailed behavior of boiling cesium in small containers would be studied to find the effect on the wall surface finish including time and temperature as variables. The effects of additives, e.g., Hf and Ti, which are oxygen



scavengers to inhibit attacks would be investigated. This should provide sound information for alloy selection or development.

- c. Since it was concluded oxide refluxing may be a mode of attack of the reactive metals such as Nb, Zr, Mo, Ti, etc., they would expose oxides of these and others to molten cesium metal at various temperatures and expose these reactive metals with high oxygen content under similar conditions. As a result of these studies, it is hoped that the mechanism will be completely understood.

## 6. Permeation

In the incore nuclear and flame-fired thermionic converter systems, the emitters are in direct contact with the heat source. The constituents and byproducts of the heat source may diffuse or permeate through the emitter material to the surface and interelectrode space. These species may affect the thermionic conversion processes significantly and thus must be carefully evaluated.

At present little is known about the sensitivity of converter performance to fuel and fission product constituents on the emitter. UC-ZrC is a potential fuel and it is believed that emission characteristics of this material as an emitter is determined by the existence of free uranium on the surface. In the case where the fuel is clad with a refractory metal emitter, uranium and carbon are among the possible species that may diffuse through to the emitter surface. The effect of carbon on the emission has not been determined. Since carbon has a high work function it may not degrade performance. Uranium, however, has a low work function and is likely to cause a decrease in emission. The type of fuel, the type, thickness and temperature of the

emitter, and the diffusion and evaporation rates all influence the magnitude of the effect of the fuel constituents on thermionic performance. The effect of materials in the interelectrode space and their possible deposition on the collector and other components are also relatively unknown.

The permeation of gases through metals has long been a subject of investigation and a considerable amount of data now exists for the materials, ceramics and gases involved in flame-fired thermionic converters. In this application, the permeation of hydrogen into the interelectrode space is a major problem. The amounts, of course, depend on the materials and temperatures involved. Since the temperature distribution over the area available for permeation may vary considerably among different converter designs, the amount of hydrogen permeation must be related to a specific converter design. There are, however, data that can be used to determine the order of magnitude of the permeation. Measurements<sup>26</sup> on the permeation of  $H_2$  through molybdenum yield values of  $0.2 \text{ cc(stp)/hr cm}^2\text{mm}$  at  $1000^\circ\text{C}$ . Conklin and Turnbille<sup>33</sup> found lower values ranging from  $0.07$  to  $0.1 \text{ cc(stp)/hr cm}^2\text{mm}$  at temperatures of  $1000^\circ$  and  $1200^\circ\text{C}$  respectively. The latter experimenters also found that a molybdenum disilicide coating had no effect on the permeation rate. Martini and McKisson<sup>34</sup> measured the  $H_2$  permeation through 10 mils of molybdenum coated with 2.5 mils of Durak-B. In this experiment the material was immersed in a propane air flame rather than one atmosphere of  $H_2$  as in the other experiments. Their results were  $0.03$  to  $0.04 \text{ cc (stp)/hr cm}^2$  at  $1200^\circ\text{C}$ .

These values are high in terms of thermionic converter performance as relatively high hydrogen pressures would build up within converters in a matter of hours. The strategic use of dry gas might considerably reduce the amount of available hydrogen. Also, it can be

shown that a reasonable amount of a titanium-zirconium alloy would getter all the hydrogen for a converter of practical design for 1000 hours.

A study has been completed<sup>35</sup> to determine the permeation rate of cesium through thin tantalum sheets. This permeation rate was found to be too small for a practical cesium-ion-dispensing hollow emitter; although it may be rapid enough to cause large losses of cesium during long-term operation of converters. No mention was made of possible long range effects that the diffusion of cesium into a tantalum emitter might have upon its mechanical, thermal, electrical, chemical and emission properties. These appear to be areas that will have to be investigated in conjunction with lifetime testing of converters using cesiated refractory metal electrodes.

#### 7. Stability Under Nuclear Radiation

A problem peculiar to the nuclear fueled heat source is the one of radiation damage. Most of the problems that have been mentioned in the previous sections can be aggravated by the nuclear radiation inherent in this source. Tests are now being planned and conducted to determine the extent of the effect of radiation damage on the properties of thermionic materials. The inpile testing that will be necessary to determine the effect of radiation damage on the overall converter performance has barely begun.

##### B. The Collector

The problems of the collector are similar to those of the emitter except that the collector is operated at a lower temperature and is not coupled as directly to the heat source. Some additional problems are encountered, however, since the collector is connected to the heat rejection system.

One of the main parameters of the collector is its work function since the efficiency of conversion becomes higher the lower

the collector work function. In a space reactor, however, efficiency considerations for the entire system put a lower limit on a desirable collector work function. One approach to improving the efficiency of the collector is to choose a material with a low work function. Another approach is to choose a material such that when the collector and cesium temperatures are optimized the composite surface of adsorbed cesium and substrate has a low work function. In either of these cases consideration must be given to the effect of material evaporated from the emitter and deposited on the collector. In some of the oxide-type collectors, it is possible for the surface to be destroyed by continual electron bombardment.<sup>13</sup> The materials released by this process could diffuse to and collect on the emitter and poison it. With the development of special matrix-type electrodes<sup>13</sup> this difficulty may be obviated.

Some very low work function collectors, approximately 0.8 ev work function near room temperature, have been studied.<sup>13</sup> These include the so-called Ag-Cs<sub>2</sub>O-Ag-Cs emitter and the Bi-Ag-Cs emitter. The experience to date with these show they lack mechanical, thermal, electrical and chemical stability.

There is now a research program<sup>35</sup> to develop special coatings with a thickness of  $10^{-5}$  to  $10^{-4}$  cm for nickel substrates for use as collectors. Tentative results show: 1) cesium-antimony compounds deposited on nickel have a work function of  $1.5 \pm 0.1$  ev and, 2) a cesium-tellurium-coated nickel collector has a work function of about  $1.2 \pm 0.1$  ev. This work is being continued and extended to other coatings. Not enough has been done to assess the mechanical, thermal, electrical and chemical stability and thereby show these will be practical for use as collectors in converters.

Under normal operating conditions collectors of cesiated refractory metals have work functions as low as 1.6 ev. Theory<sup>37</sup> and

experiments show that the higher the bare work function of a metal the greater is the amount that cesium at a given vapor pressure will lower its work function at a given temperature. It is possible to control this bare work function two ways: 1) activation with some electro-negative substance such as fluorine and, 2) control of the crystal orientation of the metal at the surface so as to have the crystal face present with the highest work function. Polycrystalline molybdenum activated with fluorine<sup>15</sup> has a work function in cesium vapor as low as about 1.4 ev. As in the case of emitters, it could well be that a combination of the crystal orientation and activation by a special additive will ultimately lead to collector work functions as low as 1 ev in cesium vapor converters. The main problems that remain include:

1) determination of conditions necessary to maintain the proper activated surface as well as the crystal orientation of the substrate and, 2) assuring that deposits from the emitter will not seriously change this condition.

### C. Cesium Purity

It is well recognized that the performance and repeatability of performance of thermionic converters can be expected only if cesium purity is closely controlled. Impurities in the cesium may have significant effects on the emitter and collector surfaces and thereby affect their work functions and chemical stability. These impurities may also inhibit the flow of electrons across the interelectrode gap. The problem of obtaining proper cesium is threefold: 1) obtaining the cesium and being assured of its chemical constituents, 2) storage of the cesium prior to use in a converter and, 3) keeping the cesium pure once it is in a converter.

When the chemical assays for cesium presented in Tables IV and V are considered, it is evident that the purity of the commercially

TABLE IV - TYPICAL CESIUM METAL ANALYSES

Element	Supplier				
	Dow 9-60	Dow 6-61	Kawecki 6-61	Am. Potash & Chemical	Dow 9-6-61*
Cs	99.9+%	99.9+%	99.9%	99.11%	
Al	0.0006	0.0005			0.0003
B	<0.0080	<0.0016			<0.0016
Ba	<0.0008				<0.0008
Ca	0.0033	0.0010	0.01		0.0030
Cr	<0.0002				0.0005
Cu	0.0002	<0.0002			0.0011
Fe	0.0021	0.0006			0.0030
K	0.0018	<0.0016	0.01	0.03	0.0035
Li	<0.0016		ND	0.00	<0.0016
Mg	0.0003				0.0003
Mn	<0.0002				0.0002
Na	0.0051	<0.0016	0.01	0.02	0.0073
Ni	0.0002				0.0003
O	0.0080	0.0036			
Pb	<0.0008	<0.0002			<0.0002
Rb	0.029	0.016	0.01	0.39	0.0047
Si	0.0042				0.0008
Sl02			0.005		
Sn	<0.0008				
Sr	<0.0002				<0.0002
Fe+Al			0.001		

\*Certified Analysis of Cesium purchased  
P.O. N 151TX - 50906 H

TABLE V - ATOMICS INTERNATIONAL CESIUM ANALYSES

July, 1962

Element	American Potash & Chemical	Mine Safety Appliance	Dow	(Kawecki) Penn Rare Metals
Ag	<0.0001	<0.0001	<0.0001	<0.0001
Al	<0.0005	<0.0005	<0.0005	0.0020
B*	0.0010	0.0010	0.0090	0.0150
Ba	<0.0001	<0.0001	<0.0001	<0.0001
Be	<0.0001	<0.0001	<0.0001	<0.0001
Ca	<0.0005	<0.0005	0.0005	0.0035
Cd	<0.0001	0.0004	<0.0001	<0.0001
Cr	<0.0001	<0.0001	<0.0001	<0.0001
Cu	<0.0005	<0.0005	<0.0005	<0.0005
Fe	<0.0005	<0.0005	<0.0005	0.0020
Mg	<0.0005	0.0010	0.0007	<0.0005
Mn	<0.0001	<0.0001	<0.0001	<0.0001
Ni	<0.0010	<0.0010	<0.0010	<0.0010
Pb	<0.0001	<0.0001	<0.0001	<0.0001
Si*	0.0070	0.0050	0.0140	0.0280
Sn	<0.0001	<0.0001	<0.0001	<0.0001
Ti	<0.0005	<0.0005	<0.0005	<0.0005
Sr	<0.0001	<0.0001	<0.0001	<0.0001
Na	0.0020	0.0020	<0.0010	0.0070
Rb	0.0700	<0.0100	<0.0100	0.0300
K	0.0040	<0.0040	<0.0040	0.0130
Li	ND	ND	ND	ND

\*High Band Si values are thought to be due to spurious pickup from glassware.

available cesium is <sup>m</sup>adequate. This fact is probably recognized by many laboratories studying cesium vapor converters. One laboratory<sup>38</sup> has reported its experience along these lines. In addition to doubting the possibility of purchasing high purity commercial cesium, this group suspected that the glass vials in which cesium is usually shipped yielded further impurities to the substance. When cesium was purified in the laboratory it was found necessary to store it in metal capsules although neither the exact method of purification nor the storage capsule description were reported. Additionally, it was found not only necessary to use pure cesium initially in the diode for the best performance, but it was also necessary to keep it pure via a distillation process when used in the converter. In essence, it was found when pure cesium was introduced in the diode initially and the diode operated that there would be a degradation in the output power with time. The difficulty was attributed to impurities introduced into the cesium by its releasing impurities from the converter. These impurities then reduced the efficiency with which cesium could be ionized, thus greatly reducing the output power in the ball-of-fire mode of operation.

#### D. Electrical Leads and Support Structures

The power generated in the converter must be transmitted to the load through electrical leads, part of which consist of the support structure for the emitter and collector. It can be shown that there is an optimum design<sup>8</sup> for the support structure such that the ratio of electrical to thermal losses is about equal to the converter efficiency. In practice, very thin (of the order of a few mils) support structures are required. As pointed out elsewhere<sup>39</sup> these components must maintain strength at the emitter and collector temperatures, must be chemically compatible with the emitter, collector and cesium, and maintain these properties over the converter lifetime.



An important aspect is the joining of the lead or support structure to the emitter or collector. In some cases where the metals are similar and the joints are accessible, welding can be performed satisfactorily. In other cases high temperature brazes, or more desirably, recrystallization catalysts are required. It has been shown, for instance, that the presence of small amounts of nickel has enhanced the recrystallization of molybdenum and tungsten at the relatively low temperature of 1200°C. Considerable development of these techniques is required, however.

#### E. Insulators and Seals

The insulators and seals in thermionic converters have several functions. They serve as part of the containment vessel, provide mechanical support for the electrodes to keep their geometric orientation accurate, provide electrical insulation between the emitter and collector and, in the reactor case, between the collector and the coolant.

For most applications alumina  $\text{Al}_2\text{O}_3$  is the best insulation material readily available today.<sup>40</sup> Brazing techniques today allow this to be used safely to temperatures of about 750°C for extended times without thermal failures. If better brazing techniques can be found, this can be used to temperatures in the neighborhood of 1200°C before its electrical, thermal and mechanical properties begin to be a problem. There are some problems, however, that may occur at the higher temperatures in any case. 1) The vapor pressure of oxygen over the  $\text{Al}_2\text{O}_3$  can be large enough to cause oxidation of the emitter, collector and seal materials. This may lead also to the formation of  $\text{Cs}_2\text{O}$  which would cause the destruction of the alumina. 2) The alumina are not pure  $\text{Al}_2\text{O}_3$ . They contain impurities that could cause further trouble at the higher temperatures such as lowering the electrical resistivity to an

unusable value, that is, it would become a very poor insulator.

Consider the incore reactor concept, however, in which the collector is cooled by a liquid metal. The collector must be insulated electrically from the coolant but have good thermal contacts. Present designs for cylindrical elements call for a collector-insulator-sheath sandwich structure. The sheath, or outer containment wall which is in contact with the liquid metal coolant would be a metal. There are several choices, but since a compressive force on the insulator is desirable, the metal should have a larger coefficient of thermal expansion than the insulator. The collector should have a thermal expansion nearly equal to that of the insulating material. Because of the high thermal conductivity requirement, BeO appears to be the best insulator for this application. Niobium, because of its compatibility with the liquid metal, may be the sheath material and either niobium or another refractory metal as the collector. An extremely important phase of this problem is the bonding of the insulator to the metal. One solution which has not been fully developed is the use of a mixture of BeO plus a few percent of CaO or MgO as a recrystallization agent. A thin film of an active metal such as vanadium, zirconium or titanium might also be used to interact with both the metal and oxide mixture. The mixture could be prepared, set in place and then fired to the required recrystallization temperature. In principle, this would recrystallize in place, yielding an insulator-metal system with good thermal and mechanical contact.

In general, problems such as the insulator-metal joints have not been solved adequately. These problems represent major obstacles to the successful development of efficient and long-lived thermionic conversion systems, particular for the nuclear systems.

## V. CONCLUSION

Significant developments have occurred recently in all areas of thermionic energy conversion. In the basics of thermionics, improvement in power densities and efficiencies is constantly occurring. Further improvement is definitely indicated by experiments on surface additives and crystal orientations as methods of controlling the work functions of emitters and collectors. Progress has been made in both nuclear and flame-fired applications with respect to coupling the converter to a heat source. There now are high-temperature data showing that some of the potential nuclear fuels and emitters are compatible at temperatures of interest to thermionics. In the flame-fired area, the lifetimes of protective coatings have been extended considerably and it is reasonable to expect further advances. These and the other materials problems discussed in this paper, which currently prevent the successful application of thermionic energy conversion, are being examined; progress is being achieved; and some solutions are being found. Thus thermionic energy conversion appears to be a source of power conversion that will be among the variety of power sources available for future military and civilian requirements.

## REFERENCES

1. H. Moss, J. Electronics, 2 305 (1957)
2. G.N. Hatsopoulos and J. Kaye, J. Appl. Phys., 29 1124 (1958)
3. V.C. Wilson, J. Appl. Phys., 30 475 (1959)
4. H.F. Webster, J. Appl. Phys., 30 488 (1959)
5. K.G. Hernquist, Nucleonics, 17 49 (1959)
6. W.B. Nottingham, J. Appl. Phys., 30 413 (1959)
7. J.M. Houston, J. Appl. Phys., 30 481 (1959)
8. N.S. Rasor, J. Appl. Phys., 31 163 (1960)
9. A. Schock, J. Appl. Phys., 32 1564 (1961)
10. L.S. Richardson et al., Metallurgy of Semiconductor Materials, Vol 15, (New York, John Wiley and Sons, 1962), p 333
11. C.K. Stanathan, ANL-6524 (1962)
12. L.K. Hansen and N.S. Rasor, Metallurgy of Semiconductor Materials, Vol 15, (New York, John Wiley and Sons, 1962), p 388
13. G.A. Haas, NRL Report 5656 (1961)
14. M.N. Huberman, Atomics International, private communication
15. R.L. Aamodt, L.J. Brown and B.D. Nichols, J. Appl. Phys., 33 2080 (1962)
16. R.C. Howard, Proceedings of the Third Government-Industry Thermionic Round Table Discussion (December 1961), Vol II
17. N.S. Rasor, AI-6799 (1961) p 21
18. L.K. Hansen and N.S. Rasor, AI-6799 (1961) p 383
19. P. Goodman and H. Homonoff, Metallurgy of Semiconductor Materials, Vol 15 (New York, John Wiley and Sons, 1962), p 311
20. L. Yang et. al., Metallurgy of Semiconductor Materials, Vol 15 (New York, John Wiley and Sons, 1962), p 365

21. L.S. Richardson et al., Metallurgy of Semiconductor Materials, Vol 15, (New York, John Wiley and Sons, 1962), pp 337-338
22. L.K. Hansen, AI-7979 (1962) p 110
23. A. Goldsmith, T.E. Waterman and H. J. Hirschhorn, Handbook of Thermo-Physical Properties of Solid Materials, I, II, III & IV (Rev) (New York, The MacMillan Company, 1961)
24. W.B. Wright, Jr., "Parametric Study of Direct Conversion Reactor Power Systems, " GA-3540 (1963)
25. J.A. Brinkman, NAA-SR-6642 (1962)
26. W.R. Martini, Atomics International, private communication. The authors are grateful to Dr. W.R. Martini for the use of this information prior to its publication.
27. S.S. Kitrilakis, M.E. Meeker and N.S. Rasor, TEECO 2-63 (1962)
28. F.G. Block and J.J. O'Grady, "The Development of an Auxiliary Electrode Thermionic Converter," Second Quarterly Technical Report, ASD (1962)
29. C.B. Magee et al., DRI-2079 (1962)
30. J.H. Ingold et al., Progress Report #4, "Thermionic Cathode Materials," (September 15, 1962)
31. A.F. Weinberg et al., "Metallurgical Factors Influencing Thermionic Emitter Characteristics," Paper 2, Dallas, Texas AIME Meeting (February 25, 1963)
32. H. Chandler and N. Hoffman, ASD-TDR #62-965 (1962)
33. L.J. Conklin and J.C. Turnbull, "Gas Permeation Study of Materials for Use in Thermionic Energy Converters," ASD-TDR-62-324 (1962)
34. W.R. Martini and R.L. McKisson, Atomics International, private communication
35. R.A. Chapman, et al., "Third Quarterly Progress Report for Hollow Cathode," Texas Instruments (1962)

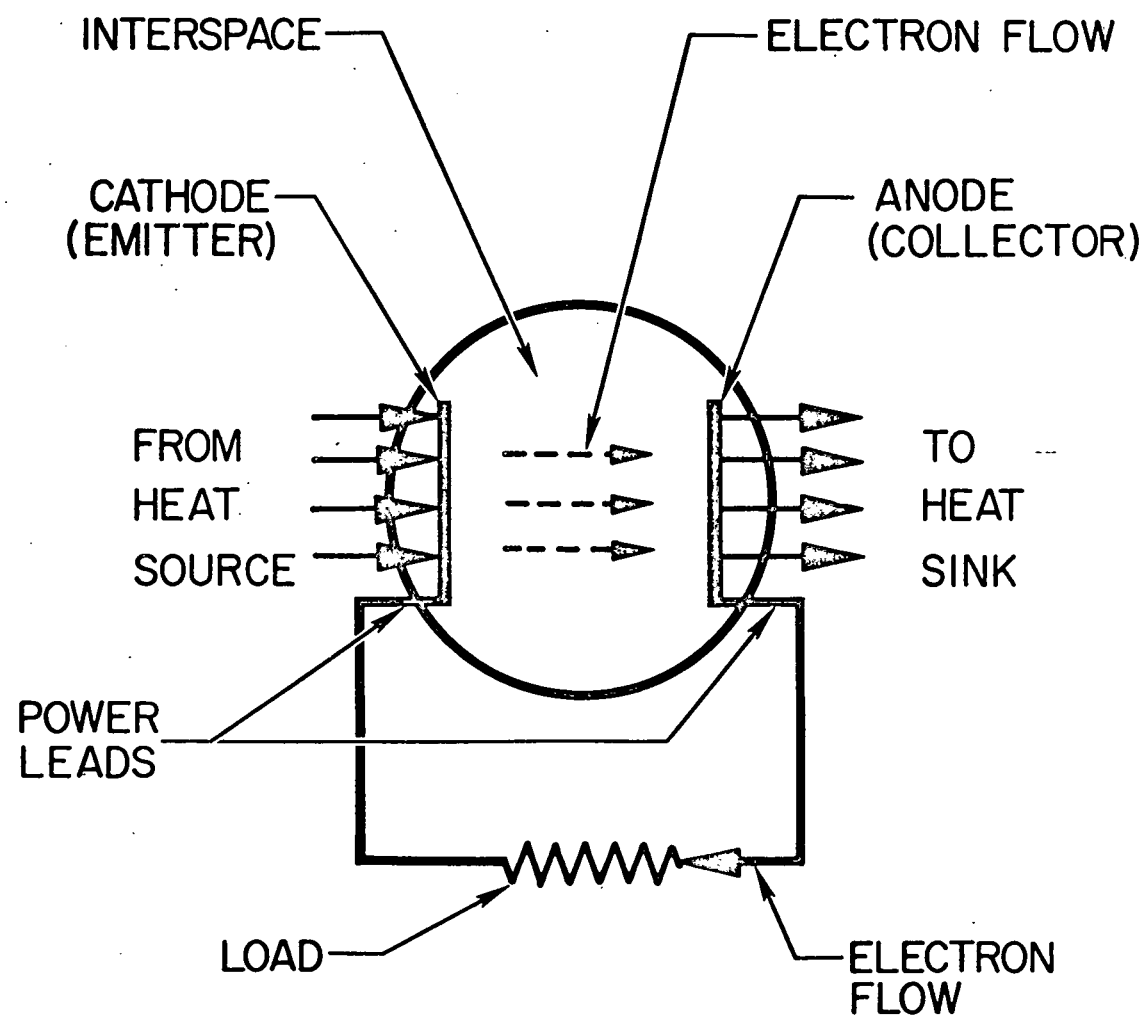
36. H.J. Caulfield, et al., First Summary Report, Basic Research in Thermionics, Part II, "Low Work Function Semiconductor Collectors," (1962).
37. C. Warner and N.S. Rasor, AI-6799, Paper B-II, (1961)
38. F.G. Block and J.J. O'Grady, Summary Technical Report, "The Development of a Low Temperature Vapor-Filled Thermionic Converter for Nuclear Applications," (1962)
39. L. Yang and F.D. Carpenter, J. Electrochem. Soc., 108, 1079 (1961)
40. D.W. Levinson, ARF-2215-6 (1962)

## TABLES

- I. Figure of Merit of Elementary Emitter Materials
- II. Results of Tests of Coatings to Protect Refractory Metals from Oxidation when Electrically Heated in Air
- III. Results of Tests of Coatings to Protect Refractory Metals from Oxidation and Flame-Impingement
- IV. Typical Cesium Metal Analyses
- V. Atomics International Cesium Analyses

## FIGURES

- 1. The Essentials of a Thermionic Energy Converter
- 2. Potential Energy Diagram for an Idealized Converter
- 3. Performance Parameters for an Idealized Converter
- 4. Properties of Some Emitters



2-13-63

Figure 1. The Essentials of a Thermionic Energy Converter

00-15577



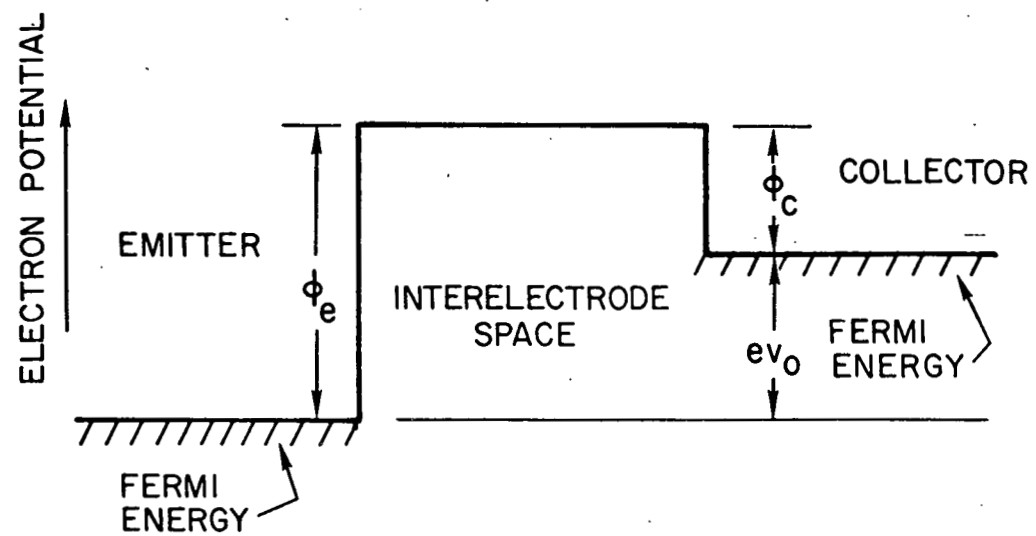
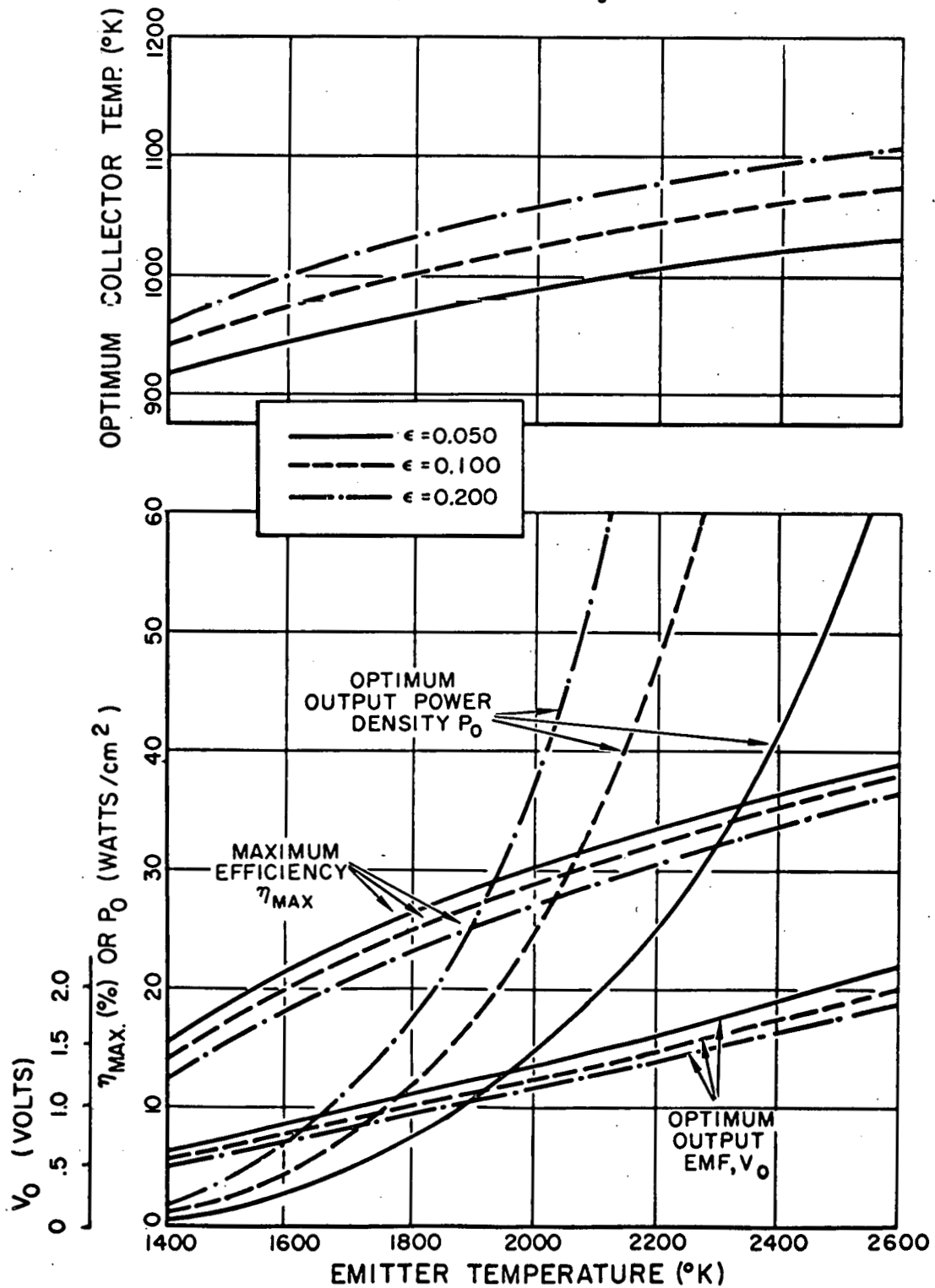


Figure 2. Potential Energy Diagram for an Idealized Converter

$$(\phi_{\text{coll}} = 1.7 \text{ ev}, K_{\text{gas}} = 0)$$



2/26/62

7590-A0331

Figure 3. Performance Parameters for an Idealized Converter

EMITTER TYPES			TYPICAL MATERIALS
ELEMENTARY (BARE)		METAL	
		COMPOUND	ZrC, UC
ADSORBED FILM	REFLUXED	METAL	Cs on { Ta, Mo, W Re, or Ir
		COMPOUND	
	DISPENSER	PORE DIFFUSION	PHILIPS CATHODES (Ba-W)
		SOLID DIFFUSION	Th-W

Figure 4. Properties of Some Emitters