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SEAL AND INSULATOR PROBLEMS
IN THERMIonic CONVERTERS
Summary Report
Contract NONR-33(00)
ARMOUR RESEARCH FOUNDATION
of
ILLINOIS INSTITUTE OF TECHNOLOGY
Technology Center
Chicago 16, Illinois

SEAL AND INSULATOR PROBLEMS
IN THERMIONIC CONVERTERS
Summary Report
Contract NONR-33400
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ARF 2215-6

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ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY
SEAL AND INSULATOR PROBLEMS IN THERMIONIC CONVERTERS

ABSTRACT

This study presents discussion of the materials requirements for seals and insulators for thermionic energy converters. Based on the requirements and published physical property data, aluminum oxide appears to be the most desirable insulator material at temperatures below its melting point.

The study includes a discussion of metal ceramic sealing technology and a bibliography of publications in the field covering 1959, 1960, and part of 1961.
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SEAL AND INSULATOR PROBLEMS
IN THERMIONIC CONVERTERS

I. INTRODUCTION

This report summarizes the results of a study program concerned with materials problems in seals and insulators for thermionic energy converters. Because the sole preoccupation of this study was with seals and insulators, other materials problems will not be discussed except where pertinent to the specific objectives stated.

The study was divided into three phases. The first of these consisted of examining published literature during the period May 1959 to May 1961. This served several purposes. It permitted statements, such as were made, of materials usage and problems therein to be assessed. Further, it assisted in the establishment of prototypic usages of seals and insulators. In addition, it brought into this author's focus the specific individuals at work in the field of thermionic energy conversion and the nature of their work.

The second phase consisted of a series of visits with selected individuals at work in the field and discussions with them regarding their problems and experiences. This was facilitated by sending a written questionnaire to a list of contractors; the nature of the replies eliminated those not at the time concerned with the engineering aspects of the devices.

During the course of the study the benefit of the experience of many other individuals at work in the field was obtained by personal contact at meetings devoted to the subject of thermionic energy conversion.

The actual experiences of the people contacted materially aided in the determination of the requirements to be met by insulator and seal materials. This is, to some degree, implicit in the energy converter design but, to a degree, also determined by actual device performance and the influence of the physical properties of the insulators and sealing systems thereon.

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As a result of an analysis of the findings of this study, recommendations are made for research programs, the results of which would help eliminate many difficulties likely, in this author's opinion, to appear in production devices operated at anticipated power levels for the requisite times. Such was, in fact, the principal objective of this program. This constitutes the third phase of this study.

II. THE LITERATURE SURVEY

The literature survey covered the two-year period between May 1959 and May 1961. The survey exhaustively covered the following publications during this period:

- Proceedings of IRE
- Transactions of IRE
- Journal of Electronics
- Review of Modern Physics
- Journal of Applied Physics
- Philips Research Reports
- Journal of the Optical Society of America
- RCA Reviews
- British Journal of Electronics
- Bulletin of American Physical Society
- Revue Generale des Sciences Pures et Appliques
- Proceedings of the Royal Society
- Proceedings of the Physical Society
- Physica
- Comptes rendus
- TAB
- Electronics
- Nucleonics
- Chemical Abstracts
- British Journal of Applied Physics
- Advances in Physics

In addition, numerous references to articles were found within the published articles above and in the abstracts, and they were included in the annotated bibliography which appears in this report as Appendix I. The results of the literature survey were disappointing in the sense that the great majority of the articles made no reference or only broad and general reference to the seal and insulator materials and the specific methods employed in their attachment. The phrases "ceramic insulator" and "brazed seal" appeared repeatedly with no further reference to precisely which ceramic or which specific brazing methods. This information was obtained
during phase II of this study and will be discussed later. In several instances specific details were forthcoming in the literature and involved commercially available, high-alumina ceramic insulators brazed into Kovar (Fe-Ni alloy) with a silver-28w/o copper (BT) silver solder.

The task of defining prototypic usages of seals and insulators was rather clearly established during the reading phase of this program, and a single prototype was entirely confirmed during subsequent discussion with various contractors.

The present state of experience indicates that production prototype devices do not as yet operate at the power levels and for the periods of time ultimately desired. These devices "fail" in the sense that performance either deteriorates with time to an undesirable degree or in the sense that the device ceases to operate altogether. As yet, the investigation of these failures as to mechanisms has not been intensive enough to indicate whether any basic deficiency in seal and insulator materials is a primary cause. To be sure, instances in which insulators have cracked or shorted, or in which seals have leaked, have occurred. As frequently as not, the failure of the devices is attributable to other causes not involving in any way yet appreciated, the seal or insulator. Definitive failure analysis is one of the programs to be recommended as a result of this study.

III. DEVICE PROTOTYPES

Many energy conversion systems (and fully as many individual device designs) are under study. These distill very quickly down to two primary device geometries—concentric and parallel plate. It is not the purpose of this report to dwell upon the merits of and difficulties associated with each. Suffice it to say that both will very probably find ultimate use. That the basic requirements of the insulator and seal in each are largely the same can be appreciated by consideration of Figure 1. Shown therein are schematic drawings of the principal components of the two types of devices. The insulator is shown cross-hatched. No attempt has been made to show a cesium reservoir, but as it now appears cesium vapor will be present in both types of device. No attempt has been made to show a heat transfer system by which the emitter is heated or by which the collector is cooled. In ultimate cases in which the emitter is not a refractory metal such as W, Mo, Ta, or Cb (fissile

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FIG. 1 SCHEMATIC PROTOTYPE THERMIONIC ENERGY CONVERTERS.
Carbides show promise for both fuel element and emitter function in nuclear fueled devices, diffusion barrier rings may be needed between such materials and the insulator. These are now shown. Similarly, coatings or other diffusion barriers may be required where certain combustion gases under consideration have access to the seal or insulator on the outside of the device. These are not shown.

The principal functions of the seals and insulators are in all cases the following:

1. To support in the structural sense the emitter with respect to the collector.
2. To electrically insulate the emitter from the collector.
3. To provide a hermetic seal between the inside of the device and the ambient environment.

To be able to perform these three basic functions certain physical and mechanical requirements are evident. These are defined and limited by operating temperatures, the requirement of compatibility with other optimum materials of construction of the device components, the possible presence of the radiation spectrum of a nuclear reactor, the presence of cesium vapor, and mechanical needs demanded by the design of the energy conversion cell and the mission to be fulfilled. These materials requirements are discussed in the following section.

IV. MATERIALS REQUIREMENTS

The basic operation of a thermionic energy converter requires a high temperature at the emitter surface and a lower temperature at the collector surface. Since the energy converter can be regarded as a heat engine, it is desirable to have this temperature difference as large as possible. This is somewhat mitigated by other requirements, not the least of which is the ability of the materials of construction to withstand long functioning time at elevated temperatures. Because it is necessary to maintain a particular cesium vapor pressure within the device during operation, the collector will also be considerably above room temperature during operation but at such a temperature that negligible primary electron emission occurs. Thus, normally, emitter surface temperatures of the order...
of 2000°K and collector temperatures in the range 500°-1300°K are currently envisaged. To be sure, there are individual designs which fall considerably away from these numbers, but these serve to generalize the insulator requirements fairly well. Thus while individual designs attempt to minimize the temperatures reached by the insulator, the insulator and the alloys with which it is sealed to the emitter and collector may reach temperatures as high as 1000°K though usually not above 800°K. For this reason, in Fig. 1A the sealing connection to the emitter is shown made back along the emitter lead in rather than at or close to the emitter surface itself.

The location of the seal in the geometry represented in Figure 1 can determine the magnitude of temperature gradient across the insulator and hence the state of stress. If the emitter side is at a somewhat higher temperature (as it tends to be) the ceramic is kept in compression by the restraint imposed by the collector. This, is, of course, desirable from the structural standpoint. Presently, the maximum tolerable insulator-seal temperature is limited by the sealing alloys and not by the insulator material.

The insulator material itself may therefore in some designs reach temperatures closer to the emitter surface temperature. This is depicted in Fig. 1B.

In summary, the insulator must possess a reasonable value of electrical resistivity at temperatures which may reach as high as 2000°K. It is hard to establish a limiting value of electrical resistivity below which an insulator would not function adequately. A value of 100 ohm-cm at the maximum operating temperature would allow leakage currents of the order of 20 ma-volt⁻¹-cm⁻² of insulator for a 1/2 cm thick insulator. While this would perhaps be tolerable, reduction of the resistivity by as much as an order of magnitude probably would not be. The specific resistivity of candidate oxides ought therefore to be as much greater as possible than 100 ohm-cm at any temperature at which it is to function.

Because heat flow away from the emitter can be moderated by design of the emitter lead, and because this heat loss is a second-order loss, the thermal conductivity of the insulator is less important than the...
electrical conductivity. For this reason the thermal conductivity is not a principal screening criterion. It is generally desirable that the thermal conductivity be low.

The insulator-seal combination must operate in cesium vapor. It must therefore not react with the cesium, nor with other materials adjacent to it, nor with other converter materials which may condense upon it as a result of vapor transport or surface diffusion. This immunity to reaction means several things. Obviously, the electrical properties must not be disturbed. This implies that the solubilities of Cs (vapor environment); of Ni, Fe, Ag, Au, Cu, Ti (seal flange materials and brazing alloy constituents); and of emitter materials such as W, Ta, Mo, VC, and ZrC must be small. Especially important, the constitution of insulator-other material system must be such as to avoid low-melting eutectics or the formation of phases of high volatility. In addition, structural strength must not be adversely affected by reactions such as the above, or by simple chemical reduction.

The insulator-seal combination must possess similar "stability" in the presence of fission products likely to be encountered (rare earth metals, iodine, barium, strontium, and others) and should have a low capture cross section for both slow and fast neutrons.

The insulator material must, in addition, be fabricable as reproducibly dense material of reliable physical and mechanical properties, and it must be available—preferably readily available.

Thus if one were to start from scratch to select an insulator material, the choice would be—from temperature requirements and availability—limited to the refractory oxides Al\(_2\)O\(_3\), BeO, MgO, HfO\(_2\), ZrO\(_2\), CaO, BaO, UO\(_2\), and ThO\(_2\) and to BN and ZrSiO\(_4\).

Data of pertinence to an intelligent selection of suitable insulating materials are presented in Table I to VI inclusive. These tables were taken from a compilation by Goldsmith et al.\(^{(1)}\) unless otherwise indicated.

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## TABLE I

**ELECTRICAL RESISTIVITY OF SOME REFRACTORY MATERIALS**

<table>
<thead>
<tr>
<th>Material</th>
<th>Resistivity ($\rho$), ohm-cm</th>
<th>Temp., $^\circ$K ($\rho = 10^8$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>$&gt; 10^{15}$</td>
<td>4 x $10^9$</td>
</tr>
<tr>
<td>$\text{BeO}$</td>
<td>$\sim 10^{11}$</td>
<td>1.6 x $10^8$</td>
</tr>
<tr>
<td>$\text{CaO}$</td>
<td>3 x $10^7$</td>
<td>$10^6$</td>
</tr>
<tr>
<td>$\text{MgO}$</td>
<td>10$^{16}$</td>
<td>10$^{10}$</td>
</tr>
<tr>
<td>$\text{ThO}_2$</td>
<td>$&gt; 10^{10}$</td>
<td>3 x $10^4$</td>
</tr>
<tr>
<td>$\text{HfO}_2$</td>
<td>$&gt; 10^{10}$</td>
<td>10$^7$</td>
</tr>
<tr>
<td>$\text{ZrO}_2^{*}$</td>
<td>$\sim 10^8$ extr</td>
<td>$\sim 5 x 10^5$ extr</td>
</tr>
<tr>
<td>$\text{UO}_2$</td>
<td>$\sim 10^1$</td>
<td></td>
</tr>
<tr>
<td>$\text{BaO}$</td>
<td>6 x $10^7$</td>
<td>$10^5$</td>
</tr>
<tr>
<td>$\text{ZrSiO}_4$</td>
<td>$\sim 10^{13}$ extr</td>
<td>4 x $10^6$</td>
</tr>
<tr>
<td>$\text{BN}$</td>
<td>1.2 x $10^{12}$</td>
<td>2 x $10^7$</td>
</tr>
<tr>
<td>$\text{TiO}_2$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Data from ref. 1
extr = extrapolated
* 2% Mg stabilized
### TABLE II

**VAPOR PRESSURES OF SOME REFRACTORY MATERIALS**

<table>
<thead>
<tr>
<th>Material</th>
<th>1500°K</th>
<th>2000°K</th>
<th>2500°K</th>
<th>&gt;3000°K</th>
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</thead>
<tbody>
<tr>
<td>AI₂O₃</td>
<td>6 x 10⁻⁸</td>
<td>1 x 10⁻⁵</td>
<td>10⁻¹</td>
<td></td>
</tr>
<tr>
<td>BeO</td>
<td>7 x 10⁻⁴</td>
<td>2 x 10⁻⁸</td>
<td>10⁻²</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>760(a)</td>
</tr>
<tr>
<td>MgO</td>
<td>2 x 10⁻³</td>
<td>10⁻²</td>
<td>--</td>
<td>760(b)</td>
</tr>
<tr>
<td>ThO₂</td>
<td>8 x 10⁻⁸</td>
<td>3 x 10⁻⁶</td>
<td>5 x 10⁻³</td>
<td></td>
</tr>
<tr>
<td>HfO₂</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>ZrO₂</td>
<td>--</td>
<td>~ 10⁻⁶</td>
<td>6 x 10⁻⁴</td>
<td></td>
</tr>
<tr>
<td>UO₂</td>
<td>10⁻⁸</td>
<td>9 x 10⁻⁵</td>
<td>3 x 10⁻¹</td>
<td></td>
</tr>
<tr>
<td>BaO</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>ZrSiO₄</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>BN</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>

* Some of these data appeared in sources other than reference 1.

(a) at 3120°K
(b) at 3900°K
<table>
<thead>
<tr>
<th>Material</th>
<th>500°K</th>
<th>1000°K</th>
<th>1500°K</th>
<th>2000°K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>0.15</td>
<td>0.58</td>
<td>1.10</td>
<td>1.75 extr</td>
</tr>
<tr>
<td>BeO</td>
<td>0.15</td>
<td>0.60</td>
<td>1.15</td>
<td>1.80 extr</td>
</tr>
<tr>
<td>CaO</td>
<td>0.25</td>
<td>0.85</td>
<td>1.65</td>
<td>2.50 extr</td>
</tr>
<tr>
<td>MgO</td>
<td>0.25</td>
<td>1.00</td>
<td>1.75</td>
<td>~2.8 extr</td>
</tr>
<tr>
<td>ThO₂</td>
<td>0.15</td>
<td>0.65</td>
<td>1.25</td>
<td>1.75 extr</td>
</tr>
<tr>
<td>HfO₂</td>
<td>0.10</td>
<td>0.75</td>
<td>1.20</td>
<td>1.60 extr</td>
</tr>
<tr>
<td>ZrO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volume changes very erratic unless stabilized</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UO₂</td>
<td>0.20</td>
<td>0.70</td>
<td>1.35</td>
<td>~2.00 extr</td>
</tr>
<tr>
<td>BaO</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>ZrSiO₄</td>
<td>0.06</td>
<td>0.33</td>
<td>0.68</td>
<td>--</td>
</tr>
<tr>
<td>BN</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Strongly anisotropic</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

extr. = extrapolated
TABLE IV (1)
THERMAL CONDUCTIVITY
OF SOME REFRACTORY MATERIALS

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal Conductivity, cal/sec-cm-*K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>500°K</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.045</td>
</tr>
<tr>
<td>BeO</td>
<td>0.034</td>
</tr>
<tr>
<td>CaO</td>
<td>0.024</td>
</tr>
<tr>
<td>MgO</td>
<td>0.05</td>
</tr>
<tr>
<td>ThO₂</td>
<td>0.025</td>
</tr>
<tr>
<td>HfO₂</td>
<td>0.004</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>0.0038</td>
</tr>
<tr>
<td>UO₂*</td>
<td>0.09</td>
</tr>
<tr>
<td>BaO</td>
<td>--</td>
</tr>
<tr>
<td>ZrSiO₄</td>
<td>0.01</td>
</tr>
<tr>
<td>BN</td>
<td>0.071/0.03</td>
</tr>
</tbody>
</table>

* 80% dense
TABLE V\(^{(1)}\)

MELTING TEMPERATURES
OF SOME REFRACTORY MATERIALS

<table>
<thead>
<tr>
<th>Material</th>
<th>Melting Temperature, (^{\circ}K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(_2)O(_3)</td>
<td>2310</td>
</tr>
<tr>
<td>BeO</td>
<td>2725</td>
</tr>
<tr>
<td>MgO</td>
<td>3220</td>
</tr>
<tr>
<td>CaO</td>
<td>2840</td>
</tr>
<tr>
<td>ZrO(_2)</td>
<td>2980</td>
</tr>
<tr>
<td>HfO(_2)</td>
<td>3170</td>
</tr>
<tr>
<td>UO(_2)</td>
<td>3150</td>
</tr>
<tr>
<td>ThO(_2)</td>
<td>3450</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>1900 (Vitreous softens 1775)</td>
</tr>
<tr>
<td>ZrSiO(_4)</td>
<td>2823</td>
</tr>
</tbody>
</table>
**TABLE VI**

FREE ENERGIES OF FORMATION
OF PERTINENT OXIDES

<table>
<thead>
<tr>
<th>Material</th>
<th>Free Energy of Formation, kcal/gm-atom oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>500°K</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>-119</td>
</tr>
<tr>
<td>BeO</td>
<td>-132</td>
</tr>
<tr>
<td>MgO</td>
<td>-132</td>
</tr>
<tr>
<td>CaO</td>
<td>-139</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>-119</td>
</tr>
<tr>
<td>HfO₂</td>
<td>-121</td>
</tr>
<tr>
<td>UO₂</td>
<td>-119</td>
</tr>
<tr>
<td>ThO₂</td>
<td>-145</td>
</tr>
<tr>
<td>SiO₂</td>
<td>-94</td>
</tr>
<tr>
<td>H₂O</td>
<td>-52</td>
</tr>
<tr>
<td>Cs₂O</td>
<td>-54</td>
</tr>
</tbody>
</table>

* Unstable above 1700°K
As shown in Table I, Al$_2$O$_3$ and BeO are electrically superior to the other compounds, especially at temperatures above 1500°K. The last column in Table I lists the temperature at which the resistivity falls below 100 ohm-cm. This is above anticipated insulator temperatures for all but a few of the substances shown. MgO is next most nearly competitive, showing superiority below 1000°K but falling rapidly above this. The principal drawbacks are very high vapor pressure (see Table II), high coefficient of expansion (Table III), and general difficulty in preparing dense pure MgO in suitable form. This latter drawback will also eliminate zircon (ZrSiO$_4$) from further consideration. To be realistic at this point, one ought not to eliminate materials with specific resistivity which is satisfactory at temperatures below 1500°K because such materials might at present be quite useful if other requirements are met.

Thermal expansion properties for most of the oxides are of the same order of magnitude. Both ZrO$_2$ and HfO$_2$ behave erratically, because of allotropy, in this respect unless stabilized. HfO$_2$ can be directly eliminated in a nuclear environment. Boron nitride demonstrates strong anisotropy of behavior as a function of the pressing direction. CaO, sharing the same structural difficulties which eliminate MgO, also has a rather large expansion coefficient and is therefore less desirable than Al$_2$O$_3$ or BeO. No thermal expansion data for BaO could be found but, like MgO and CaO, it is difficult to prepare in strong, fully dense form.

UO$_2$ is known to deteriorate electrically when irradiated, the change being of the order of one order of magnitude (decrease) for an exposure of 10$^{18}$ nvt.\(^{(2)}\) Fission processes can be expected to degrade the electrical properties of ThO$_2$ in a similar manner. In summary, Al$_2$O$_3$ and BeO are the most desirable of all substances considered and are available.

It is no accident that virtually all of the insulators in use today are of Al$_2$O$_3$-based ceramics. Alumina represents the most realistic compromise between the needed properties of all of the candidate oxides. One material, specifically BeO, is competitive as an electrical insulator material but, because of toxicity and well-known catastrophic decomposition in the presence of traces of water vapor is less desirable ultimately.

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These data indicate clearly that the insulators could operate satisfactorily at considerably higher temperatures if reliable brazing techniques were known which would permit the brazed joint (seal) to tolerate the temperature. The data also indicate a clear superiority of Al₂O₃ at presently encountered insulator temperatures. This superiority is further abetted by the fact that the thermal conductivity of Al₂O₃ is lower than that of BeO by a factor of 3 at 2000°K. (1) The thermal expansion properties of the two oxides are virtually identical (Table III).

The data quoted are all for the purest and most dense form of the oxides available; and the numbers, especially the electrical and thermal conductivities, are susceptible to considerable influence by impurities. The general influence of impurities is to lower the electrical resistivity and thermal conductivity. This effect is in all respects similar to the influence of solutes on semiconductive solids in both direction and magnitude. It is therefore of importance to evaluate the influence of transmutative injection of impurities into Al₂O₃ at flux levels corresponding to power reactor operation. This is, of course, not a factor of concern for energy converters used outside of the reactor flux. Since high-alumina ceramics have been used rather than high-purity alumina by most thermionic converter investigations, it is obvious that at insulator temperatures in the 500°-800°K range the thermophysical properties of the alumina are not seriously degraded by the impurities normally present. These ceramics are nearly single-phase Al₂O₃ with the distributed phases isolated rather than continuous. The Al₂O₃ is therefore saturated, or very nearly so, with the solutes making up the other phases. The concern about degradation of the electrical resistivity by transmutation in a reactor may thus be academic until such time as allowable seal temperatures approach the 1200°-1500°K range since initial resistivities are found to be of the order of 10⁴ ohm-cm.

It should be mentioned that other insulating materials have been tried by workers in the field and, for any of several reasons, ultimately rejected in favor of Al₂O₃. Calcium oxide was evaluated at Los Alamos and was found to disintegrate, presumably by hydration. (3) High-purity HfO₂ is a relatively rare commodity, and no reports of superiority to ZrO₂ were found. Boron nitride has not been evaluated extensively. Two factors
would tend to predict that it will not compare favorably with $\text{Al}_2\text{O}_3$. The resistivity drops rapidly with temperature, changing from approximately $10^{-12}$ ohm-cm near 500°K to below $10^{-3}$ ohm-cm at 1800°K (compare $\text{Al}_2\text{O}_3$ in Table I). The thermal expansion coefficient, while small compared to $\text{Al}_2\text{O}_3$ in a direction normal to the pressing direction is anisotropic and nearly as large as $\text{Al}_2\text{O}_3$ in the direction parallel to pressing.\(^{(1)}\) This could pose troublesome thermal stress problems. Furthermore, there is very little experience pertaining to brazing BN to metals, and the material is relatively expensive in pure form.

There are other factors of concern. It is very likely that cesium vapor at a pressure of the order of a few millimeters of mercury will be present. Therefore, the insulating materials and sealing alloys must tolerate contact with cesium vapor for the 10,000+ hours ultimately required without deterioration. Aside from the rather primitive effect of electrical shorting by condensation of cesium into interconnecting pores or surface cracks, no deterioration of the alumina insulator other than discoloration was reported to the writer by any of the investigators interviewed\(^*\) which the investigators were willing to attribute to cesium.

Static exposures for short periods (10 min) of $\text{Al}_2\text{O}_3$, $\text{ThO}_2$, $\text{ZrO}_2$, $\text{CaO}$, $\text{MgO}$, $\text{HfO}_2$, and BN were reported\(^{(4)}\) to produce no visible attack at temperatures in the 866°K to 1083°K range at cesium pressures of 20 mm Hg.

Reactions with cesium are not to be expected if one examines the free energies of formation of the oxides, including cesium oxide. Pertinent data are given in Table VI. These free energies of formation are all expressed on a per gram-atom of oxygen basis. The numbers are thus directly comparable for balanced reactions written so as to involve a complete oxygen transfer. The numbers therefore reflect the stability of the oxides with respect to one another; the more negative the value, the greater the stability. Thus, according to the table, magnesium metal can, in principle, reduce $\text{Al}_2\text{O}_3$ at 500°, 1000°, and 1500°K (its oxide is more stable than that of aluminum) but cannot at 2000°K. Similarly, hydrogen

* A list of individuals will be found in Appendix II.
will reduce cesium oxide above 1000 K but not at 500 K. Cesium thus
would not be expected to reduce aluminum oxide (or any of those shown) at
any temperature visualized to be a useful insulator temperature. This is
not to say that reactions cannot occur, for these same data would not predict
the dissociation (reduction of BeO in the presence of water, and yet traces
of water are known to somehow catalyze the dissociation of BeO, as was
mentioned. This is because the data are for the reaction

\[
\text{Metal + oxygen } \rightarrow \text{oxide shown}
\]

and do not cover the possibility of intermediate reactions which may produce
very low activity products. The rare earth metals, on the other hand, would
be expected to reduce Al2O3. These may occur as fission products, and
while they would be required to diffuse out of the fuel element, reactions are
expected to occur if they do so. The free energies of formation of the
lanthanide series rare earth metal oxides run 5 to 15 kcal/gm-atom more
negative than Al2O3 at all temperatures from 500° - 2000°K.\(^5\) This is also
true of the actinide series some of which are 40 kcal/gm-atom more negative
at all temperatures.

Still other possibilities must be considered. At the higher
temperatures, especially, the vapor pressure over Al2O3 is finite (see
Table II). It is thus possible for oxygen to be present in the converter in
sufficient concentration to oxidize emitter, collector, and seal alloys,
resulting in the possibility of eutectic melting interactions between Al2O3
(or other insulator materials) and these other oxides. It is similarly
possible for the oxygen pressure to be high enough to produce Cs2O leading
to this same mechanism of deterioration of the alumina, aggravated by the
fact that the Cs2O is very low melting (<750°K) and could act, in addition
as an effective mass transfer medium. Grossman\(^6\) has calculated a value
of 4 x 10\(^{-9}\) as a limiting oxygen partial pressure above which Cs2O would
form at a cesium partial pressure of 10\(^{-2}\) atm at 1000°K. According to
Table III, this oxygen pressure could be expected near 1500°K over Al2O3.

It is not useful to push such analyses as these too far since
the actual insulators in use now, or likely to be, are not pure crystalline
Al2O3 but, as has been mentioned, commercial high-alumina ceramics.
These materials, which vary from 85% Al2O3 to over 97% Al2O3, are

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similar chemically and virtually identical constitutionally. They consist of a polycrystalline matrix of \( \text{Al}_2\text{O}_3 \) and isolated, dispersed phases which occupy less than 10% of the bulk volume. Typical of those commercially available--whether from Raytheon, Coors, Norton, or American Lava Corp.--are the Alsimag materials, some typical data for which appear in Table VII. While these values for the "alloyed" ceramics do indicate lower electrical resistivity values than for pure, dense \( \text{Al}_2\text{O}_3 \), they are still very usefully high, and inutility of these materials would be expected to occur by softening rather than by decrease of electrical resistivity to below \( 10^2 \) ohm-cm.

The principal reasons for making additions of \( \text{MgO}, \text{SiO}_2 \), and other oxides such as \( \text{TiO}_2 \) to produce the commercial high-alumina ceramics is to improve fabricability and general mechanical ruggedness after firing, and to facilitate the formation of a fully dense material. Thus, it is unlikely that unalloyed polycrystalline alumina of high purity will be especially suited to or available for the needs of thermionic energy converters. The 96% alumina ceramics which are found to be quite usable, though more difficult to braze than those of lower \( \text{Al}_2\text{O}_3 \) content, will be applicable to temperatures far higher than presently available brazing alloys will permit. This points to an obvious need for the development of high-temperature brazes, a recommendation following from this study.

The author found that particular metal-ceramic joining methods were in use by individual investigators in the field but that, where a particular method was employed, little if any experience had been accumulated with alternate methods. There is an extensive accumulation of experience with metal-ceramic joining for the temperature range of interest here. All of these methods involve establishing an initial bond to the ceramic via a metal or alloy chemically active enough to react with the ceramic and thereby establish a bond. In some cases, the brazing or filler alloy itself will do this. In others, the initial bond is established to provide a metalized layer, after which the braze is made between this layer and the metal component. A brief review of the state of this art is pertinent to the objectives of this study and, accordingly, is included as Appendix III.
TABLE VII

PROPERTIES OF SOME COMMERCIAL HIGH-ALUMINA CERAMICS(7)

<table>
<thead>
<tr>
<th>Property</th>
<th>85% Al₂O₃</th>
<th>96% Al₂O₃</th>
<th>100% Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>fully dense</td>
<td>fully dense</td>
<td>85%</td>
</tr>
<tr>
<td>Specific resistivity, ohm-cm</td>
<td>&gt; 10^{14}</td>
<td>&gt; 10^{14}</td>
<td>&gt; 10^{14}</td>
</tr>
<tr>
<td>300°K</td>
<td>3 x 10^6</td>
<td>3.5 x 10^6</td>
<td>2.7 x 10^8</td>
</tr>
<tr>
<td>973°K</td>
<td>4 x 10^5</td>
<td>6.8 x 10^5</td>
<td>8 x 10^6</td>
</tr>
<tr>
<td>1173°K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal conductivity, (cal-cm⁻¹ sec⁻¹ °K⁻¹)</td>
<td>0.04</td>
<td>0.045</td>
<td>0.004</td>
</tr>
<tr>
<td>Softening temp., °K</td>
<td>1713</td>
<td>1923</td>
<td>2323</td>
</tr>
</tbody>
</table>

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Consideration of the mechanical properties of oxide ceramics is germane to the present study. A rather extensive compilation of such information was recently published\(^8\) and will therefore not be included in this report. The information available in no way refutes the notion that Al\(_2\)O\(_3\) is the most desirable insulator material and that the principal current temperature limitation is imposed by the brazing processes rather than the insulator material.

It thus appears that the insulators and the sealing techniques now employed will be satisfactory at insulator temperatures up to 1000°K. There is still some question of the stability of the high-alumina ceramics over long time periods in the presence of molten Cs\(_2\)O, or of oxides of the other metals (especially the more volatile oxides such as MoO\(_3\)) present in the converter. This problem will become more potentially serious as allowable insulator temperatures increase. Such temperature increases will be permitted by development of brazing alloys which will tolerate the higher temperatures. The possibility of destructive interaction between cesium vapor, molten cesium, or Cs\(_2\)O and other metals (including the sealing alloys) of the liquid metal embrittlement variety\(^9\) also exists and must be evaluated.

V. CONTRACTOR EXPERIENCE

Many specific experiences with seals and insulators have been related in prior discussion. The great bulk of energy converter construction has been made with commercial high-alumina ceramics. In one instance an 85% Al\(_2\)O\(_3\) insulating ceramic was prepared by the investigator by melting, which performed satisfactorily and in a fashion altogether similar to commercial material.

Many common experiences were found. In all cases insulator-seal failures were encountered. These failures occurred in times usually below 200 hours of operation and consisted of obvious cracks in the ceramic, electrical shorting due presumably to cesium condensation, leaks or cracks in the seal, and, in one or two instances, failure of the seal over fairly large areas which suggested melting of the brazing alloy. In all cases, discoloration of the Al\(_2\)O\(_3\) was observed. In no cases were really definitive studies of the insulator-seal failures made, and so the mechanisms of
failure, such as were expressed, were really intelligent speculation. The
importance of failure analysis cannot be overemphasized, and a program
for this express purpose should be initiated.

The insulator-seal combination was in many cases a purchased, prefabricated item in which a Kovar flange formed an integral part of the assembly. These flanges were then brazed or heliarc welded to the metal components of the converter. In most instances where pre-prepared insulators were used, exact details of their fabrication were not available though it is likely that they were made by some variation of either of two methods discussed in detail in Appendix III. This is to say that either a metallized alumina (Mo-Mn, Pt, Au, Mo-Si) was brazed to a Kovar or stainless flange, or an active brazing alloy such as Ag-Ti, Cu-Ti, or Ni-Ti was used to wet and braze the ceramic component directly to the metal component. It was generally agreed that the lower (~35% Al₂O₃) alumina ceramics were easier to braze to (where seals were made by the contractor) than the higher alumina ceramics—easier in the sense that a higher yield of good seals was obtained with whatever process was used.

Where cesium attack was used as an auxiliary criterion of the desirability of a sealing system, the copper-rich brazing alloys performed well, gold and silver alloys were somewhat more visibly attacked, and nickel-gold alloys were still more definitely attacked. A nickel-titanium alloy braze was found to be useful at 900°C but was not evaluated in a cesium environment. The so-called BT solders (silver-copper eutectic) were very frequently used for brazing pre-metallized ceramics because of good flow and filling properties, but they are relatively low melting (779°C).

Some experience was had with graded seals—that is, seals in which the braze is a layered composite to provide a transition between the thermal expansion properties of the metal and ceramic components of the device. A Mo-SiO₂ mixture fired in a reducing atmosphere provided an effective graded seal between platinized Al₂O₃ (85%) and Mo metal.

The art of wetting ceramics with metal is established. At this point it would appear that brazing to an already metallized ceramic is straightforward. Better brazing alloys (high remelt temperature, reasonable ductility, good stability, and high strength) are needed if reliable seal
operation in a cesium atmosphere is to be achieved at temperatures above 1000°K for long periods. Such development should be undertaken. This study should be undertaken with the ultimate application to the higher alumina ceramics in mind since they now appear to be potentially more desirable for higher temperature applications.

VI. RECOMMENDATIONS

Throughout the preceding sections of this report recommendations have been made for research to provide solutions to current problems or to problems which appear to be imminent. These recommendations were justified as they were stated. In recapitulation they are:

1. A program of exhaustive and definitive analysis of seal-insulator failures. Such a study would determine, by chemical and detailed metallurgical analyses, the failure mechanism. The utility of such information for intelligently coping with recurrent seal-insulator failures and for anticipating future problems is obvious.

2. A program of study of interactions between rare earth metals and $\text{Al}_2\text{O}_3$ (and high-alumina ceramics*) at elevated temperatures. The amounts of these and other fission products are likely to be small in practice, but the possibility of catalytic dissociation of the $\text{Al}_2\text{O}_3$ should be determined. Recall that trace quantities of water in the environment cause massive dissociation of BeO.

3. A program of study to determine the possibility of eutectic or peritectic interaction between the above aluminas and other oxides which may come in contact in the converter. This should include molten Cs$_2$O and solutions of other ionic oxides (refractory metal oxides, nickel oxide, rare earth metal oxides, for example) therein. The structural deterioration which would attend any incipient melting of the insulator is potentially destructive of the device. While reasonably large quantities of material might be required, the presence of a liquid phase such as Cs$_2$O could act as

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* The high-alumina ceramics are constitutionally different from pure crystalline $\text{Al}_2\text{O}_3$. We have all (including the writer) been guilty of assuming that inference may be drawn to the behavior of one, based on published properties for the other. That this may be dangerous should be obvious.
an effective mass transport medium and lead to serious corrosion of this type in the operating times visualized.

4: A program of study of stress-corrosion type interaction between cesium and the other metals of construction of the devices. Liquid metal embrittlement is still not a well-recognized phenomenon. However, many cases of record exist of failure (cracking through) of structural metals and alloys at stresses below the typical operating stress level when wetted by liquid metals or their vapor. The cracking is often the only visible sign of interaction between the two—obvious dissolution, corrosion, or intergranular penetration being absent. This phenomenon may be responsible for unexplained cracking of the sealing alloys. This program is about to commence at the time of writing.

5. High-temperature brazing alloy development. Such a program would have the objective of development of brazing alloys which would provide reliable operation as a fully hermetic seal at temperatures above 1000°K. This would probably require new metallizing procedures which would logically be a part of such a program. The development would require cognizance of the environmental factors to be encountered.

In all cases, it is of paramount importance that this work be done expeditiously and carefully, with full cognizance of possible influence by radiation attending a power reactor environment. The importance of wedding the skills and insights of the physicist, physical metallurgist, and physical chemist in such programs cannot be overemphasized.

Respectfully submitted,

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David W. Levinson
Metallurgical Advisor
Metals and Ceramics Research
REFERENCES


5. A. Glassner, USAEC Publ. ANL-5750 (1957).


7. American Lava Corp., Alsimag ceramics chart No. 611.


APPENDIX I

ANNOTATED BIBLIOGRAPHY

Auer, P. L.
"Potential Distributions in a Low-Pressure Thermionic Converter"
A plane diode model of a low-pressure cesium-filled thermionic converter is treated. It is assumed that all ions and electrons are created at the surface of the hot emitter with a Maxwellian distribution corresponding to the cathode temperature. The charged species are then assumed to move through the plasma, consisting of electrons, ions, and neutral cesium atoms, as free particles under the influence of their mutual space charge field. A method is outlined by which the potential distributions corresponding to different operating conditions may be calculated completely. In this fashion the operating characteristics of the converter may be related to the self-consistent space charge potentials. Instabilities as possible source of the tube oscillations are briefly discussed.

Auer, P. L., and H. Hurwitz, Jr.
"Space Charge Neutralization by Positive Ions in Diodes"
The neutralization of electron space charge in diodes is analyzed on the basis of the assumption that the ion density is proportional to $e^{-eV/kT}$ where $V$ is the local potential and $T$ is the cathode temperature. The neglect of electron-ion collisions enables solutions for the potential variation between electrodes to be obtained by a single numerical quadrature. Curves are presented for the potential as a function of position for a series of values of the ratio $\alpha$ of ion to electron density at the potential minimum. It is shown that for a large range of tube parameters, the electron current reaches two-thirds of its saturated value when the ion density at the cathode is about one-third the quantity $I_s/eV_o$ where $I_s$ is the saturation current and $V_o = (2kT/e\pi m)^{1/2}$. The electron current saturates completely when the ion density at the cathode is slightly above 0.81 $I_s/eV_o$ for large electrode spacing and slightly below $I_s/eV_o$ for small spacing. The anomalous behavior of the potential as a function of position when $\alpha$ lies between 0.81 and unity leads to the possibility of more than one mode of operation for a given ion density at the cathode and also causes the tube current to increase rather than decrease with increasing electrode spacing under certain conditions. Since these phenomena occur only over a narrow range of tube parameters, the effect of electron-ion collisions may prevent them from being observed experimentally.

Barmat, M.
"Direct Conversion Applied to Nuclear Fission Sources"
Direct Conversion techniques appear to offer the best solution to applications where a low or moderate power source of small size, low weight, and long life is required. Some of the fundamentals of engineering nuclear heat sources and heat-to-electricity conversion devices are presented. Construction and performance details of existing devices are given, along with descriptions of some proposed designs.

Beller, W.
"300 KW Thermionic Generator by 1967"
News article.

"Construction of a Thermionic Energy Converter"
Describes design considerations for a Cg converter with coaxial geometry. Emitter materials were Ta or Mo, and the collector was copper. Thermal barrier rings fashioned from Kovar served the double purpose of matching the expansion coefficient of the high alumina ceramic used for electrical insulator. Components were joined by brazing, the metal-ceramic brazes requiring metallized ceramics.

Performance characteristics and manufacturing feasibility were established.

Blount, E. I.
"Some Aspects of Thermionic Energy Conversion"
A general description of the operation of a thermionic device is given, and operation at maximum power and efficiency is analyzed. The various modes in which diodes achieve these conditions are discussed. The effect of leads in reducing efficiency is discussed. Two single special cases are considered, and some graphs applicable to one of them are given. The analogy with thermoelectric devices is discussed in considerable detail.

Booth, K. H. V. and I. A. Harris
"The Effect of Elastically Reflected Electrons on the Characteristic of a Thermionic Diode"
The effect of the elastic reflection of slow (< 2 eV) electrons from the collector and the emitter of a planar diode on the potential distribution and the voltage/current characteristic is worked out. Both the 'exponential' and the 'space-charge limited' regions of the characteristic are treated, and for the exponential region some new tables have been computed which include the effect of electron reflection. The characteristic of an actual planar diode is calculated as an example and is compared with the experimentally determined characteristic.
It is concluded that the elastic reflection of slow electrons in a diode with an oxide-coated cathode has a major effect on the voltage/current characteristic and the electric field distribution. The determination of contact potential associated with the diode is also affected.

Breaux, O. P.
"Thermionics"

Some discussion of materials, though mainly with regard to emitter and collector.

Brooks, R. E.
Quarterly Report No. 2, 6 Sep-6 Dec. 1958 Contr DA 36-039-sc-81257
"Industrial Preparedness Measure. The Production of S-Band Tubes and Cavities"

Development of a Factory Scallop Schedule: The pencil-tube bulb-making equipment in factory five was modified and an unsuccessful attempt was made to produce bulbs. A new rf coil design was made and although it helped to overcome some of the problems, it was still not able to produce the same quality pencil-tube bulbs as are made for other tube types.

Evaluation of Beryllia Ceramic Insulator: A new lot of beryllia insulators has been received and evaluated for compressive strength in Instron tensile-strength test equipment, for heat conduction, and in life tests. The Instron test shows that the new beryllia insulator is the strongest part of the tube-anode line assembly; it withstands compressive forces at which all other parts either yield or deform. The new beryllia insulator also has an increased mass and hence lower resistance to heat conduction. Life tests of the cavity show that this results in lower operating temperature and greater life expectancy.

Carabateas, E. N., S. D. Lezaris, and G. N. Hatsopoulos
"Interpretation of Experimental Characteristics of Cesium Thermionic Converters"

Experimental V-I curves have been obtained from a 150w cesium thermionic converter. Two different kinds of V-I curves can be clearly distinguished. One, corresponding to a collision-free operation, is obtained when the cesium mean free path is of the order of three or more times the interelectrode spacing. The other corresponding to a sheath type operation is obtained when the spacing is of the order of 30 cesium mean free paths.

Coltman, J.
Westinghouse Engineer, 20: 102-104 (1960) July
"Thermionic Generators: Materials Are The Key To Their Development"

Principally a discussion of emitter materials and their determination of device efficiency.
Data regarding the evaporation rate of a thorium monolayer as a function of coverage and temperature taken at Bartol and from other sources have been reduced to absolute values and are plotted. Evaporation rates from a thorium monolayer become excessive when temperatures which would yield 100 amp/sq cm are approached; at 10 amp/sq cm evaporation may be tolerable for certain applications. Studies were continued regarding comparison of thermionic effects of a thorium monolayer on polycrystal and single crystal tungsten. The single crystal plane currently being studied is an 832 orientation. An apparatus for growing single-grain tungsten ribbons was completed and is in successful operation. Formation of the more oblique orientations is much more probable than that of 100, 110, or 111 planes. Attempts will be made to grow single grain specimens of other materials. A study of the thermionic properties of one specimen of ZrC0.80UC0.20 was made. Contrary to a previous report from another laboratory, the Richardson constant was found to have a normal value. Life tests on thorium impregnated tungsten matrix emitters show that operating lifetimes of 15,000 hours or greater can be expected at the 1.0 amp/sq cm and 2.3 amp/sq cm levels. A water-cooled diode has shown that, as expected, an emission of 10 amp/sq cm is obtainable at 1750 degrees C (brightness).

deHoffman, F., and R. W. Pidd
Electronics, 33: 78 ff (1960) Jan. 29
"Cesium Cell For Power Conversion"

General news article--no details as regards materials of construction.

Dobretsov, L. N.
"Thermoelectric Converters of Heat and Energy"

An analysis is made of three types of thermoelectric converters: the vacuum type of thermoelectric converter without electron volume charge compensation by positive Cs+ ions produced in surface ionization on the cathode; and the plasmic converter with electron volume charge compensation by positive ions. 23 references.

Dobretsov, L. N.
Soviet Physics, Tech. Physics, 5: 343-368 (1960) October
"Thermoelectronic Converters of Thermal Energy into Electric Energy"

An english translation of the above.

Dong, Ng. -V. (France, Comm. energie atomique)
"Direct Conversion of Nuclear to Electric Energy"
"Thermionic Power Converters"

The space charge theory of Langmuir is extended to include the effects of anode emission on the performance of a vacuum thermionic power converter. The basic equation is similar to Langmuir's $I = \eta$ equation, but unlike this equation, cannot be solved for the general case. Numerical solutions can be obtained in specific cases, and were obtained for several cases of interest. Calculations indicate that for a cathode temperature of 1400°K, back emission suddenly becomes appreciable for anode temperatures above 1100°K. If the cathode-anode work function difference is large, the back emission becomes significant at lower temperatures.

Dugan, A. F.
"Contribution of Anode Emission to Space Charge in Thermionic Power Converters."

The space charge theory of Langmuir has been extended to include the effects of collector emission on the performance of a vacuum thermionic power converter. The basic equation is similar to Langmuir's $I = \eta$ equation, but it involves two additional parameters which depend on the temperatures and thermionic properties of the electrodes. An iterative technique is described for obtaining solutions in specific cases, and some sample calculations based on hypothetical diodes are presented. The calculations indicate that the effect of the collector temperature is considerably more pronounced if the emitter-collector work function difference is large.

Enoch, J., and W. A. Ranken
"Experiments and Interpretation on Cesium Diodes"

The behavior of the cesium diode at low pressures is discussed theoretically on the basis of a simple model. An exact solution for the voltage and charge distribution based on the assumptions of the simple model is given, and a more general case is discussed qualitatively. Predicted current-voltage characteristics are compared with experimental results.

Fox, R., and W. Gust
"Thermionic Emission Characteristics of a Thorium Carbide Heat Converter"

The thermionic emission characteristics of thorium carbide in a cesium space charge neutralized diode geometry has been measured. A guard ring cylindrical diode was built using thorium carbide as the emitter and nickel as the collector. The cesium pressure was adjusted so that space charge neutralization occurred. The collector temperature was adjusted so that a monolayer of cesium formed on the collector. The power input of the diode heat converter was measured from the total power used in heating the emitter. This was checked with the power expended in heating the collector plus the power output of the tube. The two measurements were in agreement. The effective emissivity and the work function of thorium carbide was also measured. A converter efficiency greater than 15% and an electrical power output greater than 15 w/cm² has been obtained. Results and characteristics of the diode will be presented.
Franklin, R. N.
"Space Charge Neutralization and Thermionic Emission"

A theoretical discussion of factors influencing space charge density distribution for the case of plane parallel electrodes in the presence of positive ions.

Fried, T. D., and L. O. Neifinger
R-TP-0090-00870 Contr. AF 04(647)-309, October 26, 1959.
"Space Charge Limited Current Flow from a Plane, Plasma 'Cathode'."

The subject of this report is to derive an equation analogous to Langmuir's for the case where $kT_e/e$ is large compared to the potential difference between anode and cathode. Study is made of a simple case--plane, parallel geometry--for which an exact solution can be found.

Gaines, G. B.
"Investigations of Rare-Earth Oxide Cathodes"

The thermionic emission from 2 samples each of gadolinium oxide and neodymium oxide was determined. At 1450°C, the emission from one gadolinium oxide sample was about 1 amp/cm². At the same temperature, both neodymium oxide samples exhibited an emission of about 0.1 amp/cm².

The oxides were put on rhenium metal by electrophoresis. Future work will involve the emission from mixtures of the two oxides.

Garvin, H. L., et al.
J. Appl. Phys. 31. 1508 (1960)
"Generation of Alternating Current in the Cesium Column"

It is found that over a substantial range of the power curve an ac signal is also being produced. This phenomenon is briefly discussed. Not concerned with material problems.

Glasstone, S., Compiler and Editor
LAMS-2396, Contr. W-7105-eng-36, July 1959

The in-pile test assembly is described, and the results of the test of the plasma thermocouple cell are given. A new type of plasma thermocouple cell was designed. Brief reports are given of other equipment, neutronics studies, and studies of carbides and carbide systems.

Glasstone, S., Compiler and Editor
LAMS-2364, Contr. W-7405-eng-36, October 1959

A "standard" design of a plasma thermocouple for in-pile testing was studied. This utilizes a ZrC-UC fuel pin 1/4 in. in diam. by 1 in. long, centered within a zirconium collector, leaving a 1-mm annular gap.

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(There was no Page 32 located in original document.)
\[ \phi = 2.94 \text{ ev and } A = 33 \text{ amp/cm}^2 \text{ deg}^2 \] was indicated. There is evidence that the energy required for electrons to escape at low fields might be several tenths ev higher than the 2.94 ev value.

Harvey, R. J., and G. N. Hatsopoulos
Ballistic Missile and Space Technology, 2: 409-41 (1960)
"Isotopic Fueled Thermionic Generators."

The progress of the thermionic generator phase in the SNAP-3 program is outlined. The advantages of the close-spaced vacuum diode over the cesium plasma diode are discussed; the vacuum diodes are usable over a wide power range, whereas the cesium devices would be limited to special applications. The performance of a vacuum diode thermionic converter is analyzed; thermal efficiency, radiation heat transfer, electron cooling, heat losses, optimum efficiency are considered. Optimum characteristic design charts were computed for a family of diodes having a spacing of 0.001 cm, a collector work function of 1.85 v, and a collector temperature of 900°K. The criteria for choosing the isotope as the heat source are discussed, a study of the available isotopes shows only two isotopes to be suitable for thermionic generators. Cm\(^{242}\) and Pu\(^{239}\). A two-stage electrically heated generator was built and tested electrically and dynamically (acceleration and vibration tests), and some of the results are reported.

Hatch, J. E.
NASA TN D575, Nov. 1960
"Analysis of Magnetic Triodes for Direct Energy Conversion Having Flat-Plate Cathodes and Anodes at an Arbitrary Angle."

No discussion of material problems.

Hatsopoulos, G. N., and E. Langberg
"Thermoelectron Engines: Future Power Sources?"

Thermoelectron engines - The basic feature of the thermionic converter is that it partially converts kinetic energy of emitted electrons into useful electrical energy which can be dissipated in an external load. There is a similarity between the thermionic converter and the steam engine. In the steam engine, water vapor works against a piston or turbine blade; in the thermionic converter electrons are evaporated from an emitter surface and do work against a retarding electric field. Thus, these converters can be thought of as thermoelectron engines.

Thermoelectron engines are technologically similar to vacuum tubes. Also, they are comparable in size, weight, and ruggedness to tubes having the same power handling capacity. Since thermoelectron engines contain no moving parts, they are likely to be especially useful in remote applications where freedom from maintenance will give them a distinct advantage over conventional generating devices.

Hatsopoulos, G. N., J. Kaye, and E. Langberg
"Prediction of Optimum Performance of Vacuum-Diode Configuration of Thermionic Engines"

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ARF 2215-6
A basic analysis is given of the close-spaced vacuum diode operating as a direct converter of heat to electricity. This analysis is arranged to yield the characteristics of this engine when operating at maximum efficiency.

Hellund, E. J.
TN-E-1FR049-332, Project 4750, AFOSR TR 59-103, Contr. AF 49 (638)-332, April 24, 1959
"Fundamental Investigations of Electrical Power Sources. Volume I: Morphology"

A survey and classification was made of various types of power sources which might possibly be used in conjunction with propulsion systems for space vehicles. Codification of these types was systematically developed with the objective in mind of providing a convenient classification by means of which a rapid evaluation of any "new" proposals can be made. A number of possible new power systems and propulsion systems were brought out. The primary goal in evaluation of all systems is to obtain an unambiguous upper limit to performance, equivalent to that derived for heat engines on the basis of the Carnot cycle. It can be readily observed from the examples given that the basic conservation laws of physics are usually sufficient to settle the question of "feasibility" in regard to any proposal.

Hellund, E. J.
TN-E-3FR049-332, Project 4750, AFSOR-TN-59-429 (ASTIA AF-214, 779), April 24, 1959, Contr. AF 49(638)-332
"Fundamental Investigations of Electrical Power Sources. Volume III; Direct Electrical Converters"

Theory, structure, performance data, and applications of photovoltaic cells and thermoelectric devices are discussed. Other direct electrical converters are briefly mentioned.

Hensley, E. B
"Thermionic Emission Constants and their Interpretation"

A critical review of the procedures used in the measurement and interpretation of thermionic emission with particular reference to nonmetallic cathodes is presented. Definitions are proposed for the terms "true work function," "effective work function," and "Richardson work function."

Hernqvist, K. G.
Nucleonics, 17: 49-53 (1959) July
"Thermionic Converters"

Lays emphasis on the fact that thermionic energy conversion devices can be built from existing materials with no especially serious problems or drawbacks.

Hernqvist, K. G.
"Rocket's Exhaust Heat is Turned to Electric Power: Thermionic Generator"

An electronic generator with no moving parts, designed to convert the heat of a rocket exhaust directly to electric power to run steering controls of a
rocket or guided missile, was announced recently by the Radio Corporation of America (RCA) and the Hunter-Bristol Division of Thiokol Chemical Corporation.

Hernqvist, K. G.
RCA Rev. 22: (1961) March (No. 1)
"Plasma Synthesis and Its Application to Thermionic Power Conversion"

The work described in this paper pertains to thermionic energy converters (T. E. C.) in which the electron space charge is neutralized by positive-ion injection into the inter-electrode space. A novel method of representing the potential energy diagram for the plasma is described; this method facilitates the understanding of the interaction between plasmas and solids. Based on this model, a detailed plasma energy balance for different types of cathode materials is given. Results of a theoretical analysis of the space-charge states corresponding to a single potential maximum or a single potential minimum with an arbitrary potential between the electrodes. The different space-charge states that are possible when ions and electrons are injected into the interelectrode space are discussed.

Experimental studies of plasma synthesis are described where ions and electrons originate at different sources. The experimental tube operating as an energy converter had a power output of about 0.55 w/cm^2 at a cathode temperature of 1100°C.

Hirsch, R. L.
"Effect of Interelectrode Spacing on Cesium Thermionic Converter Performance"

In the cesium thermionic converter, energy-dissipating interactions occur between emitted electrons and the "plasma" thus reducing the net electrical output. These interactions can be suppressed by reducing either the cesium pressure or the distance between electrodes. At very high emitter temperatures cesium is utilized primarily to neutralize space charge, and its effects on emitter work function are small. In this range the cesium pressure can be varied to approach emission limited performance. However, for operation in the moderate temperature range (1400° to 2000°C), cesium may be utilized to modify emitter work function as well as to reduce space charge. In this mode of operation the cesium pressure is fixed by these requirements, and departure from this optimum pressure results in drastic reductions in converter output. The interelectrode spacing then becomes a variable of great importance.

Houston, J. M.
"Theoretical Efficiency of the Thermionic Energy Converter"

An analysis of the efficiency of the thermionic energy converter is given in terms of \( V_C \) and \( V_a \), which represent the potential differences between the top of the potential barrier between the electrodes and the Fermi levels of emitter and collector, respectively. The analysis applies to all vacuum converters, and to gas-filled converters when the gas pressure is low.
enough so that the electron mean free path is greater than the emitter-collector spacing. In special cases, the analysis may also apply at higher gas pressures. It is shown (with certain assumptions) that optimum values of \( V_a \) and \( V_g \) exist. For \( V_a \), the optimum is determined principally by radiation losses. It is concluded that no fundamental reason exists why efficiencies of 30 per cent or more cannot be realized in converting heat to electricity by this method. This presumes no unusual losses inherent in existing material of construction.

Houston, J. M.
"Thermionic Converters"

The General Electric work on thermionic converters was detailed by Dr. J. M. Houston, who described the various means for overcoming space charge, particularly the use of cesium vapor for ionic neutralization in both low- and high-pressure designs. He observed that while efficiencies of 5 to 8% are now achieved, in 1915 the efficiency was 9 to 10%.

Howard, R. C., L. Yang, and L. Garvin
"A Nuclear Thermionic Fuel Element Test"

Hurst, H.
"Apparatus for Generating Electricity by Thermionic Emission"

A thermionic cell with two or more electrodes in a heat-resisting envelope, which may be evacuated or contain gas or vapor, is heated externally to cause a flow of electrons from an emissive electrode to a collector electrode such that, when these electrodes are connected through an external load circuit, a net current flows through the system. Pellets of radioactive material may be embedded in the emissive material or external irradiation may be carried out by exposure to a radiation source and may be made selective by shielding. Cells may be connected to systems either in series or parallel to increase voltage or current.

"Space Charge Neutralization by Fission Fragments in the Direct Conversion Plasma Diode"

Calculations are presented which show that fission fragments can produce a partial plasma in a noble gas and that the resistivity (4 ohm-cm) of the gas could be low enough to operate the system as a direct conversion plasma diode.

Jamerson, F. E.
IRE, Intern. Conv. Record Pt. 9, 1960. 66-71
"Noble Gas Plasma Diode Thermionic Converter"
A plasma thermionic converter in which a noble gas replaces Cs vapor is possible. The converter utilized a UC reactor fuel element as the cathode and source of heat and an Al anode. Ar was used as the filler gas. Fission fragments ionized the Ar to form the plasma. Under experimental conditions a cell of 0.02-amp short-circuit current, 1.1-v open-circuit voltage was obtained. The converter should change from noble-gas plasma to Cs-vapor plasma as the pressure of Cs from fission exceeded the initial pressure of noble gas filling.

Jamerson, F. E.
"Thermionic Direct Conversion Studies with Noble Gas Plasma Diode"

Johnson, F. M.
RCA Rev. 22: 21(1961) March
"Direct Conversion of Heat to Electromagnetic Energy"

Johnson, F. M.
RCA Rev. 22: 21(1961) March
"Direct Conversion of Heat to Electromagnetic Energy"

The conversion of heat into electromagnetic energy is achieved by utilizing the intrinsically unstable space-charge properties of thermionic cesium plasma diode. Experimental studies of this phenomenon are described. A physical model for the observed relaxation oscillations is proposed which is in qualitative agreement with experiments.

Kaye, J., and J. H. Welsh
Direct Conversion of Heat to Electricity
John Wiley and Sons, N. Y., 1960

The following topics are discussed: thermionic engines--high vacuum, thermionic engines--low pressure, magnetohydrodynamic converters, semiconductor devices, and fuel cells.

Kmetko, E. A.
"Anomalous Thermionic Emission of Some Borides and Carbides of Rare Earth and Transition Elements"

Thermionic emission constants, $A^*$, up to several thousand times larger than the $A^*_{\text{metal}}$ (120 amp/cm$^2$*K$^2$) predicted theoretically for metals have been reported for several compounds involving transition metals and rare earths with boron and carbon. It is suggested that such anomalously large emission constants, as well as some anomalously small ones, are due to the relatively large distances between metal atoms as a result of which the energy bands originating from the incomplete atomic f and/or d sublevels are narrow enough for nondegeneracy to occur in the experimental temperature range.

Kuczynski, G. C
J. Appl. Phys. 31: 1500 (1960) (Letter)
"Anomalous Thermionic Emission From UC and (ZrC)$^{0.8}$ (UC)$^{0.2}$"
Thermoelectric cells, as an auxiliary power supply in satellites and space missiles, were studied. Neutralizing the space charge at high-current densities, reducing the evaporation rate of the cathode, maintaining the work function of the anode at a low value, minimizing all heat and electrical losses, and converting the cell output to the voltage and current desired were the problems investigated. The resonance ionization methods showed the most promise in neutralizing the space charge. Radiation from the cathode was minimized by using highly polished reflectors and making the anode a highly reflecting surface. Progress was also made toward solution of the other problems. (NSA, 1960, No. 17980)

Leisenring, J. G.  
SAE Preprint 159 C (1960) April  
"The Thermionic Power Converter and its Applications"

A simplified description of the thermionic converter and its operating principles are presented to provide a basis for the discussion of thermionic converter applications. Application requirements and limitations are discussed in relation to the converter as an electrical power generator or high-temperature sensor in space, airborne, ground or sub-surface system.

Leisenring, J. G.  
"Collector Design for Solar-Thermionic Space System"

This paper describes thermionic converters, their operating characteristics, and their use in power conversion systems. It presents detailed analysis of a solar-thermionic space power system. A solar collector design study is part of this analysis.

Leovic, W. S., and M. W. Mueller  
Elec. Eng. 79: 979(1960)

Describes solar Cs diode, with a Ta emitter and Cu collector. Uses alumina spacers, rings, and insulators, brazing where required, to fasten to Kovar and other metal parts. Emphasizes need for cleanliness in fabrication. Performance of diode is described.

Lewis, H. W., and J. R. Reitz  
"Thermoelectric Properties of the Plasma Diode"

The thermoelectric properties of a gas diode containing a high density of positive ions are discussed in some detail. The complete circuit of diode and load is treated as a thermocouple. Expressions for both the Seebeck emf and thermoelectric conversion efficiency are obtained as a function of cathode and anode temperatures. The interior of the diode is divided, for convenience, into three regions: (1) the emitter sheath, (2) main body of plasma, and (3) the collector sheath. The collector sheath is the region of large temperature gradient; the approximate temperature distribution in the sheath is obtained by solving a greatly simplified heat-conduction equation. Finally, the results of this analysis are compared with experiments performed by Grover, Roehling, Salmi, and Pidd.
Lewis, H. W., and J. R. Reitz
"Open-Circuit Voltages in the Plasma Thermocouple"

Extends earlier work to a plasma diode in which a "trickle current" flows, small compared to the cathode emission but large compared to the anode emission current. An expression obtained for the emf of the cell reduces to kT log (ja/j), in the case when electrons near the anode have the temperature T of the cathode (j = current density of the anode, ja = saturation current density anode would emit at temperature T). The analysis is used to explain the results of Pidd and others on the effect of introducing cesium vapor, and the advantage of using a cylindrical diode.

Lewis, H. W., and J. R. Reitz
"Efficiency of the Plasma Thermocouple"

The efficiency of a thermionic converter containing cesium ions is calculated for the regime in which the plasma density is sufficiently high so that the random current density, nev/4, is large compared to the actual current density. Under these circumstances positive space-charge barriers are set up at the cathode and anode, and the plasma region is many free paths in length. The output voltage $V_L$ is determined for various currents by a consistent solution of the electrical and thermal conduction problems. The efficiency of the over-all circuit is

$$n = \frac{V_L - IR_0}{V_L + W_a + 2(k/e)T_a + (P_F + P_j)/I'}$$

where $W_a$ is the work function of the collector, $T_a$ the temperature of the electron gas in contact with the collector, $P_F$ the radiation loss through the thermocouple, $R_0$ and $P_j$ the resistance and power loss, respectively, of the lead wire which completes the circuit. Efficiencies up to 32% are obtained for a typical thermocouple circuit.

Lewis, H. W., and J. R. Reitz
"Efficiency of the Plasma Thermocouple"

The efficiency of a thermionic converter containing cesium ions is calculated for the regime, in which the plasma density is sufficiently high so that the random current density, nev/4, is large compared to the actual current density. Under these circumstances, positive space-charge barriers are set up at the electrodes, and the plasma region is many free paths in length. The output voltage $V$ is determined for various currents by a consistent solution of the electrical and thermal conduction problems. The efficiency of the thermocouple is then deduced from the calculated current-voltage characteristic and the appropriate electron temperature distribution. Over-all efficiencies up to 32 per cent are predicted for a typical thermocouple circuit.
Lindley, B. C.
Nuclear Power, 5: 100-103 (1960) June
"The Direct Generation of Electricity, Part I"

Sources of power used at present are discussed, and direct conversion of thermal energy into electricity is concluded to be feasible because of reduced costs. Direct conversion may be accomplished by a thermoelectric generator (assembly of solid semiconductor thermocouples) and by a thermionic generator in which electron emission from cathode to anode occurs. Equations are derived for the thermal efficiencies of the two generators, and graphs are given for the efficiency vs. temperature for various arrangements of thermoelectric generators with reactors. It is concluded that the only systems worthy of further study are the reactors with thermoelectric or thermionic fuel elements.

Lindley, B. C.
Nuclear Power, 5: 80-83 (1960) July
"The Direct Generation of Electricity. Part II"

Generation of electricity by magnetohydrodynamic (MHD) means and by an electrochemical fuel cell is discussed. (1) MHD. If a stream of an electrically conducting fluid interacts with a magnetic or electric field, the kinetic energy of the stream may be converted to electric power. In order to do this, the fluid must be a gas and, at low gas temperatures, a substance with low ionization potential must be injected in order to induce ionization, e.g., an alkali metal such as Cs. Several conceptions of a MHD generator are described, in which transverse and radial magnetic fields are used and in which induction and pulsed streams are used. An estimate of the duct size of a 100-Mwe MHD generator is presented as a function of the gas electric conductivity. (2) Fuel Cell. The fuel is supplied to the cathode and the oxidant to the anode, the two electrodes being connected through an electrolyte. An important disadvantage of such a cell is its low dc voltage even with extensive series connection. The chemical reaction rates will have to be increased for economic operation. There are three fuel cell types: cells using \( \text{H}_2 \) and \( \text{O}_2 \) with aqueous electrolytes, redox cells, and high-temperature cells operating above 500°C with molten salts. Fuel gases from coal or oil gasification processes (\( \text{H}_2, \text{CO}, \text{hydrocarbons} \)) appear to be promising in conjunction with a high-temperature fuel cell. The best direct generation methods are concluded tentatively to be a gas-cooled reactor with thermionic diode fuel elements and a MHD generator coupled to a very high-temperature reactor. Fuel cells may find application as an economic means of increasing the operating load factor of nuclear installations.

Luke, K. P. and F. E. Jamerson
"Low-Frequency Oscillations in a Filamentary Cathode Cesium Diode Converter"

Mazur, P.
"A Mathematical Model of a Neon-Cesium Vapor Thermionic Diode"
A differential equation for the electrostatic potential in a gas diode has been derived and numerically integrated on the IBM 704. The gas consists of a neon-cesium mixture of which the neon acts as a good scatterer of cesium but a poor scatterer of electrons. The cesium ions, consequently, distribute themselves in a complete Boltzmann distribution while the electrons migrate from emitter to collector with a mean free path for "close" collisions greater than the diode spacing.

Moizhes, B. Ya., and G. E. Pikus
Fizika Tverdogo Tel. 2: 756-774, (1960) April (in Russian)
"On Theory of a Plasma-Thermoelement"

Physical processes in the plasma thermoelement were investigated considering local thermodynamic equilibrium and disregarding the generation and recombination in the volume. In the latter case the current was determined by the diffusion of carriers and the load intensity by the contact potential difference. Calculations were made of the volt-ampere characteristics and of efficiency factors for cases in which energy exchange between electrons and atoms is absent and for cases in which the plasma is isothermal.

Morgulis, N. D. and A. G. Naumovets
Fizika Tverdogo Tela, 2: 537-542 (1960) March (in Russian)
"Application of Thermionic Emission for Direct Transformation of Heat into Electrical Energy"

Direct transformation of heat into electric energy was attempted by applying thermionic emission from cathodes in cesium vapor. The method utilizes the partial compensation of electron volume charge by Cs ions, which appears due to thermal ionization at uncoated areas on the cathode, producing a short-circuit electron current and considerable energy transformation efficiency. The thermal ionization is also used in studies of the absorption characteristics of coated cathodes with various coatings.

Morgulis, N. D. and A. G. Naumovets
Radioteknika i Elektronika (USSR) 4: 1065-6 (1959) June (in Russian)
"The Problem of Converting Thermal Energy into Electrical Energy Using Thermionic Emission"

Essentially a review of the principles involved. No cogent discussion of materials problems pertaining to seals and insulators.

Quarterly Report No. 4, 1 July-30 September, 1959 of David Sarnoff Research Center, Princeton, N. J.
"Thermionic Emission Studies"
(Contract DA 36-039-sc-78155)

The thermionic emission from the rare earth oxides Y$_2$O$_3$, La$_2$O$_3$ and Sm$_2$O$_3$ was measured, and the corresponding $\phi$ and $\Lambda$ values have been derived. Work on these materials will be discontinued, at least for the
time being. Contact potential differences between vacuum-cleaved silicon crystals and a tungsten ribbon were measured. Work function values were obtained for three crystals containing different amounts of impurities. By cleaving each type of crystal at least twice, it could be shown that the method leads to reproducible values for each sample. A grown n-p-n Si junction was used as a target in a low-velocity beam scanning tube. For the first time, the p-n junctions were observed on the display tube without using a biasing potential across the crystal. Current-voltage characteristics were measured in a new Cs activated tube. Measurements on this and earlier tubes were correlated, and a provisional interpretation of the results obtained to date is suggested.

Nergaard, L. S.
RCA Rev. 20: 191-204 (1959) June
"Thermionic Emitters"

A vacuum tube is considered as a chemical system undergoing continuous reaction. It is proposed that the emitter reacts with everything in the tube via the gas phase. If the tube contains reducing agents in the form of getters or electrodes of reducing metals such as titanium, these reducing agents help maintain cathode activity via the gas phase. Thus getters not only prevent poisoning but contribute to keeping the emitter in the reduced state necessary for emission.

Nottingham, W. B.
J. Appl. Phys. 30: 413-417 (1959) March
"Thermionic Diode as a Heat-to-Electrical-Power Transducer"

The high-vacuum thermionic diode is shown to be capable of converting heat to electric power. For this purpose, a low-work-function collector, a small spacing and sufficient temperature difference between the emitter and the collector are necessary. A detailed understanding of both thermionic emission and space-charge phenomena is needed for evaluating the effectiveness of this transducer. With \( V_f \) defined as the critical bias potential that gives zero potential gradient at the collector, the maximum available power is given by the relation \( 3.7 \times 10^6 V_f^{1/2} (V_f - V_c/2) \) watts/m\(^2\). Here, \( V_f \) is the voltage equivalent of the temperature \( T/11,600 \). In the range of emitter temperature from 1200-1700°K, the most optimistic conversion efficiency lies between 3 and 4 per cent for a diode of 0.001-inch spacing. With a suitable choice of emitter inhomogeneity, the introduction of cesium vapor should improve the efficiency of this device.

Nottingham, W. B., G. N. Hatsopoulos, and J. Kaye
J. Appl. Phys. 30: 440-441 (1959) March
"Addendum Remarks on a Diode Configuration of a Thermoelectron Engine"

1. The results of Hatsopoulos and Kaye agree with the theory of Nottingham.
2. The load conditions for maximal power output are different from those for maximal efficiency. For a numerical example given, the respective values are 10.7 and 12.4 per cent. (3) More research is necessary before correct allowance for power radiation from a porous, gray emitter can be made; the ultimate efficiency is thus not yet predictable but cannot exceed the values calculated by Hatsopoulos and Kaye.
Nottingham, W. B.
ASTIA AD-238, 296 (1960)
"Cesium Plasma Diode as a Heat-to-Electrical-Power Transducer"

The plasma diode which depends on the ionization of cesium at a hot surface cannot be worked out in all of its detail at present because of a lack of certain fundamental experimental data. It is possible to make use of published results of Taylor and Langmuir and a detailed analysis of recent thermionic studies to carry the understanding of the plasma diode far enough to make a direct comparison with experiment. This analysis first involves an understanding of the phenomenon of surface ionization. General properties of a plasma and space-charge considerations control the delivery of ions to neutralize electron space charge. When applied to the experimental data available, an interesting result comes as an important simplification. Essential to the theory of the high-vacuum diode is the knowledge of the emitter temperature and the diode spacing. The electrical characteristics of the plasma diode have been found to be very closely duplicated by those of a high-vacuum diode characterized by an effective distance that is reduced from the actual diode spacing.

Nottingham, W. B.
(Contract DA 36-039-sc-78108, Proj. 3-99-00-000)
"The Thermionic Energy Converter"

General theory of the plasma diode energy converter. A simplified method for the computation of electrical properties of a closed-space thermionic converter. The thermionic diode as a heat-to-electrical-power transducer.

Oman, H., and G. Street, Jr.
"Experimental Solar Thermionic Converter for Space Use"

Describes a converter operating at high Cs pressure (2mm Hg) employing solar heating of emitter and radiant cooling of the collector. Optimum emitter temperature was 3600°R, a temperature whose maintenance during operation required heat input of 50 to 100 watts/cm². This necessitates concentration of solar flux of the order of 1000.

A drawing of the experimental converter was given but no details of its materials of construction, though it was implied that the emitter was tungsten.

Parfenov, V. A.
Nauka i Zhizn, 26: 69 (1959) (July) (in Russian)
"A Thermo-Electronic Generator"

A description of a thermoelectronic generator for artificial satellites for the Earth and Moon published in the Western press is described. The project features direct conversion of thermal power into electric energy. The generator consists of two metal plates separated by only several thousandths of a millimeter and built into a vacuum tube. One plate is heated to the temperature of about 1200°, the other to 500°C. The electrons travel from the hot...
to the cooler plate. Connected up by a conductor, electric current can be thus produced. Thermal energy for the generator will be supplied by an atomic reactor or by the Sun.

Pidd, R. W.  
"Plasma Thermocouple Converts Energy Directly"

General description of a nuclear fueled Cs diode.

Pidd, R. W.  
SAE Journal, 68: 60-61 (1960) April  
"Cesium Diode can Convert Nuclear Heat to Electricity"

General news information--no specific details other than on performance of device.

Pidd, R. W., G. M. Grover, E. W. Salmi, D. J. Roehling, and G. F. Erickson  
"Characteristics of a Plasma Thermocouple"

The operation of a cesium plasma thermocouple is described for a range of hot-junction temperatures from 1600°C to 2600°C and for a range of cesium pressures from 10^{-5} mm Hg to 2 mm Hg. Electromotive force and short-circuit current data are presented for cells containing three different emitter substances: Ta, ZrC, and (ZrC)(UC). In the range of pressure and temperature variation studied, the observed electromotive forces are between 1 and 4.5 volts. Short-circuit current depends markedly on the current emission properties of the hot electrode. The largest short-circuit current density observed for the (ZrC)(UC) emitter, is 62 amperes per square centimeter.

Ranken, W. A. and T. G. Frank  
_Aero/Space Engineering, 19: 58-59 (1960) May_  
"Utilization of Plasma-Cell Energy Conversion in Nuclear Reactors"

The plasma cell is discussed in connection with its ability to directly convert heat to electricity. This fact shows considerable promise as a basis for the design of space nuclear-electric power supplies. The cell is capable of transforming thermal or fission energy into electrical energy without moving parts, giving highly reliable power supplies. Temperatures in excess of 2600°C can be attained while the heat sink operates at 1500°C. A high-temperature heat sink is desirable, since all outer space power stations must dump waste heat by radiation. Comparative current voltage characteristics for an emitter temperature of 2540°C and a Cs pressure of 0.5 mm Hg are given.

Ranken, W. A., G. M. Grover, and E. W. Salmi  
"Experimental Investigations of the Cesium Plasma Cell"

Some aspects of the performance of a cesium plasma cell with tantalum emitter are evaluated in terms of experimental determinations of the effects of variations in such parameters as cesium vapor pressure, emitter temperature, and emitter-collector separation distance. Experiments relating to the...
effect of collector serrations and to the feasibility of radiation shielding are described. Voltage-current characteristics are presented for several emitter temperatures and for a wide range of cesium vapor pressure.

Rasor, N. S.  
"Figure of Merit for Thermionic Energy Conversion"

The optimum performance for emission-limited thermionic energy conversion is derived in convenient analytical form. The steps which are thereby indicated to reduce fundamental performance limitations are enumerated and briefly discussed. A figure of merit is defined with brief description of its usefulness and significance. A comparison of thermionic and thermoelectric conversion is thereby afforded by the analysis.

Rasor, N. S.  
AI-4248 (Atomics International), Canoga Park, Calif.  
"Summary of Thermoelectric and Thermionic Conversion Technology"

The features of thermionic emission and thermoelectricity were studied and compared. An extensive derivation of the basic performance of the thermionic converter was made. Thermoelectric conversion was found to be less thermally efficient than thermionic conversion. A comparison of fraction Carnot efficiency, usable energy transport, extraneous energy transport, and figure of merit was made for thermoelectric and thermionic converters. The best demonstrated performances for converters are summarized along with their apparent status.

Rittner, E.  
"On the Theory of the Close-Spaced Impregnated Cathode Thermionic Converter"

The tables associated with the exact Langmuir space charge theory have been represented to a maximum relative error of 0.01% by approximation formulas which are suitable for use with digital computers. Application of the exact theory to a thermionic converter comprising two close-spaced planar impregnated cathodes has permitted a critical evaluation of the approximate space charge theory of Nottingham. The influence of the electrode separation, the emitter and collector work functions, and of the emitter temperature has been investigated. Spectral emittance measurements on a cathode surface at two wavelengths has resulted in a more firmly based estimate of the radiation heat transfer between two impregnated cathodes and of the maximum efficiency of an ideal design.

Sakuntala, M., et al.  
"Electromotive Force in a Highly Ionized Plasma Moving Across a Magnetic Field"

When a cloud of highly ionized gas flows across a magnetic field, an emf is produced in the gas which is proportional to the speed of flow. Oscillographic probe measurements have been carried out giving the flow speed as
a function of position. By drawing currents from the probes the plasma resistance can be found at various distances from the plasma generator. The resistance is shown to be due to the motion of positive ions.

Salmi, E. W.
"Plasma Thermionic Converters"

Describes a 3-stage, Cs-filled nuclear fueled converter with UC-ZrC emitters, a 1 mm spacing between emitter and collector, and emitter supports fashioned from thin-walled Cb tubing. Emitter temperatures are ~2100°C, collector temperatures 400°C. Concentric tube geometry is employed with the collectors in thermal contact with a water-cooled outer jacket. The possibility of stacking 15-20 cells in series in a rod of the order of 2 ft in length for use as fuel element rods for a water tank reactor is considered good. Materials for the collector and collector insulators (electrical) were not mentioned. The design of the emitter supports provides adequate electrical conductivity with simultaneously adequate thermal resistance.

Shock, A.
"Effect of Magnetic Fields on Thermionic Power Generators"

It is demonstrated that the high currents present in large thermionic power generators produce magnetic fields which result in a considerable reduction of electron transmission and energy conversion efficiency. To overcome the adverse effect of the self-induced field, the report presents the concept of a magnetothermionic power generator, employing an externally produced magnetic field parallel to the current direction. Analysis indicates that this concept will permit efficient operation of large generators. In addition, by use of a modulated field coil current, it offers the possibility of the direct generation of alternating current, at a controlled frequency.

Shock, A.
Elec. Eng. 79: 973 ff (1960)
"Magneto-Thermionic Power Generation"

An analysis of heat flow and energy flow in a diode with a magnetic field normal to electrode surfaces. Points out that conduction losses through leads, supports, etc., are minor (<10% of total), a fact pertinent to the specification of material for these parts.

Simpson, J. W.
Elec. World 153: 60 (1960) June
"Westinghouse Combines Converters in Reactor; Thermionic and Thermoelectric Generator Inserted into a Test Reactor at Waltz Mill"

Snyder, Nathan W. (editor)

B. Thermionics

Eight papers are presented (pp. 125-211). There is occasional mention of
the use of alumina for insulators (p. 142) and the use of Ni-Ti brazing of the ceramic to metal components. These are papers presented at the space power systems conference, Santa Monica, Cal., and are individually referenced elsewhere in this report. They are:

Nottingham, Wayne B.
"Review of the Physics of Thermionics"

Lewis, H. W.
"Plasma Thermionics"

Wilson, V. C.
"Cesium Converter Studies"

Rasor, N. S.
"Parametric Optimization of the Emission-Limited Thermionic Converter"

Hernqvist, Karl G.
"Experimental Research on Plasma Thermionic Energy Converters"

Steele, H. L.
"Theory of the Cs Plasma Energy Converter with a W Cathode"

Bowman, Melvin G.
"Chemistry of Fuel Element Cathode Materials"

Howard, R. D., L. Yang, H. L. Garvin, and F. D. Carpenter
"A Nuclear-Thermionic Fuel Element Test"

Stauffer, L. H.
ARS Journal 31: 322-326 (1960)
"Voltage-Current Characteristics of Tungsten Electrodes in Cesium Vapor"

Toy, S. M.
NAA-SR-Memo-4692 (Atomics International, Canoga Park, Cal.)
November 25, 1959
"Thermionic Nuclear Fuels for Direct Conversion Reactors"

A proposed program for the evaluation of thermionic nuclear fuels for direct conversion reactors is described. Physical and mechanical properties of selected thermionic metals, carbides, and oxides are given.

Von Doenhoff, A. E., and D. A. Premo
IRE Trans. on Military Electronics, MIL-3, No. 2: 46-51 (1959) April
"A Brief Survey of Direct Energy Conversion Devices for Possible Space-Vehicle Application"

A brief review is given of various types of devices for converting heat or radiant energy directly into readily available electrical form. These devices include the thermoelectric generator, the photovoltaic cell, the thermionic converter, and the photoemissive converter. The discussion is from the point of view of possible space-vehicle application. An attempt is made to indicate in a general way the present state of development, the advantages and difficulties associated with each device, and to suggest general lines of future research.
Watt, B. E.
"Design Considerations for a Plasma Thermocouple Reactor"

General features of a nuclear reactor-plasma thermocouple power system are investigated. Only simple plasma cells are considered, for which all the experimental data and most of the theory were presented elsewhere. From the available information it is concluded that the reactor should be a heterogeneous system with alternating hot junctions (reactor fuel) and cold junctions (liquid metal coolant preferred), and must contain a large number of cells. Uncertainties in many of the important parameters and in the design concepts leave the conclusions open to debate and emphasize the need for more experimental and theoretical work.

Waymouth, J. F.
"The Measurement of Thermionic Emission in Hot-Cathode Discharge Tubes"

A method has been discovered for measuring the zero-field thermionic emission current from hot emitters in gas discharge tubes of the fluorescent lamp type. It depends on detecting the vanishing of the space-charge potential minimum in front of the emitter when the current ceases to be space-charge limited. When this potential minimum is present, mercury ions can get trapped in it, and oscillate, producing rf noise stops. This marks the disappearance of the space-charge potential minimum, and hence marks the maximum zero-field thermionic emission. The method appears to be generally applicable to hot-cathode discharges in various gases.

Webster, H. F.
"Calculation of the Performance of a High-Vacuum Thermionic Energy Converter"

The performance of a high-vacuum thermionic energy converter was evaluated from Langmuir's 1923 paper on the thermionic diode. The results are presented in the form of a generalized set of curves which show output voltage as a function of current drawn from the device. These general curves were then applied to a few specific cases to determine what emitter-collector spacings, and emitter and collector properties will be required to produce a practical energy converter.

Wilson, V. C.
"Conversion of Heat to Electricity by Thermionic Emission"

A heat engine and electric generator is described which is a vacuum or gas-filled device containing a hot emitter and a cold collector. Heat at the emitter lifts electrons out and to a high (negative) potential in the system. By collecting the electrons on a low work function surface, part of the potential energy may be converted into electrical energy. Cs vapor-filled tubes have been built and tested as thermionic converters. A hot surface ionized part of the Cs vapor to neutralize space charge between the emitter and collector. The-Cs vapor was also used to adjust the work functions of the two surfaces.
A thermionic converter has been built which converts 9.2 per cent of the input heat into electricity.

Wing, L. D. and K. E. Cameron
ARS Journal 31: 327-334 (1960)
"Solar Collectors for Use in Thermionic Power Supply Systems in Space"

Yaffee, J.
Aviation Week 71: 92-101 (1959) Nov. 23
"Unit Converts Waste Rocket Heat to Power"

Zener, C.
"Notes on Thermionic Power Generation"

The purpose of this note is to examine the possibilities that the same advantages of multiple staging which are found in the case of thermoelectric power generation will also be found in thermionic power conversion.

Zinn, W. H.
Technical Progress Reviews, Vol. 3, No. 1 (1959)
"Power Reactor Technology"

General Research and Development: Section one of this volume is devoted to reactor applications and discusses the uses of process heat, process heat generation and consumption, and reactors for producing process steam. The second section discusses thermionic energy conversion and in particular the basis of operation, efficiency equation, estimates of attainable efficiencies, high-vacuum thermionic converter performance, experiments on a cesium-vapor-filled thermionic converter, and the Los Alamos plasma thermocouple. In the third section the reactor physics of $H_2O$-moderated critical assemblies is discussed. The fourth section discusses heat transfer and fluid flow. Recent investigations are reported on the collapse of parallel-plate fuel assemblies, nucleate boiling, liquid-metal heat transfer, liquid metals with internal heat generation, and water flowing parallel to tube bundles. Section five is devoted to reactor kinetics and dynamics. Current investigations are reported on delayed neutrons in reactor kinetics, reduced delayed-neutron group representations, approximations for reactor accident calculations, oscillation experiments on large heavy-water reactors, and transfer functions of distributed parameter systems. In the sixth section reactor safety and containment are discussed. A review of shielding presented in the seventh section. In section eight the radiation effects on semiconductors and magnetic materials along with the corrosion of stainless steel in a nitrogen atmosphere are reported.

Progress on Specific Reactor Types: The four sections comprising this part of the volume are devoted to lightwater reactors, boiling-water reactors, fluid-fuel reactors, and fluidized-bed reactors.

Zwick, E. B., and R. L. Zimmerman
"Space Vehicle Power Systems"
A review is given of systems utilized for generation of secondary and/or propulsion power: chemically-fueled power, open and closed cycle; solar power, closed cycle; nuclear power, closed cycle; thermionic and thermoelectric power; solar photovoltaic and solar recycling fuel cell power; typical systems, general physical construction and limitations, comparison of systems and selection for various missions. However, no specific discussion of materials usage in thermionic devices was given.
MEETINGS AND CONFERENCE PROCEEDINGS

M. Bowman
Paper 1286-60, American Rocket Society, Santa Monica, Calif.
September, 1960
"Chemistry of Fuel Element Cathode Materials"
This paper was concerned primarily with selection of optimum fuel element cathodes in the system UC-ZrC. Properties of the carbides and their inter-solid solutions are discussed and compared with some alternate materials.

Casey, E. F. and G. Street, Jr.
CP-59-904 (1959) June, AIEE Meeting, New York, N. Y.
"A Thermionic Power Supply Using Solar Heat For Space Application"
This paper deals with the possibilities of thermionic application to a space power supply using solar energy as a heat source. It discusses the six major components of a space power generating system. Some major problems of satisfactory application, possible solutions, and recommendations are given.

Fox, R. H.
"Some Important Parameters of the Plasma Diode"
A relationship is derived that predicts the power radiated from the emitter to the collector of the plasma diode. The radiated power loss predicted by this relationship for a tungsten emitter and a nickel collector at widely different temperatures is found to be five times greater than the prediction of the conventional relationship which assumes gray-body conditions. The effective work functions of the emitter and collector are found to be a function of the electrode separation and the grain sizes of the emitter and collector materials. An upper limit of the thermoelectric power output of the cesium plasma is evaluated and found to be small compared with the total electrical power output of the diode.

Two nonconventional methods are described for obtaining a high heat-converter efficiency with the plasma diode. One method uses barium vapor for depressing the emitter work function and cesium vapor for space-charge neutralization. In the second method, the emitter is at such a high temperature that there is appreciable evaporation of emitter material. The efficiency of the plasma diode is derived for the case when electron scattering is small. The efficiency is given as a function of the temperatures, work functions, and emissivities of the cathode and anode, and the electrical and thermal conductivities of the electrical leads.
Hernqvist, K. G.
"Experimental Research on Plasma Thermionic Energy Converters"

Theoretical analysis of a cesium plasma device. A new method of presenting the potential energy diagram is given as is a detailed plasma energy balance for different types of cathode materials.

Hirsch, R. L. and J. W. Holland
"Problems Associated with the Development of a Thermionic Conversion Reactor"

Howard, R. C., et al.
"A Nuclear-Thermionic Fuel Element Test"


Huffman, F. N.
AIEEE Meeting, New York, N. Y., June 21-26(1959)
"Conceptual Design of a Thermionic Space Power Plant"

Outlines in elementary fashion the basic principles of thermionic conversion presenting a conceptual design for a 25KW plant.

Johnson, K.
"Dynamic vs. Direct Conversion"

Lewis, H. W.
"Plasma Thermionics"

Nottingham, W. B.
"Cesium Plasma Diode as a Heat-to-Electrical Power Transducer"

The new interest in the direct conversion of heat-to-electrical power has stimulated research in both the application of the high vacuum diode and the plasma diode to accomplish this purpose. The theory of the high vacuum diode is relatively simple and the experimental verification of the theory is satisfactory. The plasma diode which depends on the ionization of cesium at a hot surface cannot be worked out in all of its detail at present because of the lack of certain fundamental experimental data. It is possible to make use of published results of Taylor and Langmuir and a detailed analysis of recent thermionic studies to carry the understanding of the plasma diode.
far enough to make a direct comparison with experiment. This analysis first involves an understanding of the phenomenon of surface ionization. General properties of a plasma and space-charge considerations control the delivery of ions to neutralize electron space charge. When applied to the experimental data available, an interesting result comes as an important simplification. Essential to the theory of the high vacuum diode is the knowledge of the emitter temperature and the diode spacing. The electrical characteristics of the plasma diode have been found to be very closely duplicated by those of a high-vacuum diode characterized by an effective distance that is reduced from the actual diode spacing. This fact supports the opinion that the efficiency of the plasma diode may be tremendously improved over that of vacuum diodes of practical design.

Nottingham, W. B.
Paper 1286-60, American Rocket Society, Santa Monica, Calif. September, 1960
"Review of the Physics of Thermionics"
Title is self-explanatory.

Rasor, N. S.
Paper 1233-60 American Rocket Society, Santa Monica, Calif., September, 1960
"Parametric Optimization of the Emission Limited Thermionic Converter"
This paper is a theoretical appraisal of the degradation to be expected in optimized emission limited devices by non-essential effects.

Steele, H. C.
"Theory of the Cesium Plasma Energy Converter with a Tungsten Cathode"
Not concerned with device materials other than specifying lifetime requirements where lowest temperature will be of the order of 450°C.

Teutsch, W. B.
"Conversion of Heat to Electricity in Solids and Plasmas"
The general aspects of thermoelectricity are reviewed in light of recent developments. The theory of conversion of heat to electricity in solid thermoelements is reviewed. The physical significance of the various parameters that determine the figure of merit of a solid thermoelement is discussed. Conversion of heat to electricity in a cesium cell is considered in some detail. The cesium cell is primarily a thermionic device in which the added cesium becomes partly ionized so that it may be regarded as a plasma. For very high cesium pressures, such a device may be described in a manner completely equivalent to the discussion for solid thermoelements.
Wilson, V. C.
Paper 1281-60 American Rocket Society Meeting, Santa Monica, Calif.,
September, 1960
"Cesium Converter Studies"
Discussion of the effects of variation of cesium pressure, anode and cathode
temperature and of an applied axial magnetic field on device performance.
Devices constructed using alumina insulators and Ni-Ti brazing alloys.

Wilson, V. C.
"Thermionic Converter"
This paper includes: calculations to determine optimum condition to obtain
maximum power outputs and maximum efficiencies; theoretical and experi­
mental results for closely spaced vacuum converter and for two methods of
operating gas-filled converters; possible applications in use of solar energy
and atomic power for space vehicles, etc.

Wilson, V. C.
"Thermionic Emission"
The theory, construction, and operating characteristics of close-spaced
vacuum thermionic converters and gas-filled thermionic converters are
reviewed.

Wilson, V. C.
"Electric Energy Sources and Conversion Techniques for Space Vehicles"
Electric generators for space vehicles must be dependable, have long life,
and be light weight. If the generator is a heat engine and so requires
radiating away unused heat, it must be a high-temperature heat engine.
This paper investigates and discusses thermionic converters in relationship
to requirements for space vehicle electric generators.
ANONYMOUS

General Studies in High-Power Microwave Concepts
AFCRL TN 60-974, Scientific Rept. No. 24, 1 Apr-30 June, 1960
August, 1960 (Contract AF 19(604) (1930)

Cesium plasma tube techniques discussed.

Solar Power for Space Vehicles: A Summary of Recent Boeing Research
Boeing Report D7-3040 (1959) Sept. 4

Recent results of Boeing solar-power investigations are summarized in this document. Both photoelectric and heat-to-electricity energy conversion are being investigated.

GE Markets Vacuum Thermionic Converter

A thermionic converter that is capable of using solar energy to provide a light, compact power supply for space vehicles is described.

Gold Gets Role in Outer Space: General Electric Uses Heat From Radioisotopes to Fuel its Thermionic Converter

Exotic Devices for Future Power Needs: Thermoelectrics, Magnetohydrodynamics and Thermionics

Direct Conversion of Nuclear Energy to Electricity

General Electric Co.
Chemical Week Feb. 18, 1961 p 91

G. E.'s new plasma thermionic converter, that will be built directly into nuclear fuel elements to transform core heat directly into electricity will use cesium gas and a uranium-beaming emitter plate. High-temperature heat would be converted directly, while low-temperature heat escaping through the walls of the fuel elements would generate steam power as in present-day reactors.

Cesium Cell Converts Heat Directly to Alternating Current: Developed by
General Dynamics Corporation
Plasma Thermocouple
Electronics 32: 11 (1959) April 24

Plasma thermocouple, first to convert nuclear reactor power directly into electricity, was announced this month by Los Alamos Scientific Lab. A single cell placed in a reactor far exceeded its expected lifetime by operating for almost 12 hours with an open-circuit voltage of 3.8 volts and a short-circuit current between 30 and 40 amps. The experimental thermocouple, resembling a frozen fruit juice can, uses a 3/4-in. long rod containing enriched uranium. Rod is suspended in center surrounded by cesium gas. It was discovered last year that when cesium gas is substituted for one of the thermocouple's two contact metals, several hundred times as much direct current power is produced. In the reactor's core the neutron flux activates uranium fission heating in the can's center; flow of reactor coolant outside can drops temperature of cesium plasma.

Thermionic Generator Tube
Electronics 32: 11, (1959) Dec. 11

Thermionic generator tube has converted rocket exhaust heat into useful levels of power during preliminary evaluation tests announced by RCA and Thiokol Chemical Corp. The RCA tube has produced up to 270 watts of power directly from the heat source—an output of nearly 80 watts per pound of its 3-1/2 pound total weight. In tests the device was coupled to a Thiokol solid-fuel rocket motor. RCA and Thiokol engineers say actual and simulated rocket tests show the feasibility of using light-weight thermionic tubes to produce the power needed during a missile's launching and upward flight. They say thermionic devices could power a rocket's guidance, telemetering and related electronic gear during the operating life of the rocket motor.

Power Sources for Space
Electronic Equipment Engineering, 8: 34-40 (1960) May

Need for small, reliable power generators for satellites and space vehicles has focused attention on the direct conversion of heat energy into electrical energy. The four basic techniques under investigation are fuel cells, thermoelectricity, thermionic conversion, and magnetohydrodynamics.

Nuclear and Thermal Sources Still Costly
Electronic Design 7: 10-11 (1959) May 27

Conversion of thermal to electrical energy, by thermoelectric generators and thermionic converters, which have no rotating parts, offers reliability and long life. Dr. A. D. Steele described the 5 w thermoelectric generator, developed by the Minnesota Mining and Manufacturing Co. under the A. E. C. Snap III program. The unit, publicly displayed at the White House earlier this year, uses lead telluride p- and n-elements heated by alpha particles emitted by polonium 210.

Theoretical and experimental results for close-spaced thermionic vacuum- and gas-filled converters were outlined by Dr. V. C. Wilson of the G. E. Research Lab. Dr. Hatsopoulos of M. I. T. comparing thermoelectric and thermionic converters, concluded that relatively low-temperature thermoelectric devices could be thermally cascaded with higher-temperature thermionic units to achieve high over-all conversion efficiency of heat to electricity.
Thermionic energy converters are discussed.

Four Advanced Power Generators Pose Hot Materials Problem

Four new direct power generating systems are described by Westinghouse. These systems operate at high temperatures and, therefore, their success depends on the development of new and better materials.

Practical thermionic converters are being produced in quantity by GE and are expected to be on the market in October 1960.

Efficiency of 15-17% has reportedly been obtained with a new vapor thermionic converter developed by General Electric Power output of 23 watts was obtained at 1530°C. GE says the cesium-vapor converter is a "practical" device and can be reliably produced in quantity for space and military applications.

A method of converting thermal energy to electric energy is outlined in which a pair of electrode surfaces with differing work functions is supported in a vacuum-tight enclosure and kept at different temperatures; the electrode with the higher work function is maintained at temperatures above 1400°K and the other at least 700°K below that of the first. Cesium vapor is introduced into the enclosure to coat the cool electrode completely and the hot electrode partially and to neutralize the space charge between the electrodes; in this way, the electrode voltage approaches the contact potential between the two electrode surfaces. In the preferred embodiment of this method, the hot electrode is molybdenum, the cool electrode is oxidized silver, and the support is a ceramic insulator. A plot of the logarithm of electron emission vs. 1/T for various cesium vapor temperatures illustrates the kind of performance that may be obtained.
Heat into Electricity

"Thermoelectron engine" invented at Massachusetts Institute of Technology operates on electron stream, without moving parts; two metallic plates are spaced 10⁻³ in. apart in a vacuum; one plate heated to about 2200°F, the other maintained at 1000°F. The electrons boil off hit plate onto cold plate, and suitable external connections permit flow of electricity. Present thermal efficiency of 12 per cent may eventually be increased to 30 per cent.

On the Conversion of Thermal Energy to Electrical Energy by Means of Thermionic Emission
Radiotekhnika i Elektronika, 4: 1065-1066 (1959)

Power from Plasma

Fission to Power Shortcut Found: Thermionic and Thermoelectric Generator Built into Nuclear Fuel Assembly and Inserted into a Reactor
Steel, 147: 102 (1960) July 18
APPENDIX II

LIST OF CONTRIBUTING INDIVIDUALS

This list is to acknowledge the contributions helpfully made by specific individuals to this study. Personal contact was made either by a visit to the company or at meetings and symposia held during 1961.

Robert Allen  
Seymour Bortz  
Richard Blair  
Samuel Bradstreet  
William Colner  
John J. Connelly  
Leonard Grossman  
Loren Hansen  
George Hatsopoulos  
Robert Howard  
Lazarus Lazaridis  
William Martin  
Ned S. Rasor  
John Satkowski  
Robert Scapple  
Paul Stephas  
Charles Warner  
Chester Weeks  
Alfred Weinberg  
Paul Winslow  
Ling Yang

Atomics International  
Armour Research Foundation  
Hughes Aircraft Company  
Electro Refractories and Abrasives Corp.  
Hughes Aircraft Company  
Office of Naval Research  
General Electric Vallecitos Atomic Laboratory  
Atoms International  
Thermo Electron Engineering Corp.  
General Motors  
Thermo Electron Engineering Corp.  
Atoms International  
Atoms International  
Atoms International  
Atoms International  
Atoms International  
Atoms International  
Atoms International  
Hughes Aircraft Company  
General Electric Vallecitos Atomic Laboratory  
Atoms International  
Atoms International  
Atoms International  
Hughes Aircraft Company  
General Atomics

Many miscellaneous bits of information were obtained from many other individuals, the specific details of which are now beyond recall. To these individuals the writer wishes to express thanks and apologies.
APPENDIX III

METAL-CERAMIC JOINING*

A. Telefunken Process and Modifications

One of the earlier practical methods of joining a metal to a ceramic was developed at Telefunken, Germany, \(^{(1, 2, 3)}\) and bears the name of the Telefunken or the molybdenum process. This is essentially a three-step process in which molybdenum powder is sintered onto the ceramic at approximately 1350°C in an atmosphere of high dew point hydrogen. A nickel layer is then sintered to the molybdenum surface at a temperature of approximately 1000°C to improve the wettability during subsequent silver brazing of the metallized ceramic to a metal. The parameters of the process have been indicated to be extremely critical by numerous investigators, a quantitative study having been made by Bender. \(^{(4)}\) This study clearly outlined parameters of time and temperature of firing in the first two steps and the maximum powder sizes of the Mo, Ni, and often substituted NiO. A summary of these parameters and procedures has been outlined by Bender in a later work. \(^{(14)}\) Nolte and Spurck \(^{(5)}\) have modified the basic Telefunken process by the addition of manganese powders to the molybdenum powders to enhance the adherence of the molybdenum to the ceramic and lower the firing temperature by 100°C. It was pointed out by these investigators that Mn is capable of bonding other powders—e.g., tungsten, iron, nickel—to ceramics. They indicate that the criterion for selection of the molybdenum over other refractory metals is the similarity of thermal expansion characteristics to those of the ceramic. A further modification of the basic process was the introduction of nickel and copper electroplating to the Mo-Mn surface instead of a second firing of Ni or NiO powders. A typical application of this

\(^{(+)}\) References in this appendix will be found in the bibliography at the end of this appendix.

* This review is the product of the joint efforts of J. F. Rudy, H. Schwartzbart and D. W. Levinson of the ARF staff.

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process has been outlined by Coykendall\(^6\) in the production of an annular ceramic tube for a tetrode to withstand accelerations up to 1000G.

Other variations of the process have been introduced such as substitution of molybdenum trioxide for molybdenum powder\(^7\) which is reduced by dry hydrogen in the first firing operation to molybdenum, and the replacement of the molybdenum-manganese entirely by tungsten-iron\(^8\) depending on the properties of the ceramic being metallized and the subsequent soldering or brazing filler metal.

B. Reactive Hydride Method

In 1947, Bondley\(^9\) introduced the use of TiH\(_2\) as a paint-on coat to the ceramic prior to brazing with the filler alloy. The method essentially relies on the decomposition of the TiH\(_2\) at an early stage of the heating cycle to provide finely divided Ti to alloy with the brazing filler metal and thus wet the ceramic. Subsequent investigators have shown that ZrH\(_2\) may be substituted for TiH\(_2\) with superior results\(^6, 10\) with further improvement gained by the addition of a small amount of manganese to the hydride.\(^6\) Excellent results with the TiH\(_2\) process have been attained when used in conjunction with silver-based filler alloys, especially with RTSN filler alloy (60% Ag).\(^11\) Bondley\(^12\) has shown the applicability of this process to soldering; but, in this case, the superiority of TiH\(_2\) over ZrH\(_2\) is specifically mentioned. Unfortunately, the hydride process yields best results under vacuums of less than 1 micron; this makes the selection of low temperature soldering alloys critical with regard to the vapor-pressure of the solder constituents.

A unique application of the hydride process is described by Hume\(^13\) in which ZrH\(_2\) was painted on a ceramic, evaporated to 1 mil thickness, and a silver filler alloy bonded as a pre-tin to the ceramic under vacuum in an induction coil. The pre-tinned ceramic was then inserted into an aluminum bushing, set into a graphite boat, evacuated, and the aluminum melted by induction. A sound aluminum-to-ceramic bonded part resulted.
Recent work at Armour Research Foundation has resulted in the bonding of a metal pin to ceramic using a mixture of TiH$_2$ and MoO$_3$ as the bonding agent. A procedure for making such joints in production was developed.\(^{(15)}\)

C. Active Metal and Alloy Joining

The work of Pearse and Zingeser\(^{(10)}\) cited above in connection with ZrH$_2$ joining also revealed the use of Ti or Zr in metallic form in conjunction with Ag, Cu, and Al. These metal combinations made satisfactory joints between a metal and a ceramic. This process was found to be effective when performed under inert gas or vacuum. Beggs\(^{(16)}\) has shown procedures for fabrication of many types of parts composed of alumina, forsterite, and zircon joined to Cu, Ti, and Zr, using a shim material of Ti or Zr when brazing the Cu or Ni and an Fe shim when brazing the Ti or Zr. In this application, under inert gas or vacuum, joints were made at temperatures ranging from 875$^\circ$C to 1015$^\circ$C.

A variation of this method is accomplished by using titanium-cored silver filler alloy wire. Evans\(^{(28)}\) has fully described a production process for a particular part utilizing titanium-cored BT brazing filler wire. This commercially available wire resulted from an investigation of silver-based alloys containing titanium conducted at Armour Research Foundation.\(^{(17)}\) In this study it was shown that silver alloy containing approximately 5% Ti had excellent melting, flow, and bonding characteristics. Greater amounts of titanium increased the brazing temperature considerably and decreased the workability of the alloy. The titanium-cored silver filler alloy was prepared in an effort to introduce a greater amount of Ti to the braze for high-temperature applications. The addition of 8% titanium to the silver permitted maximum wettability, but it was possible to produce such an alloy only in cored form. This has been found to result in inhomogeneities after application which it is claimed caused ceramics like zircon and forsterite to crack although not affecting alumina.\(^{(4)}\) A homogeneous alloy of Ag + 5% Zr, however, has been prepared that not only wets and flows but eliminates the cracking of the forsterite and zircon. This alloy may be used successfully
under vacuum only. It has been pointed out that Ag-Mn and Pb-Ti (the latter for low temperatures) have shown promising characteristics with the advantage of being usable in a hydrogen atmosphere.

Titanium-cored nickel wires are available commercially for ceramic-to-metal bonding. These metals are adjusted in the eutectic proportion; the composite wire melts and wets both ceramic and metal when the eutectic temperature is exceeded. Titanium-cored copper wires should be just as successful.

Glasses have been sealed about iron-nickel-cobalt wires using pure Zr and Ti in the form of preplaced wires. This was a specialized application in which the joint was to be exposed to chemical attack, and a chemical resistant filler metal was needed.

D. Miscellaneous Methods

Knecht describes a method involving the gradation of metal-ceramic powders, graduating the coefficients of expansion between the ceramic and the metal to be bonded. The bond is made under pressure in the solid state in a manner similar to powder metallurgical practices. It has been reported that strong bonds can be developed on alumina ceramics with vapor-deposited Inconel-copper films which can then be brazed with silver filler alloy. On the other hand, Evans pointed out that, although strong bonds between the vapor-deposited film and the ceramic may be formed, subsequent brazing destroys the bond. The preparation of a molybdenum metallized ceramic surface by the reduction with hydrogen of a painted-on MoO₃ has been mentioned earlier in this section. The same procedure may be employed using CuO by first firing the CuO to the surface of the ceramic and then following with a hydrogen reduction. The metallic copper film resulting may then be soldered. Note that the use of CuO involves a two-step process whereas MoO₃ requires one firing.

Metals having tightly adhesive oxides, i.e., Cr₂O₃ on stainless steel, have been shown to bond to ceramics by a fused glass method. Research along this line has been conducted also at Armour Research Foundation in the brazing of waveguide windows. The method appears simple and inexpensive due to the fact that processing is possible in oxidizing atmosphere.
E. Evaluation of Existing Methods

The Telefunken process, including its various modifications, has been developed to a point where the important factors are well under control. Strong, reproducible bonds may be expected. It also has inherent control of the areas to be wetted. It is, however—and this is its greatest drawback—a multi-step process requiring three firings to complete a seal, two of which are in excess of 1000°C. At these high temperatures, distortion due to temperature and discoloration of some ceramics by hydrogen must be reckoned with.

The hydride method eliminates some of the objections to the Telefunken process but introduces one or two in its own right. The process requires rigid control, particularly in the ratio of hydride to filler alloy. It has the advantage of being a one-step process. The discoloration inherent in the Telefunken process is eliminated due to the substitution of inert gas or vacuum for hydrogen. Firing temperatures are normally lower, and the process has been successfully used with copper, silver-copper alloys, lead, and low-melting filler alloys. Control of the area to be wetted is difficult due to the high fluidity imparted to the filler metal by the hydride. Two investigators(6, 28) have reported a change from the hydride process to the Telefunken process or the active metal process because of poor reproducibility using the hydride. Furthermore, a drawback to the hydride method concerns the application of the hydride to the ceramic. Some skill is required to apply the hydride uniformly particularly where the geometry of the joint is irregular. The application technique plays a great role in the subsequent joint uniformity.

A truly one-step process, amenable to high production, lies with the active alloy or metal technique. It has been shown that many of the refractory oxides may be joined to metals through proper choice of alloys bearing Ti or Zr. These bonds are strong with excellent reproducibility. Assembly usually is no more difficult than with metal-to-metal brazing. As with hydrides, the fluidity of the active alloys makes control of the wetted area difficult.
A major drawback to the process in the light of present technology is the low ductility of the presently available alloys and inhomogeneity. The silver-titanium cored wire flows and wets ideally with 8% Ti. Unfortunately, an 8% Ti-Ag alloy is difficult to work into wire. The alloy has little ductility even though the Ag-Ti intermetallic compound is relatively ductile. As previously discussed, this necessitates using cored wire which, upon melting, results in inhomogeneities. The same criticism is applicable to the zirconium alloys in that the addition of Zr to Ag in proportion to assure wetting and flow results in a non-homogeneous alloy. Bender has shown that, even at 5% Zr in Ag, wetting and flow is erratic but is improved over Ag alloys with lower Zr contents. This would indicate a need for more than 5% Zr for a dependable process. Despite present difficulties, the formulation of ductile, homogeneous, active alloys will result in this basic method developing into an outstanding production process for a great range of service temperature requirements.

Other methods such as pressed powder technique, metallic oxide seals, ceramic-glaze seals, glaze and metal powder seals (not discussed) have utility in specialized applications depending on service temperature, materials being joined, and joint geometry. A full critique of the foibles of many of these processes is given by Evans in his selection of a process to butt-join a ceramic tube to a metal plate.

F. Joint Design

In the design of a ceramic-metal component, a most important consideration is the relative thermal expansion coefficients of the two bodies being joined. Few, if any, metals have coefficients of expansion similar to ceramics. This is particularly true if the entire range of temperatures encountered in a brazing cycle is considered. The fact, however, that mismatches of materials possessing different thermal coefficients are bonded is not a result of chance but of careful consideration of the individual expansion curves, the thermal cycle, the section size and strength of the ceramic, the strength and dimensions of the metallic body, the expansion coefficient and ductility of the filler alloy, and geometry of the component being joined. Understanding of these factors leads to rough analysis of the stresses developed during the bonding.

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Several authors have presented thermal expansion curves of typical ceramics and metals. (8, 18, 16, 12, 23) The metals are divided into low and high expansion groups, notably Cu and Ag at the high extreme and the Fe-Ni alloys at the low extreme. Between these extremes are other metals of interest in ceramic bonding: namely, Mo, Fe, Ti, Zr. Further distinction among the metals is made on the basis of those alloys having sharp inflections in their expansion curves as a function of temperature, e.g., an allotropic transformation. These alloys are of notable importance as the phenomenon occurs in the low expansion group of alloys (Fe-Ni) that are most commonly bonded to ceramics. This condition often results in a reversal from compressive stress on a ceramic at operating temperature to tensile stress at room temperature or vice versa.

Regarding the ceramic itself, an enormous range of coefficients of expansion is encountered from quartz at the lowest to forsterite as one of the highest. Fortunately, there exists some overlapping of coefficients between the high ceramics and the low metals. As mentioned in the previous paragraph, the metals involved are those with the expansion curve inflection. Thus, the problem becomes complex.

Palmer(21) cites the quite obvious fact that, after a component having a metal seal surrounding an annular ceramic is brazed and then cooled, radial compressive stresses result in the ceramic. Under these circumstances, little difficulty is encountered since the compressive strength of the ceramic will normally exceed the yield strength in tension of the metal. A metal bonded within a ceramic presents a somewhat different problem. Under these circumstances, the ceramic will be stressed in radial tension. In each geometry, assuming the metal has the greater coefficient of expansion, the tangential and longitudinal stress (those stresses in planes which are parallel to the bonding plane) will be tension on the metal side of the bond and compression in the ceramic.

A match of thermal coefficients of expansion is important in geometries of this type. If a near match is not possible, then the metal part must be designed of small enough section that it will yield before the tensile strength of the ceramic is exceeded. For example, a much closer match of thermal expansion may be attained between forsterite and Kovar.

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than alumina and Kovar; yet alumina-Kovar is generally accepted as a mechanically superior structure. In this case the magnitude of the residual stress is compromised by the ability of the ceramic body to take the stress. Although much less stress is generated in the forsterite than in the alumina, the forsterite fails due to its lower tensile strength.

The subject of design is given an excellent treatment in a paper by Cronin. He gives an example of an approach to the stress relationships through consideration of the thermal expansion versus temperature curves of the components of a contemplated assembly.

Consider the plot in Figure 2. Then consider an assembly consisting of only a thin (0.020 in.) Kovar cylinder surrounding a 3 in. disk of ceramic of diameter equal to the inside diameter of the Kovar. When the assembly is heated to 900°C, the Kovar I.D. will expand to 3.030 in. whereas the ceramic will expand to 3.023 in. If, theoretically, the ceramic is replaced by a piece 3.030 in. while at temperature and the cooling cycle begins, the ceramic will merely follow its own contraction curve, being unyielding, down to point D. The Kovar, however, will undergo deformation and, instead of following its own curve, will follow the contraction curve of the ceramic. Consequently, at room temperature a strain, ED, has been set up in the Kovar and the ceramic is stressed in compression.

If the joint were made at 665°C, which is the cross-over point between the ceramic and Kovar, the strain AB which existed at 900°C would reduce to zero. Thus, the stresses developed during the thermal cycle under these conditions are temporary and would leave a stress-and-strain-free assembly at room temperature.

If instead of replacing the ceramic with a larger circular section, gap AB were filled with silver alloy, the Kovar would be subjected to radial forces pulling it inward due to the contraction of the silver alloy. This would be counteracted by a metal such as molybdenum on the ceramic (the Telefunken process) that would act to force the Kovar outward due to its lower coefficient of expansion.
FIG. 2 — STRESS-STRAIN RELATIONSHIPS OF SOME TYPICAL SEALING MATERIALS (AFTER CRONIN)
It can be seen that the design problem can be complex, with the above type of analysis being only a first step in the determination of the result. Cooling rates, for example, can influence the answer as to whether, as in the above example, compression or tension results in the ceramic. Geometry and ambient temperature also play important roles.

The transparent glass-to-metal seal as opposed to the opaque ceramic-to-metal seal is readily amenable to stress analysis. Work has been done and is continuing using transmitted polarized light to obtain optical stress patterns. Development of these techniques will greatly aid designers of ceramic-metal seals when such data can be applied to similar opaque ceramic systems.

We have discussed the effects of relative coefficients of thermal expansion on the design of ceramic-metal seals. It has been shown that the brazing filler alloy can affect the stresses and strains in the completed assembly. This leads to the consideration of the ductility and thickness of the brazing filler alloy. For purposes of present discussion, a criterion for the selection of a suitable filler metal is that it should allow sufficient movement between the metal and ceramic components in the joint to relieve stresses, thereby avoiding the imposition of high tensile stresses on the ceramic. The movement which can occur increases with increasing ductility and thickness of the intermediate brazing alloy. The Armour Research Foundation has recently developed a process called fiber metal shim brazing which is an effective means of maintaining a large gap for brazing. This technique also affords a convenient method of mixing metals, such as an active metal plus Ni, Cu, or Ag, in the interface.

G. Bonding Mechanisms

It is interesting and pertinent to discuss the mechanism of bond formation in metal-ceramic seals. One point in question in much of the theoretical discussion is whether a glassy phase forms at the interface. Pulfrich, in his original patent of 1939 for the firing of molybdenum on ceramic, claimed that the molybdenum particles are wetted by a ceramic eutectic at the surface. Some MoO$_3$ is present to aid the eutectic formation. The eutectic then solidifies and forms a crystalline matrix about the
molybdenum powders at the surface. He did note, however, that MnO₂, ZrO₂, BaO, and CaO as constituents in the base ceramic promoted the molybdenum interaction. No consideration of the possibility of glass formation was made since, based on the original assumption, a crystalline matrix was to develop. Pulfrich made a point of stating that a glassy phase was to be avoided, since a glass would impair the low loss properties of the ceramic. Later investigations added TiO₂, HfO₂, and ThO₂ to the list of oxides promoting the molybdenum interaction. Gross suggested that the ZrO₂ improved the bond merely through a strengthening of the ceramic. Kuhner countered with a hypothesis of the improved bond being caused by the formation of a molybdenum zirconate as a reaction product. This has never been proved, however.

Not much light was shed on this basic question even after Nolte and Spurck introduced manganese to the molybdenum to stimulate the reaction. These investigators claimed that "refractory metals combine indifferently with ceramics whereas Mn combines with both through the formation of eutectics or solid solutions of the metals and ceramics." At any rate, metallographic examination always revealed a completely crystalline structure through the entire composite with no evidence of a chemical change or interaction.

It was not until 1953, when a magnifying metallographic technique known as the taper section technique was developed by Pincus, that a different conception evolved. With a magnification of 10:1 in the metallographic section, Pincus observed a glass formation at the (Mo-Mn)-alumina interface. He postulated a mechanism of the formation of MnO in the presence of high-dew-point hydrogen, the MnO attracting Mo by dissolving residual oxides surrounding the molybdenum particles. With this first evidence of glass and a liquid phase, he showed the use of oxide equilibrium diagrams in predicting bond formations. Using the taper section technique, Pincus later developed a comprehensive mechanism for the bonding of molybdenum using Al₂O₃ as the base ceramic. Al₂O₃ was chosen as the ceramic because it contained none of the elements suggested by previous investigators as aids to the bonding process. He found that the basis for the process is a controlled degree of oxidation of the metal; a
chemical reaction zone between metal oxide and ceramic forms an interaction zone including glass causing bonding of the metal and ceramic through this interface in a graded, continuously coherent structure physically compatible with the ceramic.

Ryshkewitch\(^{(31)}\) states that bonding of a Mo-Mn mixture to alumina depends on the presence of a few per cent of silica in the ceramic. This component, which is commonly present even in high-alumina ceramics, has several roles. (a) it lowers the temperature at which liquid forms in the system MnO-Al\(_2\)O\(_3\), (b) it stabilizes this liquid as a glass, and (c) on reduction by hydrogen at 1400°C to Si, it interacts directly with the molybdenum metal. In the absence of SiO\(_2\), MnO-Al\(_2\)O\(_3\) liquid forms only above 1500°, and Al\(_2\)O\(_3\) is not significantly reduced; consequently, adhesion is very poor even with firing temperatures well above 1400°C.

In contrast, Ti, Zr, or Cb powders (or the decomposition products of the hydrides) adhere to pure alumina, probably because these metals can reduce alumina at least partially. This reduction causes an ionization of the active metals which can then dissolve to a limited extent in the surface layers of the oxide and subsequently diffuse under a concentration gradient. This creates a suboxide layer which grades into metal on one side and normal oxide on the other.

Such a layer is created by a different route in the case of techniques involving the deposition and fusion of an oxide flux (CuO, or NiO + CuO + Fe\(_2\)O\(_3\)) on a ceramic, followed by reduction.\(^{(31)}\) The molten sealing oxides react with or dissolve in the surface layers of the ceramic forming a strongly bonded layer. Subsequent reduction of this layer produces a complex consisting of a metal film bonded to a partially oxidized transition zone which in turn adheres to the underlying oxide. In both cases adhesion is probably due to the fact that the bonding oxide layer penetrates both the metal and the substrate oxide, and its structure grades between these two phases.

Numerous investigations have been made to associate surface tension of metals and ceramics interfaces with the bonding of ceramics.\(^{(32-36)}\) Zackay and Mitoff,\(^{(32, 33)}\) have used a sessile drop method to determine the
surface tensions of three silicate glasses on solid Cu, Ag, Au, Ni, Pd, Pt, and Ta. Contact angles were determined and found to be unaffected by glass composition or solubility of gases in the base metal. Oxygen and hydrogen atmospheres favor wetting due to reactions forming oxides and hydrides. Such reactions would be expected to promote wetting through reduction of the glass-metal interfacial tension as well as change the surface tension of the solid. Under pure helium, in the absence of chemical reaction, these investigators noted small variations in wettability that appeared to be associated with the polarizing power of the metal \( (Ze/r^2) \). They observed a trend of increased wetting with decreasing polarizing power. This hypothesis, however, is not yet unequivocally established.

Although Kingery’s work is extensive in relating surface and interface energies with wetting behavior, caution must be exercised in applying the energy data to predict the result. An example of this is the above experimental work of Zackay that contradicts Kingery’s predictions for wetting, under helium, of silicon by sodium silicate.

Allen et al. have measured surface tensions for numerous pure metals and alloys on \( Al_2O_3, Si_3N_4, MoSi_2 \) and SiC. In all cases the surface tension coefficients were negative with increasing temperature; this implies wetting if the temperature is raised sufficiently. These investigators also show that less than 1% Ti markedly reduces the interface energy when alloyed with Sn. This measurement is in agreement with the known experimental facts pertaining to the active metal bonding method. That less than 1% Ti greatly increases the wettability of Ag on ceramic has been reported in a recent program conducted at Armour Research Foundation.

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* Zackay has indicated that surface chemical reaction greatly influences the wetting of a metal by a molten glass. Kingery’s predictions are based on the pure metal with no oxides or hydrides present. Although Zackay’s data were obtained under purified helium, the degree of purity can certainly not be 100%. Under ideal conditions, the predictions, therefore, may concur with the experimental data. It becomes rather obvious that, in practice, results will often deviate from predictions because laboratory conditions are unattainable.
Additional work on surface tensions in very recent investigations has shown some new surface-active metal combinations. Selenium, for example, imparts surface activity to Fe, as does oxygen and sulfur. Recent work at the Foundation has shown that Li imparts surface activity to silver; Ag + 3% Li brazing alloy was found to wet and bond to Vycor glass readily under inert gas.

H. Factors Affecting the Mechanical and Electrical Properties of Seals

It has been previously shown that the sealing zone between a metal and ceramic is complex, and displays fairly extensive cation diffusion and the formation of intermediate oxide or glassy layers. One might expect that this area should be weaker than either the ceramic or metal, and that its strength should be strongly affected by the development of the bonding layer. It is a rather surprising fact, therefore, that seals commonly fail in the ceramic adjacent to, but not directly at, the metal-ceramic interface. This might be due to the following factors:

(a) The surrounding ceramic is weakened during the sealing process. Mechanisms for such a deterioration are certainly available; for example, infiltration of Ti and other impurity ions, as well as liquids, can catalyze harmful grain growth in the ceramic. Furthermore, if these liquids solidify to glasses, strength will be much reduced in the permeated areas. However, these processes also occur in the seal zone itself—and probably to a greater extent than in the neighboring ceramic; consequently, there is no reason for the deterioration to be greater outside the bonding layers than at the seal interface.

(b) The bonding layer can undergo limited plastic deformation above its elastic limit whereas the adjacent ceramic fails by cracking. In the case of active metal or hydride seals on a pure oxide, the plasticity argument is supported by observations on alumina and zirconia ceramics containing very thin films of titanium. Such
composites show a ductile type of indentation,\textsuperscript{(42)} and have even been bent through an angle of about 3 1/2 degrees at 660°F.\textsuperscript{(43)}

Ductility at the seal interface is a desirable condition since this area is normally a zone of weakness. However, if plastic deformation is a possibility, the strength of the joint is set by that of the ceramic itself (minus residual stresses caused by expansion discrepancies) and it is in the ceramic that failure occurs. This limited ductility probably has its highest development in active metal or hydride seals on pure oxides. Where bonding occurs through a glassy phase rather than through suboxide layers, one might predict that plastic deformation at low temperature will be at a minimum and that the seal will fail right at the interface. In this case, the strength of the seal will probably depend on the amount of glassy phase present and on such other factors as the extent of penetration of the glass into the ceramic, the development and characteristics of the oxide layer on the metal, and its solution in the glass.
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