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High Power Densities from High-Temperature Material Interactions

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Work performed for
U.S. DEPARTMENT OF ENERGY
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Prepared for
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Under Interagency Agreement EC-77-A-31-1062

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HIGH POWER DENSITIES FROM HIGH-TEMPERATURE MATERIAL INTERACTIONS*

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Abstract

Thermionic conversion (TEC) and metallic-fluid heat pipes (MFHPs) offer important and unique advantages in terrestrial and space energy processing, and they are well-suited to serve together synergistically. TEC and MFHPs operate through working-fluid vaporization, condensation cycles that accept great thermal power densities at high temperatures. TEC and MFHPs have apparently simple, isolated performance mechanisms that are somewhat similar. And they also have obviously difficult, complexed material problems that again are somewhat similar. Intensive investigation reveals that aspects of their operating cycles and material problems tend to merge: "In short, high-temperature material effects determine the level and lifetime of performance." Simplified equations verify the preceding statement for TEC and MFHPs. Material properties and interactions exert primary influences on operational effectiveness. And thermophysical-chemical stabilities dictate operating temperatures which regulate the thermoelectic currents of TEC and the vaporization flow rates of MFHPs. Major high-temperature material problems of TEC and MFHPs have been solved. These solutions lead to productive, cost-effective applications of current TEC and MFHPs--and point to significant improvements with anticipated technological gains.

Energy Efficacy and High-Temperature Materials

"If there is a single general trend that applies to the various combinations of heat sources a conversion methods, it is the one toward higher source temperature and higher sink temperature--and consequently lighter weight systems. For this reason, the workshop felt that high-temperature-materials data was of prime importance...." This is a quotation from W. A. Ranken of the Los Alamos Scientific Laboratory, one of 150 experts who attended a recent symposium at NASA Lewis Research Center on "Future Orbital Power System Technology Requirements". The inexorable evolution toward high space-system power levels is a movement to not only high temperatures but also high efficiencies and high power densities.

Similarly high-temperature, high-power-density topping promises higher efficiency, lower cost and less pollution per watt of electricity on earth 2-20. And very important in these trends are two direct energy devices that process great power densities effectively through high-temperature material interactions alone: The thermionic energy converter and the heat pipe operate on thermal inputs only and have no moving parts. Their working fluids cycle continuously through evaporation, condensation and return flow by a self-induced voltage or a capillary-pressure difference (Fig. 1). Specially selected materials serve as interacting evaporators and condensers as well as containers for these working fluids. In such combinations thermionic-energy-conversion (TEC) and heat-pipe processes function at low temperatures. But their high-power-density capabilities prevail at high temperatures (Figs. 2 and 3). "In short, high-temperature material effects determine the level and lifetime of performance."21

Temperatures for optimum TEC and for some important terrestrial topping applications appear in Fig. 2. Corresponding heat-pipe utilization could occur at temperatures near those for appropriate emitters and collectors. Possible heat-pipe service in projected space applications comprises the entries in Table 1.22-29. Metallic fluid heat pipes (MFHPs) and TEC are also a synergistic combination for efficient high-temperature, high-power-density production of weight-effective space power near and above the megawatt level.26, 27. Aiming at this goal the USSR reported in 1976 on "the tests of three 'Topaz' reactors" ('thermionic nuclear power plants') that demonstrated... long-term stable and reliable operation with good reproducibility of parameters.28.

TEC and MFHP Power Densities and Problems

TEC heat inputs can reach the order of 100 W/cm², as implied by Fig. 2. There TEC outputs range up to tens of W/cm² (POL) and tens of percent efficiency (nOL):

\[
P_{OL} = (\phi_E - \phi_C - V_D - V_A - V_L)(J_{ES} - J_R) \quad (1)
\]

\[
n_{OL} = (J_{ES} - J_{BE})^{1/2} \left(\frac{2.45 \times 10^{-6} n_{EC}(T_E^2 - T_C^2)(2 - n_{EC})^{1/2}}{\left[2.45 \times 10^{-6} n_{EC}(T_E^2 - T_C^2)(2 - n_{EC})^{1/2}\right]} \right)^{1/2}
\]

\[
\left[1.05 + 7.5 \times 10^{-5}(T_E - 1000)\right]^{1/2} \left(T_E^4 - T_C^4\right) \quad (2)
\]

In these equations, \(\phi_E\) and \(\phi_C\) are emitter and collector work functions, \(V_D\) is the interelectrode voltage drop, \(V_A\) is the equivalent auxiliary input voltage for enhancement, \(V_L\) is the voltage loss required for optimum leads (equal to the expression within the square brackets in the numerator of (2)). \(n_{EC}\) is the TEC electrode efficiency (equal to (2) with \(V_L\) deleted from the numerator). \(T_E\) and \(T_C\) are emitter and collector temperatures, the last term in the denominator of (2) approximates non-electronic thermal transport. \(J_{BE}\) is reverse electronic flow (including reflections, backscattering, back emission \(J_{BE}\), and other effects that diminish output current), and \(J_{ES}\) is the current density.
for emitter saturation:

$$J_{ES} = A(1 - R_E)T_E^2 \exp(-\phi_E/kT_E)$$  (3)

where $A$ and $k$ are Richardson and Boltzmann constants and $R_E$ is the emitter reflection coefficient.

Equation (2) is a simplified, yet reasonable estimate applicable for low cesium concentrations, reduced enhanced-mode pressures, close electrode spacings, and small interelectrode losses. Under such conditions, the back emission ($J_{BE}$) approximates $1.3e28$ J/cm$^2$.

$$J_{BE} = A(1 - R_{BE})T_C^2 \exp(-\phi_D/kT_C)$$  (4)

where $R_{BE}$ comprises $R_C$ (collector reflection coefficient) and similar coefficients for all interelectrode mechanisms that return collector-emitted electrons to their source — except those for noncollisional repulsion by the emitter sheath. With negligible interelectrode losses and reflections, back emission equals that for collector saturation:

$$J_{CS} = A(1 - R_C)T_C^2 \exp(-\phi_D/kT_C)$$  (5)

The preceding equations verify a previous assertion: High-temperature material effects ($\phi_E$, $R_E$, $T_E$, $\phi_D$, $R_D$, $T_C$, $J_{CS}...$) determine the level of TEC performance — completely. This generalization includes enhanced-mode operation also because $\phi_A$ represents a small fraction of TEC output recycled to increase efficiency. With this rather limited background a tabulation of TEC characteristics may now be apropos:

### Thermionic-Energy Conversion (TEC) Advantages

Electricity directly from heat
No moving parts or inherent mechanical stresses
High temperatures: high Carnot efficiencies
Great power densities — with
- Broad near-maximum-efficiency plateaus
- Rapid responses to load or heat variations
  - (constant temperature)
- Low weights
- Small volumes
- Modularity

Modularity in TEC Applied Research and Technology (ART)

TEC ART is essentially independent of other system components
Development and testing on the lab bench are effective
Converters are scalable
Module building blocks adapt to system size and shape
- Repetitious rotational fabrication modes apply
- Nearest-neighbor load sharing minimizes unit-failure effects
- Modular designs allow TEC-unit replacements

Economy: research, development, fabrication, application
Adaptability
Reliability
Maintainability

Although TEC accepts great thermal power densities, MFHPs excel in this capability: They can receive and deliver thousands of W/cm$^2$ radially and tens of thousands axially. Such performance falls within an envelope of mechanistic limitations identified by the following sketch.

A simplified, yet informative expression for maximum heat-pipe thermal power $Q_{\text{max}}$ results from reduction of a complicated quadratic equation by neglecting inertial and interphase effects:

$$Q_{\text{max}} = \left( \frac{2A}{r_p} \right) \left( \frac{r_p}{r_1} \right) \left( \frac{16}{\pi^2} \right) \frac{g}{g_0} \frac{k}{k_0} \pi \sin \theta$$  (6)

In this equation the first factor is the "wick number" ($N_w$); the second, the "liquid-transport factor" or "zero-g figure of merit" ($N_l$); and $g/g_0$ is the "one-g wicking height" ($H_p$). The subscripts $w$, $l$, and $p$ designate "wick," "liquid" and "pore." And $A$ is area; $g$, gravity vector; $k$, permeability; $l$, length; $r$, radius; $\theta$, inclination angle from horizontal; $\lambda$, heat of vaporization; $\mu$, viscosity; $\rho$, density; and $\sigma$, surface tension.

Equation (6) verifies that, aside from internal geometry, high-temperature-material properties ($A$, $r_p$, $r_1$, and $g$) and their effects determine the level of MFHP performance. Perhaps this context makes the general characteristics of heat pipes more meaningful:

The Heat Pipe

Is a thermal-energy transporter, transformer, and isothermizer;
Is a compact, lightweight, self-contained, self-pumped system;
Operates with no mechanical or electrical inputs — and no moving parts;
Allows diverse temperature ranges, high thermal-power densities, and low temperature gradients:

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature</th>
<th>$Q_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium (Li)</td>
<td>1500°C</td>
<td>0.1</td>
</tr>
<tr>
<td>Molten copper (Cu)</td>
<td>4000°C</td>
<td>3.75</td>
</tr>
</tbody>
</table>

The preceding simplified algebraic expressions indicate that properties and interactions of materials at high temperatures dictate TEC and MFHP performances at their maxima. But an introductory quotation states that "high-temperature
material effects determine the level and lifetime of... performance." And because thermally exponential tendencies of corrosion-rate constants can be crucial, the fact that "high-temperature material effects determine the... lifetime" is often more important. In practice, thermophysical-water stablity limits operating temperatures, hence TEC thermal emission and MFHP vaporization rates. Therefore, can high-performance TEC and MFHPs withstand thermally accelerated deterioration and live productively to economically old ages?

Answering this question requires first a diagnosis of some of the most destructive ravages possible during high-temperature TEC and MFHP operation: Both devices are subject to internal alkali-metal corrosion and solution-accelerated by low concentrations of impurities like oxygen. Inter-terrestrial service both must survive external attacks by hot corrosive gases. For space applications both must oppose sublimation of their exterior surfaces into the hard-vacuum ambience. And the near-vacuum within TEC admits of vaporization, condensation at compaction, that could cause function alterations and coat insulators. Also wherever interfaces of differing materials encounter high temperatures, reaction and diffusion loom as major concerns. Accentuated effects of the latter phenomenon occur when composition discontinuities promote void formations (Kirkendall) that diminish transport cross sections. Finally thermal creep, expansion coefficient mismatches, and solid-phase transitions demand attention in temperature cycling and gradients.

But as subsequent discussion reveals, solutions for these problems are available to make high-temperature TEC and MFHPs viable.

**Successful Limitation of Alkali-Metal Corrosion**

Since the 1960's TEC technologists have considered cesium (Cs) corrosion under control to the extent that it no longer poses problems. As reference 35 states "... the materials used are not attacked by Cs." In addition, utilization of ultra-pure Cs, strict Cl-aminities, effective getters and high-temperature vacuum bake-outs insure long lifetimes for TEC interiors.

The same general approach produces acceptable results for MFHPs, where Li usually provides the ultimate corrosion test. But in 1973, reference 36 asserted, "It has been concluded that W-26%Cr/1 (SiC) heat pipes promise a lifetime of many years at 1800 °C."

This achievement is particularly noteworthy because the heat-pipe cycle concentrates corrosion-accelerating impurities at the evaporator surface. Therefore localized thermochemical attack intensifies continuously in the performance-affecting fine structure of the wick as indicated in Fig. 4-4.

Such alkali-metal-corrosion effects catalyzed by oxygen (O) dramatize the importance of oxide getters as metallic-fluid preloading processors, as in situ purifiers and as alloy constituents. Of course good getters release much enthalpy and undergo nearly as great negative free-energy changes upon combining with O — like the metals in lower Fig. 539-91. A qualitative version of some of these data simplifies their presentation somewhat in Fig. 642. A great difference between free energies of oxide formation for two metals indicates a strong O-gettering preciosity for the one with the more-negative free-energy change. But this is a generalization based on equilibrium concepts. And degrees of rates of approach to equilibria are not estimable from free-energy values. In fact solid-state transport usually controls gettering rates after initial superficial reactions.

However Figs. 5 and 6 provide some interesting TEC and MFHP insights: One is the observation that TEC Cs can scavenge impurity oxygen, then surrender it to the Ta or Nb envelopes. This clean-up process might have caused early relatively uncontrolled TEC tests, which often began with high performances typical of O-additive enhancement, to taper off to lower efficiencies with continued operation.

Consensus places O solubility in Ta and Nb near one percent at several hundred degrees centigrade (a) or less than five percent above 1500 °C. But Cs dissolved on these refractory metals. So popular Ta and Nb alloys incorporate small amounts of hafnium (Hf) and zirconium (Zr), respectively, to getter solid-solution O, fix it as distributed oxides, and reduce brittleness. But welding and other hot processing tend to segregate slag and other impurities at interfaces. Thus, because Li can attack Ta, Nb, Zr, and Hf oxides successfully, Li heat pipes of such alloys often succumb to intergranular and weld perforations. However, as previously stated, properly processed W alloys serve admirably as high-temperature Li heat pipes. This statement is also true for Mo and some Mo alloys.

Although Li can getter O from most oxides, it is subject to gettering by a few metals like those at the bottom of Fig. 5. One of these, lanthanum (La), is present in the order of a tenth percent in Haynes Alloy 188 (cobalt (Co) -40 percent, nickel (Ni) -22 percent, chromium (Cr) -22 percent, tungsten (W) -14 percent). But welding and other hot processing tend to segregate oxides and other impurities at interfaces. Thus, because Li can attack Ta, Nb, Zr, and Hf oxides successfully, Li heat pipes of such alloys often succumb to intergranular and weld perforations. However, as previously stated, properly processed W alloys serve admirably as high-temperature Li heat pipes. This statement is also true for Mo and some Mo alloys.

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In this vein Ti-alloy, Li heat pipes should also be available soon for long-lived, weight-effective space applications ranging to over 1300 K. Such availability was unexpected for years because some authoritative heat-pipe publications state that the only alkali metal compatible with Ti is Cs. But a preponderance of non-heat-pipe literature indicates that Ti should serve well with any alkali metals as working fluids, including Li. Contract verification of this assertion is underway.

Such additional success in limiting alkali-metal corrosion will enhance TEC as well as MFHP technologies.

**Protection Against External Hot Corrosive Gases**

Advantageous terrestrial utilization of TEC and MFHPs demands operation with direct access to fossil-fuel combustion products at high temperatures. And such service requires efficacious protective coatings on heat-receiving surfaces. But subject to high velocities and mechanical stresses is unnecessary because MFHPs can collect low thermal-power densities and transform them to appropriate, nearly isothermal TEC inputs.

Silicon-carbide (SiC) claddings for TEC in toping of power plants (TOPP) arose as a promising solution to this hot-corrosion problem. 14-16,40-54 During pre-1970 Office of Coal Research contract studies, Reference 2 reports on the thermal-shock stability, thermal-expansion compatibility, molten-slag resistance and hot-corrosion protection of SiC-clad TEC. Recent EPRI-supported work on coal-fired recuperators and regenerators further supports SiC as a high-temperature heat-receiving surface.

Now Thermo Electron Corporation (TECU) is testing a series of SiC-clad TEC tubes in fossil-fuel combustion products. One with a 1730 K emitter passed 3500 hours (early December 1980) and is continuing. Tests after over 5000 hours for another SiC-clad converter with a 1630 K emitter yielded gratifying results:

"Electron microprobe analysis showed no evidence of any reaction between the interfaces of the tungsten, graphite, and silicon carbide. X-ray diffraction patterns of the silicon carbide were compared to those from unired silicon carbide. The patterns were essentially identical and showed primarily silicon carbide. Knoop microhardness tests indicated there was no change in the hardness during the life test. The hardness at the dome was KHN 2600. The following impurities were found on the dome area of the hot shell: aluminum, magnesium, potassium, and iron. The first three probably originated from the furnace firebrick and the iron from the melted fluid pipe. Significantly, no chemical reactions between these elements and the silicon carbide were indicated. Apparently, no change or degradation to the composite shell resulted from the 5000 hours of operation."

TECU also revealed that TEC fabrication based on chemical vapor deposition (CVD) with suitable SIC claddings is more economical than conventional fabrication for lower-temperature superalloy protection. The lamellar W. graphite (C), SIC dome (emitter, thermal-expansion adapter, protective coating) can also be manufactured on reusable mandrels. So directly-fired TEC appears cost-effective as well as feasible.

TECU has also demonstrated adaptability of their methods to produce SiCl-clad MFHP envelopes.

**Coping with External and Internal Vaporization**

Some lower-temperature terrestrial applications of TEC and MFHPs anticipate external not-corrosion protection by superalloys as previously mentioned. Such materials often serve well considerably hotter than 1400 K in combustion products because of adherent protective-oxide formations (see numerous NASA LeRC publications on superalloys). Therefore it is not illogical to assume that the absence of corrosive attack in the chemically benign hard vacuum of space should allow satisfactory service by these superalloys at even higher temperatures. But of course this assumption fails to eventuate.

As Fig. 7 testifies the most important superalloy constituents (Co, Cr, Fe and Ni) vaporize separately at about a mil per year between -1150 and -1250 K. Of course escape rates from alloys differ from those of pure materials because of dilution, association, and diffusion effects. But Fig. 7 enables estimates of high-temperature vaporization into vacuum for non-associated surface components. And a mil per year is significant for lightweight space structures.

Much slower vaporization rates as well as higher melting points, great strengths and much lower densities make Ti alloys excellent candidates for MFHPs in space (Fig. 8). Ti sublimes at only 0.1 mil/year near 1300 K. But such service temperatures for unprotected Ti envelopes on earth would be inconceivable. Here long-term use of unclad Ti generally occurs at temperatures below 10 K.

For satisfactory sublimation rates at temperatures above 1300 K, alloys of Mo and W or even of Nb and Ta, with proper precautions, can serve well for TEC and MFHPs (Fig. 7) — bare for space and other vacuum environs and suitably clad for usual terrestrial applications.

As previously described, MFHPs function through evaporation, condensation, wicking cycles for fluid metals: Internal pressures tend to center around one atmosphere, often between 0.1 and 10 atmospheres. But although metal vaporization prevails in MFHPs, wick and envelope materials must be thermally stable to maintain geometries essential to performance.

However vaporization, deposition problems demand special attention in TEC, where high temperatures and surface phenomena dictate performance. Line-of-sight or maze shielding can preclude insulator short-outs. But emitter-vapor deposition can be critical on the collector. Adsorption of only a few atomic layers, less than 10⁻¹⁵ cm, of a different material on an electrode can drastically alter its work function and electron reflectivity — hence its TEC per-
formance (Lqs. 11 to 5) Thus emitter-vapor deposits on the collector are as important as they are unavoidable:8

"The hot, close-up emitter practically covers the several-hundred-degrees-cooler collector. And the emitter vapor pressure is several orders of magnitude higher than that of an emitter-vapor deposit on the collector. So in low-pressure converters the arrival rate of emitter vapor on the collector is several orders of magnitude greater than the departure rate of its accumulated emitter-vapor deposit. This arrival-to-departure ratio approaches the actual emitter vapor pressure divided by its vapor pressure at the collector temperature and that quotient multiplied by the square root of the collector-to-emitter temperature ratio." Accordingly in TLL, emitter-vapor deposits tend to build up on collectors. Therefore utilizing the material deposited on it by the emitter as the collector is a simple, general solution for this TLL vaporization, deposition problem. Other answers are possible but exceptional.8,21

In any event coping with internal and external vaporization in TLL and MHPS essentially reduces to selection of the proper materials, which are available and viable.

Controlling Interfacial Reactions and Diffusion

Aside from the previously discussed working-fluid influences, reaction and diffusion effects are really not problematic in standard MHPS. Selection, electron-beam welding and high-temperature, hard-vacuum baking of identical wick and envelope materials, which have proven thermophysicalchemical stability, practically eliminate such problems to over 1600°C. And external hot-corrosion protection developed for TLL applies at least for small and intermediate heat pipes, which offer the advantage of near-isothermality.

In high temperature fossil-fuel combustion products, the 1190 SCC, C, W dome for TLL showed "no change or degradation...from 5000 hours of operation" with a 1600 K emitter. In vacuum, a cylindrical diode with a 1973 kW emitter 0.23 mm from a 1073 kNb collector generated 8 W/cm² at 0.26 V and 14 percent electrode efficiency for over 5 years before a 1973 contact termination stopped it. So interfacial reactions and diffusion appear well under control in standard TLL also.

Introduction of new high-performance electrodes sometimes causes difficulties. For example NASA LeRC proposed a Cs diode with an emitter and a collector of La hexaboride (La₆B₁₂) in the late 1960's and again during the reactivation of its TLL program in 1974/9. In 1977 NASA LeRC and USSR technologists both demonstrated high-performance TLL with nonoriented La₆B₁₂ electrodes.8,21 Controlled deposition of polycrystalline metal-hexaboride films8,21, with preferred or etch-relieved 100 or C100 orientations for La₆B₁₂, promise even better performance in practical TLL configurations (similar to CWP'd 110-W electrodes in cylindrical diodes). And gratifyingly the published consensus in 1974 indicated that brazing, diffusion and reactions between La₆B₁₂ and its support were not problems. But today the inability to maintain a 1700 K La₆B₁₂ emitter on a refractory-metal base for over 100 to 200 hours is still frustrates practical applications. However history teaches that such diffusion and reaction problems usually yield to concentrated applied research.

In general the problem of "contact diffusion interaction of materials" causes major difficulties originating at high-temperature interfaces.6,71 Other pertinent examples are the previously mentioned solution effects of alkali metals and oxygen (particularly in niobium and tantalum) as well as the intermingling of fuel with its immediate container in nuclear power generators like the in-core thermionic-converter of heat-pipe configurations.

In the latter area reference 70 presents results obtained by a group of USSR scientists who contributed theoretically and experimentally to the understanding of fuel, clad interactions. In turn reference 71 corrects their simple diffusion equation, then derives more rigorous versions through Laplace transformation of the differential rate expression, "small-system" approximation, and finally complete inversion with subsequent simplification:

\[ C(x,t) = C(0,0) \left[ 1 + \cos \left( \frac{x^2}{D} \right) - \cos (\frac{x^2}{D}) \right] \exp \left( -\frac{x^2}{D} \right) \]

where C is concentration of A in B varying over a short time t and very small distance x in accordance with a dominating diffusion coefficient D for A in B and a layer-growth constant k.

Diffusion is of course a critical influence as an entity at high-temperature interfaces. But more crucially it generally dictates rates of corrosion and other chemical reactions in practical systems -- after the initial superficial interactions deplete local compositions. To further elucidate the last observation, consider the simplistic but heuristic example of pure-metal oxidation controlled by migration in an ideal solution (after Evans21, from Hurlen6). For this situation the absolute reaction-rate theory (Eyring, Laidler and Glassstone) yields an expression for one-dimensional net transport of a species (corrected from Ref. 7c):

\[ v = \left( \frac{a_i}{n_i} \right) \exp \left( -\frac{G_i}{RT} \right) \exp \left( -\frac{e_i}{RT} \right) \]

where \( v \) is the net transport rate; \( a \), the equilibrium distance between migrating charged particles; \( k \), Boltzmann constant; \( T \), degrees Kelvin; \( h \), Planck constant; \( k_B \), standard chemical activation energy; \( R \), gas constant; \( c \), concentration of mi-
Simplifying assumptions and transformations lead to an approximate expression for film thickness \( y \) related to an equivalent oxide volume \( V \) and to \( a \) values across the film:

\[
\frac{dy}{dt} = V(\gamma), \quad \frac{d\gamma}{dx} = \frac{F}{aG}, \quad \text{and} \quad a = \frac{1}{2}
\]

(9)

\[
\frac{dy}{dt} = \sum K_i c_i y \left( \exp(-a_i z_i aG/RT) \right)
\]

(10)

where \( t \) is time and \( \gamma \) = \((Vz_i z_i aG/RT)\exp(-a_i z_i aG/RT)\).

From this simplified yet unwieldy equation Evans extracts some of the more common reduced forms used to correlate corrosion data.

For high temperatures and large film thicknesses the exponential of Eq. (10) submits to series expansion with small-terms elimination:

\[
\frac{dy}{dt} \approx \left( \sum K_i c_i \right) y \quad \text{or} \quad y^2 = K_i t + \text{const.}
\]

(11)

And the classic parabolic corrosion expression results.

In contrast for low temperatures and small film thicknesses a bracketed exponential term in Eq. (10) approaches negligibility:

\[
\frac{dy}{dt} \approx \left( \sum K_i c_i \right) \exp(T_i z_i aG/2RTy)
\]

or \( y^{-1} = \text{const.} - K_i t \) log \( t \)

(12)

This is the inverse-logarithmic relationship for corrosion.

A cubic version derives from corrosion models invoking assumptions of semiconductor properties for the oxide film. The result is equivalent to assuming corrosion conditions validating \( \exp(p) \) as an approximation of \( \exp(p) - \exp(-p) \) in Eq. (10):

\[
\frac{dy}{dt} \approx \left( \sum K_i c_i (z_i aG/2RTy)^2 \right) y^2
\]

(13)

Or \( y^3 = K_i t + \text{const.} \)

Rather than semiconduction, catalysis assumed in corrosion modeling can lead to linear time dependency. And all these variations evolve from an admittedly simplistic, even unattainable system of a pure metal limited in corrosion by transport through an ideal solution. Complications of alloys, nonideal multicomponent solutions, steep temperature gradients, inhomogeneities and myriad other realities are normal effects in actual interfacial diffusion and reactions. But this somewhat superficial description begins to indicate the problems and underscores the importance of life testing.

The preceding amplification began with a comment on new high-performance TEC electrodes like LaB₆. Gratifyingly, unoriented and CVD'd 110-W electrodes with negligible interelectrode losses can provide optimal TEC for applications requiring -1000- to -1000 K collectors. Furthermore high performance W and Mo electrodes with stable or steady-state supplies of enhancing O are in the offing. And for such TEC materials "interfacial reactions and diffusion appear well under control."

Meeting Other Thermophysical Challenges: Expansion Matches, Creep...

One of the first considerations in anticipation of a laminar composite, particularly of unforgiving refractory materials like tungsten and silicon carbide, is the match of thermal-expansion coefficients. An excellent example of such an evaluation from the late 1960's appears in Ref. 7: Fig. 9(a) comprises prepublished data; Fig. 9(b) data obtained during the published study. Separately the sets of results reveal near-matches for W and SiC thermal expansions. Together they predict practical coincidence.

The significance of this comparison was impressive in the late 1960's, even as it is today 77:

"Six molybdenum tube samples, coated with various thicknesses of thick grain CVD silicon carbide have been received from Chemetal and subjected to a series of thermal shock tests, both in a vacuum furnace and in a natural gas flame. The objective was the evaluation of the coating adhesion. Temperature cycling in the vacuum furnace covered the range from approximately 400 to 1500 K. The samples were inspected after one, three, and six temperature cycles. Following these tests, the surviving samples were subjected to natural gas flame heating and ambient air cooling for a total of approximately 40 cycles. The conclusion reached in these preliminary tests is that when a thin intermediate layer of tungsten is used, the molybdenum substrate-CVD silicon carbide coating will withstand the thermal stresses over the temperature range of interest. No evidence of layer separation was disclosed in metallographic examination of tube samples."

The contribution of this thermal-expansion-match observation is critically important to MFHPs for terrestrial use as well as to TEC.

Incidentally, a reference-2 silicon carbide sample "temperature cycled over 7300 times" in hydrocarbon-combustion products "to about 2800° F in about one minute," followed by a "two-minute..."
cool-off to about 700° F. Coal ash was deposited on the surface of the test sample during the cool-down portion of the test cycle ... The only visible effect on the silicon carbide was an erosion of about 0.02 inch where the pressurized flame impinged on the sample. "It was apparent that the temperature of this point was considerably higher than the measured temperature of the test sample ... As before, solidified coal ash was evident on the tube surface, but sectioning and metallographic examination ... showed no coal ash penetration of the silicon carbide. The solidified coal ash observed on the test sample was a result of the final cool-down. During the temperature cycling, good run-off of the coal ash was observed at the high temperatures, leading to the conclusion that the final air heater would indeed be self-cleaning."

Subsequent references on SiC service in fossil-fuel combustion products support and augment reference-2 findings48-54. For example, TECO recently heated its SiC, L, W dome at 1875 K for over 70 hours, sprayed water on it at 1875 K 10 times (1000 K between the water-cooled spot and the rest of the dome), poured liquid nitrogen on it at 1875 K 10 times, then cycled it from 1875 K to 900 K over 150 times, then from 2025 K to 900 K over 100 times taking about one minute for each cycle -- all with no ill effects to the SiC, L, W dome.

Interestingly, TECO uses L to more carefully adapt silicon-carbide thermal-expansion to that of W. And Chemetall utilizes W for thermal-expansion adaptation of SiC to Mo. The latter lamination has yet to undergo long-term high-temperature exposure to fossil-fuel combustion products, successfully experienced by the former. But results of both approaches are gratifying.

In addition to the thermal-expansion effects, refractory-material strength and creep at high temperatures are of course important in TEC and MFHP applications. In this vein, just subsequent to mentioning SiC and C, two referential observations are pertinent: First "it is interesting to note that the treated SiC exhibits an increase in strength with an increase in test temperature up to about 2200° F" ...78. And second "graphite possesses high thermal conductivity, a low modulus of elasticity, a low coefficient of thermal-expansion, and relatively satisfactory strength increasing with increase in temperature to 2700° C" ...79. Conceivably such protective clads and thermal-expansion adapters might also serve as structural members at high operating temperatures.

High temperature structural members are subject to the thermal creep80-82. This phenomenon is the time-dependent plastic deformation of a material under sustained loading at temperatures above about half its melting point value. Like many other thermophysical effects, creep is complex, even in pure polycrystalline metals. Here in general high-temperature creep resistance relates to high levels for the melting point, elastic modulus, stability of fine grain size, crystal-structure constant for self-diffusion, and valence state. Departing from pure metals introduces considerations of strengthening by solution, precipitation, dispersion and composite effects. In practical applications, permutations of complicating influences are myriad. For example, reference 47 states that "the maximum U level in Na necessary to avoid embrittlement of Nb at 700° C has been estimated to be less than 10 ppm."

The preceding scarce tactics are really intended only to indicate that published creep values for a given material can vary considerably with little or no apparent reason. But such information is particularly important for MFHPs and TEC in systems with ~1000 K emitters. And for these applications, satisfactory materials are few as the creep-strength curves of Fig. 10 illustrate.

In any event high-temperature TEC and MFHPs based on the creep resistance of W and W alloys have demonstrated in vacuum capabilities for many years of service. Ta, Nb and Mo alloys afford effective creep resistance for selected applications also. Figure 10 shows such alloys: T-111 (Ta, W, ZrF); ASTAR-B11C (Ta, W, 3Re, 0.7Hf, 0.35C); Nb, 1Zr; FS-85 (Nb, 28Ta, 10W, 1Zr); TZC (Mo, 1.7Ti, 0.25Cr, 0.15C); and TZM (Mo, 0.5Ti, 0.08Br, 0.03C).

Weight-effectiveness in space and cost-effectiveness in general drive toward minimal wall thicknesses allowed to in Fig. 8. For such conditions the previously mentioned "stability of fine grain size" is very important. This state not only maintains creep resistance, but also avoids recrystallization grain dimensions and intergranular paths approaching containment-wall thicknesses. The latter occurrence promotes fluid leaks as well as strength discontinuities.

Specially selected additives can increase creep resistance, retard recrystallization and control solid-phase transitions often accompanied by abrupt changes in properties like thermal expansion. Referring again to titanium may exemplify the last observation:

"Thermophysically, Ti undergoes a solid-phase alteration at about 1160 K. Here rising temperatures change the closely packed-hexagonal "alpha" structure to the body-centered-cubic "beta" configuration. However this transformation, like the a-to-y transition for iron at 1180 K, causes no great difficulties. The Ti a-to-y phase-change temperature rises with Al additions and falls (even below room temperatures) with inclusions of Mo, Fe, Cr or V. Commercially available pure (99.6 percent) Ti and Ti, 5AI, 2.5Sn are alpha alloys. Ti, BMo, BV, 2Fe, 3AI is a beta alloy, and the most widely used Ti, 6AI, 4V is an "alpha-beta" alloy.

Like Ti, refractory metals Zr and Hf, also in periodic group IVA, undergo solido-phase transitions43-46,84. In contrast group VA Mo and W exhibit no solid-phase changes.

The considerations raised in this section represent some obvious difficulties that have been overcome on the path to successful applications of high-temperature TEC. Many other less impressive thermophysical challenges have arisen, then fallen under the pressure of applied research.
High-Temperature TEC and MFHPs: In Brief

In addition to the detailed similarities of TEC and MFHPs emphasized in the introductory sections, a generalized parallel can be drawn: The two operating cycles appear as invitingly simple and isolated as their material problems seem forebodingly difficult and complexed. The first observation is deceptive; the second, candid. Both areas required intense study and experimentation, which resulted in recognition of their singular relationship. "In short, high-temperature material effects determine the level and lifetime of ... performance."

Simplified equations verify material properties and interactions as primary influences on the operational effectiveness of both TEC and MFHPs. And being essentially evaporation, condensation cycles, TEC and MFHPs experience flow limitations in thermal emission and vaporization because of temperature restrictions redounding from thermophysical-chemical-stability considerations. Thus attaining practical lifetimes generally implies limiting performances in exchange.

But as previous discussions reveal, major high-temperature material problems of TEC and MFHP have been solved. The solutions are workable and economically and lend directly to applications that are productive and cost-effective. In fact current performance and cost levels imply improved outputs, efficiencies, and economies for TEC topping of combustors, central-station power plants and other advanced conversion systems heated by high-temperature energy sources.

And anticipated technological gains point to even greater improvements for future TEC and MFHP applications by more fully utilizing high-power densities from high-temperature material interactions.

References
### TABLE I. SOME SPACE APPLICATIONS FOR METALLIC-FLUID HEAT PIPES

<table>
<thead>
<tr>
<th>SYSTEM ELEMENT OR PRIMARY FUNCTION</th>
<th>HEAT-PIPE SERVICE</th>
<th>TEMPERATURE, K</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ENERGY SOURCES</strong></td>
<td></td>
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</tr>
<tr>
<td>Solar Concentrators</td>
<td>Isothermalize receivers and processors</td>
<td>To &gt; 2000</td>
</tr>
<tr>
<td></td>
<td>Isothermalize receivers and transport thermal power (TTP)</td>
<td>To ≤ 1850</td>
</tr>
<tr>
<td>Nuclear Reactors</td>
<td>Cool reactors, flatten temperature profiles, TTP, transform TP densities (TTPD), if required</td>
<td>To &gt; 1850</td>
</tr>
<tr>
<td></td>
<td>Cool and isothermalize radioisotopes. TTP (TTPD)</td>
<td>To ≤ 1675</td>
</tr>
<tr>
<td></td>
<td>TTP, TTPD, heat, isothermalize</td>
<td>To ≤ 1600</td>
</tr>
<tr>
<td></td>
<td>TTP, heat, isothermalize</td>
<td>To ≤ 1300</td>
</tr>
<tr>
<td></td>
<td></td>
<td>To ≤ 1000</td>
</tr>
<tr>
<td><strong>THERMAL-TO-ELECTRIC CONVERTERS</strong></td>
<td></td>
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<tr>
<td>Thermal-Power Input</td>
<td></td>
<td></td>
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<tr>
<td>TEC emitters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TE hot shoes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>New materials</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Current materials</td>
<td></td>
<td></td>
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<tr>
<td>Best possibility</td>
<td></td>
<td></td>
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<tr>
<td>Ready availability</td>
<td></td>
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</table>
TABLE I. - Continued. SOME SPACE APPLICATIONS FOR METALLIC-FLUID HEAT PIPES.

<table>
<thead>
<tr>
<th>SYSTEM ELEMENT OR PRIMARY FUNCTION</th>
<th>HEAT-PIPE SERVICE</th>
<th>TEMPERATURE, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>B H-T heat exchanger ('H-T-HE)</td>
<td>TIP, Act as H-T-HE</td>
<td>To ~ 1400</td>
</tr>
<tr>
<td>New materials</td>
<td></td>
<td>To ~ 1150</td>
</tr>
<tr>
<td>Current materials</td>
<td></td>
<td>To ~ 1050</td>
</tr>
<tr>
<td>Potassium Rankine</td>
<td></td>
<td>-400 to -1100</td>
</tr>
<tr>
<td>Thermal-Power Rejection</td>
<td></td>
<td>To ~ 950</td>
</tr>
<tr>
<td>TEC collectors (depending on system power)</td>
<td>Isothermalize, Cool, TTP</td>
<td>To ~ 800</td>
</tr>
<tr>
<td>TE cold shoes (depending on system power)</td>
<td>Act as HEC, TTP</td>
<td>-400 to -850</td>
</tr>
<tr>
<td>New materials</td>
<td></td>
<td>-350 to -500</td>
</tr>
<tr>
<td>Current materials</td>
<td></td>
<td>-800</td>
</tr>
<tr>
<td>B Heat-exchanger cooler (HEC) (system power)</td>
<td>Cool, isothermalize, TTP</td>
<td>-350 to -430</td>
</tr>
<tr>
<td>New materials</td>
<td></td>
<td>&gt;500</td>
</tr>
<tr>
<td>Current materials</td>
<td></td>
<td>To &gt; 920</td>
</tr>
<tr>
<td>Potassium Rankine</td>
<td></td>
<td>To &gt; 1270</td>
</tr>
<tr>
<td>ELECTROCHEMICAL CELLS</td>
<td></td>
<td>-300 to -430</td>
</tr>
<tr>
<td>Fuel Cells (FC)</td>
<td></td>
<td>To &gt; 420</td>
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<tr>
<td>Noble-metal catalyst</td>
<td></td>
<td>To &gt; 720</td>
</tr>
<tr>
<td>Apollo (Bacon) cell (high reject. temp. HRT)</td>
<td></td>
<td>-280</td>
</tr>
<tr>
<td>Molten carbonate (high reject. temp. HRT)</td>
<td></td>
<td>To &gt; 450</td>
</tr>
<tr>
<td>Solid oxide (high reject. temp. HRT)</td>
<td></td>
<td>To &gt; 450</td>
</tr>
<tr>
<td>Electrolysis (regen. FC: energy storage)</td>
<td></td>
<td>To &gt; 450</td>
</tr>
<tr>
<td>Current practice</td>
<td></td>
<td></td>
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<tr>
<td>Thermal + electrolytic processing (HRT)</td>
<td></td>
<td></td>
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<tr>
<td>Batteries</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Current practice</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkali-metal, organic-electrolyte (HRT)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkali-metal, solid-electrolyte (HRT)</td>
<td></td>
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</tr>
<tr>
<td>PHOTOVOLTAIC CELLS</td>
<td></td>
<td></td>
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<tr>
<td>Concentrated radiation (raise low efficiencies)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermally reformed radiation (raise low eff.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>High-temperature environments</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### TABLE I: Conclusion. Some space applications for metallic fluid heat pipes.

<table>
<thead>
<tr>
<th>Other Aerospace Applications</th>
<th>Heat-Pipe Service</th>
<th>Temperature, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space radiators</td>
<td></td>
<td>To &gt; 1100</td>
</tr>
<tr>
<td>Heat exchangers, recuperators, regenerators</td>
<td></td>
<td>To &gt; 1850</td>
</tr>
<tr>
<td>Heat-pipe, phase-change-material</td>
<td></td>
<td>To &gt; 1100</td>
</tr>
<tr>
<td>Thermal capacitors</td>
<td></td>
<td>To = 350</td>
</tr>
<tr>
<td>High-temperature structures (Ollendorf patent)</td>
<td></td>
<td>T_e's to &gt; 2000</td>
</tr>
<tr>
<td>High-power-density, high-voltage</td>
<td></td>
<td>T_C's to &gt; 1000</td>
</tr>
<tr>
<td>Electrical processing and electronics</td>
<td></td>
<td>To &gt; 1100</td>
</tr>
<tr>
<td>High-power density switching with plasma devices</td>
<td></td>
<td>To &gt; 2000</td>
</tr>
<tr>
<td>Heat-pipe-cooled magnetics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Leading-edge cooling for re-entry vehicles and hypersonic aircraft</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Materials processing, testing, and fabrication in space</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tritium production (n + ^7Li + T → He* + 4.6 MeV and n + ^6Li + He* + T + n → 2.47 MeV) and recovery with Li heat pipes in blankets of thermonuclear reactors (D + T → He* (3.5 MeV) + n (14.1 MeV))</td>
<td>&gt; 1400</td>
<td></td>
</tr>
</tbody>
</table>
THERMONIC ENERGY CONVERTER ELECTRONS

ESCAPE THE HEATED_EMITTER,
PASS THROUGH THE INTERELECTRODE_GAP,
ENTER THE COOLED COLLECTOR,
DEVELOP VOLTAGE ACROSS THE ELECTRODES,
FLOW BACK TO THE EMITTER EXTERNALLY,
PERFORM ELECTRICAL WORK, AND
RECYCLE CONTINUOUSLY.

THE HEAT-PIPE WORKING FLUID

VAPORIZES IN THE HEATED "EVAPORATOR,"
FLOWS AS A VAPOR THROUGH THE "ADIABATIC
SECTION,"
GIVES UP ITS HEAT OF CONDENSATION IN THE
COOLED "CONDENSER,"
FLOWS AS A LIQUID BACK TO THE EVAPORATOR
THROUGH THE "WICK" ARTERIES,
MOVES TO THE VAPORIZING SIDE THROUGH
THE WICK CAPILLARIES,
AND RECYCLES CONTINUOUSLY.

Figure 1. - TEC and heat-pipe cycles.

Figure 2. - Performance and tapping temperatures for thermionic energy conversion with 30 Acm², 18% back emission and negligible interelectrode losses.
Figure 3. - Heat-pipe operating ranges.

REFLUX-CAPSULE TEST FLUIDS

1. Vaporize, sweep noncondensible corrosion products to capsule tops, condense.

2. Form, dissolve, and drain nonvolatile corrosion products to capsule bottoms, diluting nonvolatile corrosion products in test-liquid pools.

HEAT-PIPE WORKING FLUIDS

3. In contrast, transport dissolved corrosion products through wick arteries to evaporator tops, move to evaporating surfaces through wick capillaries, vaporize, leaving continuously concentrating nonvolatile corrosion products in evaporator wicks.

4. Then, sweep noncondensible corrosion products to condenser ends, liquefy, and recycle.

Capsule, coupon, or ordinary "low methods do not approximate heat-pipe life testing.

But, a suitable cylindrical screen changes an ineffective capsule into a heat-pipe for effective, economical life testing.

Figure 4. - Heat-pipe materials compatibility: life testing.
Fig. 5  Free-energy data for oxide formation (after Richardson and Jeffes, 1948).

1 kcal = 4. 1868 kJ; 2.303 R = 19. 546 J/mol deg C; 2 atm = 101. 325 N/m²; 1 atmosphere = 96606 kJ.

(Refs. 38 to 41.) (Courtesy of American Society of Metals.)
Figure 6. - Stability relationships of refractory oxides. Solid lines represent constant standard free energy of formation from the elements. The darkest area is the region of greatest stability (ref. 42).

Figure 7. - Vaporization of pure metals and lantha-nium hexaboride.
RELATIVE MONTNER

►

ARAWTER

IDASED ON ASK

RESSUK VESSEL COOEI

FOR HIGH-PRESSURE HEAT-PIPE ENVELOPES

( DENSITY AT T

ULT. STRENGTH AT T

METAL

DENSITY AT T

ULT. STRENGTH AT T

0055

CU CDA 102

AI 6061 T6

Ti 35A

COMMERCIALMELY PURE

Ti, 02 Pd

30455

Ti, 8AI, 1Mo, 1V

Ti, 6AI, 4V

Ti, 8Mo, 8V, 2Fe, 3Al

Figure 8. - Relative weight parameters.
Figure 9. - Linear thermal expansions for Mo, W, and SiC from ref. 2.

Figure 10. - Creep strength of some refractory metals and alloys for 1 percent creep in 10,000 hours.