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High Power Densities from High-Temperature Material Interactions

James F. Morris
National Aeronautics and Space Administration
Lewis Research Center

Work performed for
U.S. DEPARTMENT OF ENERGY
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Prepared for
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Abstract

Thermionic energy 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. TEL 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, complicated 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 TEL and MFHPs. Material properties and interactions exert primary influences on operational effectiveness. And thermophysical-chemical stability dictates operating temperatures which regulate the thermoelectric 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 competitive, cost-effective applications of current TEL 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 the experts who attended the 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 conversion 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, 14, 16-20. 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 level20, 27. Aiming at this goal the USSR reported in 1976 on "the tests of three 'Topaz' reactors" ("thermo electric nuclear power plants") that demonstrated... long-term stable and reliable operation with good reproducibility of parameters28.

TEC and MFHP Power Densities and Problems

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

\[ J_{ES} = A(1 - R_E)T_C^2 \exp(-\phi_E/kT_C) \]  

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 censtrum concentrations, reduced enhanced-mode pressures, close electrode spacings, and small interelectrode losses. Under such conditions, the back emission \( (J_{BE}) \)

\[ J_{BE} = A(1 - R_{BE})T_C^2 \exp(-\phi_E/kT_C) \]  

where \( R_{BE} \) comprises \( R_E \) (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:

\[ J_{ES} = A(1 - R_L)T_C^2 \exp(-\phi_L/kT_C) \]  

The preceding equations verify a previous assertion: High-temperature material effects \( (\phi_E, R_E, T_E, \phi_L, R_L, T_C, J_{ES}, \ldots) \) determine the level of TEC performance — completely. This generalization includes enhanced-mode operation also because \( V_A \) 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 \( W/\text{cm}^2 \) radially and tens of thousands axially. Such performance falls within an envelope of mechanistic limitations described 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:

\[ Q_{\text{max}} = \frac{(2A_k)^{\frac{1}{2}}}{v_1 r_1^2 \rho_1} \left( \frac{r_1}{r_1^2} \right) \left( \frac{1 - \rho_1 g \eta_1 \sin \theta}{\rho_1} \right) \]  

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 \( 2\eta_1/\rho_1 \) 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; \( l \), heat of vaporization; \( u \), viscosity; \( \rho \), density; and \( \eta \), surface tension.

Equation (6) verifies that, aside from internal geometry, high-temperature-material properties \( (A_k, \rho, \eta, \rho_1, \) and \( \rho_1) \) 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 isolator;
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:

\[
\begin{align*}
15,000 \text{ W/cm}^2 & \text{ at } 1500^\circ \text{C} & 1^\circ \text{C/cm} & 150,000 \\
\text{Lithium (Li) heat pipe} & & 0.1 & 4000 \\
\text{Molten copper (Cu)} & & 3.75 & \text{W/cm}^2/\text{C}
\end{align*}
\]

The preceding simplified algebraic expressions indeed 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 trends of corrosion-rate constants can be crucial, the fact that "high-temperature material effects determine the ... lifetime" is often more important. In practice, thermophycochemical stability 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 more 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. Interstellar 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 ambiance. And the near-vacuum within TEC admits of vaporization, condensation and complicating corrosion 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 is unlikely to be of much concern. As reference 35 states "... the materials used are not attacked by Cs." In addition, utilization of ultra-pure Cs, strict Cl-anliness, effective getters and high-temperature vacuum bake-outs ensure 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-26Re/Li (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.

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. 5A-B. A qualitative version of some of these data simplifies their presentation somewhat in Fig. 6. 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 or 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 amound water than five percent above "1500°C". But dissolved oxygen embrittles these refractory metals. So popular Ta and Nb alloys incorporate small amounts of hafnium (Hf) and zirconium (Zr), respectively, to getter 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, iron (Fe) -2 percent). It is noteworthy that a Haynes 188, lithium heat pipe has been and is running with an evaporator temperature of -250 K for over 19,000 hours (mid-November 1980) at the NASA Lewis Research Center. This heat pipe was part of a project to determine advantages of very high-temperature, hard-vacuum preloading bake-outs on Li and sodium (Na) compatibilities with several superalloys during heat-pipe operation. In practically all such preceding compatibility studies, access to corrosion-accelerating impurities had been assured. Unfortunately, the project objective was thwarted at the outset because the supplier was forced to use metal-felt wicks, which are difficult to clean up, rather than the stipulated screen. As a result, bake-out achieved only in the order of 10^-4 torr rather than the specified lower than 10^-7 torr. Subsequently the other (non-HA188) superalloy, Li heat pipes failed early with destroyed wicks and severe internal wall attacks. Two Haynes 188, Li heat pipes developed leaks in stress cracks caused by welding after 200 hours. But sectioning and microscopic examination revealed no Li effects on wicks or walls (unpublished results from W. B. Kaufman, W. E. Frey and J. F. Morris of NASA Lewis Research Center).
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 exposure 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) clads for TEC in topping power plants (TOPP) arose as a promising solution to this hot-corrosion problem.14-18,40-54 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 (TECO) 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 1680 K emitter yielded gratifying results54:

"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 unfired 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 flue 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."

TECO also revealed that TEC fabrication based on chemical vapor deposition (CVD) with suitable SiC cladding 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.

TECO has also demonstrated adaptability of their methods to produce SiC-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 superalloys39). 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 1400 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 10⁻¹⁰ cm, of a different material on an electrode can drastically alter its work function and electron reflectivity—hence its TEC per-
formance (Eqs. (1) to (5)). Thus emitter-vapor deposits on the collector are as important as they are unavoidable:

"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 convertors 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 approximates the actual emitter vapor pressure divided by its vapor pressure at the collector temperature with that quotient multiplied by the square root of the collector-to-emitter temperature ratio."

Accordingly in ILC, 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 ILC vaporization, deposition problem. Other answers are possible but exceptional.

In any event coping with internal and external vaporization in ILC and MHPIs 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 MHPIs. Selection, electron-beam welding and high-temperature, hard-vacuum baking of identical wick and envelope materials, which have proven thermophysical stability, practically eliminate such problems to over 1600°C. And external hot-corrosion protection developed for ILC applies at least for small and intermediate heat pipes, which offer the advantage of near-isothermality.

In high-temperature fossil-fuel combustion products, the 1100 SiC, C, W dome for ILC showed "no change or degradation ... from 5000 hours of operation" with a 1600 K emitter. In vacuum, a cylindrical diode with a 1973 K W emitter 0.23 mm from a 1073 K Nb collector generated 8 W/cm² at 0.7 eV and 14 percent electrode efficiency for over 5 years before a 1973 contract termination stopped it. So interfacial reactions and diffusion appear well under control in standard ILC 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 (La₆B₆) in the late 1960's and again during the reactivation of its ILC program in 1974). In 1977 NASA LeRC and USSR technologists both demonstrated high-performance ILC with nonoriented La₆B₆ electrodes (3-5). Controlled deposition of polycrystalline metal-hexaboride films with preferred or etch-relieved 100 or 110 orientations for La₆B₆, Nb, or Nb₅Si, promise even better performance in practical ILC configurations (similar to CWP'd 110-K electrodes in cylindrical diodes). And gratifyingly the published consensus in 1974 indicated that brazing, diffusion and reactions between La₆B₆ and its support were not problems. But today the inability to maintain a 1700-K La₆B₆ emitter on a refractory-metal base for over 100 to 200 hours (85°C) 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 (5,7). 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 or heat-pipe configurations.

In the latter area reference 70 presents results obtained by a group of USS 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:

\[
C(x, t) = C(0, 0) \left[ 1 + \cos \left( \frac{x^2}{D} \right) - \cos \left( \frac{x^4}{D} \right) \right] \exp \left( - \frac{x^2}{D} \right)
\]

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 Evans 7, from Hurlen 7). 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):

\[
v = \frac{1}{k} \exp(-\Delta G^f/RT) \left[ \exp(-aRFD/RTdx) - (c + \lambda \Delta dc/dx) \exp(-(1 - a)RFD/RTdx) \right]
\]

The pre-bracket factor, specific rate for a unit concentration without fields, involves no net transport. The first term in the brackets covers retardation. Also in (8) \( v \) is the net transport rate; \( \lambda \), the equilibrium distance between migrating charged particles; \( k \), Boltzmann constant; \( T \), degrees Kelvin; \( h \), Planck constant; \( R \), standard chemical activation energy; \( c \), 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 $\alpha$ values across the film:

$$\frac{dy}{dt} = V \dot{\alpha}, \quad \frac{d\alpha}{dx} = \frac{dc}{dx}, \quad \alpha = \frac{G}{F} \beta$$

where $t$ is time and $\dot{\alpha} = (Wk/1n)exp(-G/RT)$.

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

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

$$\frac{dy}{dt} = K/C_y \exp(\frac{\alpha}{C_y}) / y$$

where $y^2 = K \alpha / C_y$ or $y^1 = K \alpha / C_y$.

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:

$$\frac{dy}{dt} = \left[ \sum_{i} K_i C_i \exp(\frac{\alpha_i}{C_i}) \right] / y$$

or $y^1 = K_i \log t$.

This is the inverse-logartimic 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 $\exp(1/z_1,2G/2RT)$ in Eq. (10):

$$\frac{dy}{dt} = \sum_{i} K_i C_i \exp(\frac{\alpha_i}{C_i}) / z_1,2G/2RT)$$

or $y^3 = K_i \exp(\frac{\alpha_i}{C_i})$.

Rather than semiconduction, catalysis assumed in corrosion modeling can lead to linear time dependence. 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 LaCr. Gratifyingly, unoriented and CVD'd 110-K electrodes with negligible interelectrode losses can provide optimal TEC for applications requiring -1000- to -1100 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.'
material under sustained loading at temperatures many other thermophysical effects, creep is com-

plex, even in pure polycrystalline metals. Here

in general high-temperature creep resistance
relates to high levels for the melting point,
High-Temperature TEC and MFHP's, in Brief

In addition to the detailed similarities of TEC and MFHP's 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 complex. 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 MFHP's. And being essentially evaporation, condensation, cycles, TEC and MFHP's experience flow limitations in thermal emission and vaporization because of temperature restrictions redounding from thermophysical-stability considerations. Thus obtaining 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 economical and lead 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 ever greater improvements for future TEC and MFHP applications by more fully utilizing high power densities from high-temperature material interactions.

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<td>To - 1600</td>
</tr>
<tr>
<td>TEC emitters</td>
<td></td>
<td>- 1300</td>
</tr>
<tr>
<td>TE hot shoes</td>
<td></td>
<td>- 1000</td>
</tr>
<tr>
<td>New materials</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Current materials</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat possibility</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ready availability</td>
<td></td>
<td></td>
</tr>
</tbody>
</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 '1.-T-HE)</td>
<td>TTP, 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></td>
<td>To - 800</td>
</tr>
<tr>
<td>TE cold shoes (depending on system power)</td>
<td></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></td>
<td></td>
</tr>
<tr>
<td>New materials</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Current materials</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potassium Rankine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ELECTROCHEMICAL CELLS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fuel Cells (FC)</td>
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<td></td>
</tr>
<tr>
<td>Noble-metal catalyst</td>
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<td></td>
</tr>
<tr>
<td>Apollo (Bacon) cell (high rej.-ct. temp. HRT)</td>
<td></td>
<td></td>
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<tr>
<td>Molten carbonate (high reje.-ct. temp. HRT)</td>
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<td></td>
</tr>
<tr>
<td>Solid oxide (high reject. temp. HRT)</td>
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<td></td>
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<tr>
<td>Electrolysis (regen. FC:Energy storage)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Current practice</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal + electrolytic processing (HRT)</td>
<td></td>
<td></td>
</tr>
<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>
<td></td>
</tr>
<tr>
<td>PHOTOVOLTAIC CELLS</td>
<td></td>
<td></td>
</tr>
<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>
<tr>
<td>Cool, isothermalize, TTP</td>
<td></td>
<td>-350 to -430</td>
</tr>
<tr>
<td>Heat; cool, isothermalize, TTP</td>
<td></td>
<td>&gt;500</td>
</tr>
<tr>
<td>Cool, isothermalize, TTP</td>
<td></td>
<td>To &gt; 920</td>
</tr>
<tr>
<td>Cool, isothermalize, TTP</td>
<td></td>
<td>To &gt; 1270</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-300 to -430</td>
</tr>
<tr>
<td></td>
<td></td>
<td>To &gt; 420</td>
</tr>
<tr>
<td></td>
<td></td>
<td>To &gt; 720</td>
</tr>
<tr>
<td></td>
<td></td>
<td>To &gt; 450</td>
</tr>
</tbody>
</table>


### TABLE I: Concluded. 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>OTHER AEROSPACE APPLICATIONS</strong></td>
<td></td>
<td></td>
</tr>
<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; 1300</td>
</tr>
<tr>
<td>Thermal capacitors</td>
<td></td>
<td></td>
</tr>
<tr>
<td>High-temperature structures (Ollendorf patent)</td>
<td></td>
<td>To &gt; 350</td>
</tr>
<tr>
<td>High-power-density, high-voltage</td>
<td></td>
<td>T_e's to &gt; 2000</td>
</tr>
<tr>
<td>Electrical processing and electronics</td>
<td></td>
<td>T_C's to &gt; 1000</td>
</tr>
<tr>
<td>High-power density switching with plasma devices</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat-pipe-cooled magnets</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Leading-edge cooling for re-entry vehicles and hypersonic aircraft</td>
<td></td>
<td>To &gt; 1100</td>
</tr>
<tr>
<td>Materials processing, testing, and fabrication in space</td>
<td></td>
<td>To &gt; 2000</td>
</tr>
<tr>
<td>Tritium production (n + ^1_1H + T = He^4 + 4.6 MeV and n + ^7_3Li = He^4 + T + n = 2.47 MeV) and recovery with Li heat pipes in blankets of thermonuclear reactors (D + T = He^4 (3.5 MeV) + n (14.1 MeV))</td>
<td></td>
<td>&gt; 1400</td>
</tr>
</tbody>
</table>
Figure 1. - TEC and heat-pipe cycles.

Figure 2. - Performance and tapping temperatures for thermionic energy conversion with 30 Acm², 16% back emission and negligible interelectrode losses.
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 Jeffsy, 1948)\(^1\)

1 \(1 \text{cal} = 4.1868 \text{kJ}, 2 \text{mol} = 19,154.6 \text{J/mol deg C};\)

1 \(1 \text{atm} = 101.325 \text{KN m}^2; 1 \text{V corre.} = 96,602 \text{kJ}.\)

(Ref. 36 to 41.) (Courtesy of American Society for 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 lanthanum hexaboride.
RELATIVE WEIG-T PARAMETER
(BASED ON ASME PRESSURE VESSEL CODE)
FOR HIGH-PRESSURE HEAT-PIPE ENVELOPES

DENSITY AT T
ULT. STRENGTH AT T
METAL
DENSITY AT T
ULT. STRENGTH AT T
"0455

Cu CDA 102
Al 6061 T6
Ti 38A
COMMERCIALIY PURE
Ti, 0.2 Pd
30455
Ti, 8Al, 1Mo, 1V
Ti, 6Al, 4V
Ti, 8Mo, 8V, 2Fe, 3AI

RELATIVE WEIGHT PARAMETER
FOR LOW-PRESSURE-HEAT-PIPE ENVELOPES AND ALL WICK STRUCTURES
RWP = (METAL DENSITY AT T/30455 DENSITY AT T)
APPLIES WHERE ASME PRESSURE-VESSEL CODE YIELDS WALL THICKNESSES TOO THIN FOR FABRICATION, JOINING, PROCESSING, HANDLING, AND/OR OPERATION.
EXAMPLE: 1" - DIAM. SPACE HP AT 10 ATM. WITH A 40,000 psi (ULT. STR.) ENVELOPE.
HOOP-STRESS WALL THICKNESS (ASME P-V CODE): 7 MILLS (THINNER WALLS RESULT FOR LOWER OPERATING PRESSURES AND HIGHER ENVELOPE STRENGTHS). USUALLY PREFERRED WALL THICKNESSES: TENS OF MILLS

296 K (70°F) 700 K (1300°F) 1033 K (1800°F)
Aluminum 0.33 0.34 ---
Copper 1.11 1.11 ---
Titanium 0.56 0.57 0.58
30455 1.0 1.0 1.0

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.