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James F. Morris
National Aeronautics and Space Administration
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Work performed for
U.S. DEPARTMENT OF ENERGY
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Prepared for
Sixteenth Thermophysics Conference, High
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HIGH POWER DENSITIES FROM HIGH-TEMPERATURE MATERIAL INTERACTIONS*

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

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. 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, complected 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 thermophysicochemical stabilities dictate operating temperatures which regulate the thermoemissive 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 and 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"[1]. 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[1,22-25]. 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 that 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_t/cm^2, as implied by Fig. 2. There TEC outputs range up to tens of W_e/cm^2 (P_{OL}) and tens of percent efficiency (η_{OL}):

$$P_{OL} = (\phi_E - \phi_C - V_D - V_A - V_L)(J_{ES} - J_R) \qquad (1)$$

$$\eta_{OL} = (J_{ES} - J_{BE})\left\{\phi_E - \phi_C - V_D - V_A - 2\left[2.45\text{x}10^{-8}\,\eta_{EC}\left(T_E^2 - T_C^2\right)\Big/(2 - \eta_{EC})\right]^{1/2}\right\}\Bigg/\left\{J_{ES}(\phi_E + 2kT_E) - J_{BE}(\phi_E + 2kT_C) + 5.7\text{x}10^{-12}\left[0.05 + 7.5\text{x}10^{-5}(T_E - 1000)\right]\left(T_E^4 - T_C^4\right)\right\} \qquad (2)$$

In these equations ϕ_E and ϕ_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)), η_{EC} is the TEC electrode efficiency (equal to (2) with $2V_L$ deleted from the numerator), T_E and T_C are emitter and collector temperatures, the last term in the denominator of (2) approximates nonelectronic thermal transport, J_R 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

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for emitter saturation:

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

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[21,26,29-31]

$$J_{BE} = A(1 - R_{BE})T_C^2 \exp[-(\phi_C + V_D)/kT_C] \qquad (4)$$

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:

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

The preceding equations verify a previous assertion: High-temperature material effects (ϕ_E, R_E, T_E, J_{ES}, ϕ_C, R_C, T_C, J_{CS}...) 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

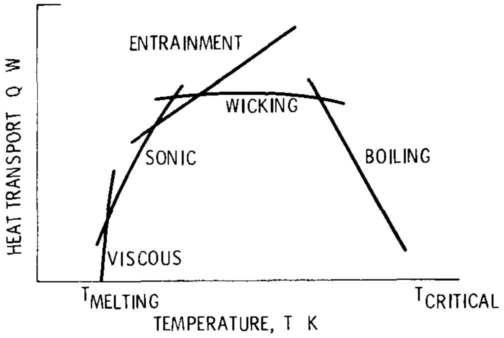
Electricity directly from heat
No moving parts or inherent mechanical stresses
High temperatures: high Carnot efficiencies
Great power densities - with
Broad near-maximum-efficiency plateaus
Rapid responses to load or heat variations
  (constant temperature)
Low weights
Small volumes
Modularity

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_t/cm^2 radially and tens of thousands axially. Such performance falls within an envelope of mechanistic limitations typified by the following sketch.



HEAT PIPE PERFORMANCE LIMITS

A simplified, yet informative expression for maximum heat-pipe thermal power Q_{max} results from reduction of a complicated quadratic equation by neglecting inertial and interphase effects[32-34]:

$$Q_{max} = \left(\frac{2A_w K_w}{r_p L}\right)\left(\frac{\sigma_l \rho_l \lambda_l}{\mu_l}\right)\left(1 - \frac{\rho_l g L r_p \sin\psi}{2\sigma_l}\right) \qquad (6)$$

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 $2\sigma_l/g\rho_l$ is the "one-g wicking height" (N_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; ψ, inclination angle from horizontal; λ, heat of vaporization; μ, viscosity; ρ, density; and σ, surface tension.

Equation (6) verifies that, aside from internal geometry, high-temperature-material properties (λ_l, μ_l, ρ_l and σ_l) 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
  isothermalizer;
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:

15,000 W/cm² at 1500° C	°C/cm	W/cm/°C
Lithium (Li) heat pipe	0.1	150,000
Molten copper (Cu)	4000	3.75

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 tendencies of degradation-rate constants can be crucial, the fact that "high-temperature material effects determine the ... lifetime" is often more important. In practice, thermophysicochemical 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. In 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 ambiance. And the near-vacuum within TEC admits of vaporization, condensation complications that could cause work-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 cleanliness, 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-26Re/Li (SiC) heat pipes promise a lifetime of many years at 1600° 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[37].

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. 5[38-41]. A qualitative version of some of these data simplifies their presentation somewhat in Fig. 6[42]. A great difference between free energies of oxide formation for two metals indicates a strong O-gettering proclivity 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 and greater than five percent above ~1500° C[43-46]. 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 solid-solution O, fix it as distributed oxides, and reduce brittleness[47]. 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 and iron (Fe) ~2 percent). It is noteworthy that a Haynes 188, lithium heat pipe has been and is running with an evaporator temperature of ~1250 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[37]. 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[37]. 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 subjection 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 of power plants (TOPP) arose as a promising solution to this hot-corrosion problem[2,14-18,48-54] 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 diodes in fossil-fuel combustion products. One with a 1730 K W emitter passed 3500 hours (early December 1980) and is continuing. Tests after over 5000 hours for another SiC-clad converter with a 1630 K W emitter yielded gratifying results[54].

> "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 laminar 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 hot-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[55]). 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[37] (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 870 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 fraction of an atomic layer, less than 10^{-7}cm, of a different material on an electrode can drastically alter its work function and electron reflectivity -- hence its TEC performance (Eqs. (1) to (5)). Thus emitter-vapor deposits on the collector are as important as they are unavoidable[56]:

> "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 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 TEC, 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 TEC vaporization, deposition problem. Other answers are possible but exceptional[18,21].

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

In high-temperature fossil-fuel combustion products, the TECO SiC, C, W dome for TEC showed "no change or degradation ... from 5000 hours of operation" with a 1630 K emitter. In vacuum, a cylindric diode with a ~1973 K W emitter 0.23 mm from a ~1073 K Nb collector generated 8 W/cm^2 at 0.76 V 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 TEC 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 (LaB_6) in the late 1960's and again during the reactivation of its TEC program in 1974[57]. In 1977 NASA LeRC and USSR technologists both demonstrated high-performance TEC with nonoriented LaB_6 electrodes[58-60]. Controlled deposition of polycrystalline metal-hexaboride films[61], with preferred or etch-relieved 100 or 210 orientations for LaB_6 [62-67], promise even better performance in practical TEC configurations (similar to CVD'd 110-W electrodes in cylindric diodes). And gratifyingly the published consensus in 1974 indicated that brazing, diffusion and reactions between LaB_6 and its support were not problems. But today the inability to maintain a 1700 K LaB_6 emitter on a refractory-metal base for over 100 to 200 hours[68,69] 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[70,71]. 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 or 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:

$$C(x,t) \approx C(0,0)\left[1 + \cos\left(\frac{kx}{D}\right) - \cos\left(\frac{k^2t}{D}\right)\right]\exp\left(-\frac{k^2t}{D}\right) \tag{7}$$

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[72], from Hurlen[73]). For this situation the absolute reacton-rate theory (Eyring, Laidler and Glasstone) yields an expression for one-dimensional net transport of a species (corrected from Ref. 72):

$$\begin{aligned} v = (\lambda kT/h)\exp\left(-\Delta G_0^{\ddagger}/RT\right)[c\ \exp(-\alpha\lambda zFd\phi/RTdx) \\ - (c + \lambda\ dc/dx)\exp((1 - \alpha)\lambda zFd\phi/RTdx)] \end{aligned} \tag{8}$$

The pre-bracket factor, specific rate for a unit concentration without fields, involves no net transport. The first term in the bracketed factor represents acceleration by the field. The second term in the brackets covers retardation. Also in (8) v is the net transport rate; λ, the equilibrium distance between migrating charged particles; k, Boltzmann constant; T, degrees Kelvin; h, Planck constant; $\Delta G_0^{\ddagger}$, standard chemical activation energy; R, gas constant; c, concentration of migrating species; α, symmetry factor; z, migrating-particle charge; F, Faraday equivalent; ϕ, inner potential; and x, distance in the transport direction.

Simplifying assumptions and transformations lead to an approximate expression for film thickness y related to an equivalent oxide volume V and to Δ values across the film:

$$dy/dt = Vv(y),\ \Delta\phi/y = d\phi/dx,$$

$$\Delta c/y = dc/dx,\ \Delta G = F/\Delta\phi \ \text{and} \ \alpha = 1/2 \qquad (9)$$

$$dy/dt = \sum_i \pm K_i c_{i,y}[\exp(-\lambda_i z_i \Delta G/2RTy)$$

$$- (1 + \lambda_i \Delta c_i/yc_{i,y})\exp(\lambda_i z_i \Delta G/2RTy)] \qquad (10)$$

where t is time and $K = (V\lambda kT/h)\exp(-\Delta G_0^\ddagger/RT)$. 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-term elimination:

$$dy/dt \approx \left[\sum_i \mp K_i\lambda_i c_{i,y}(z_i\Delta G/RT + \Delta c_i/c_{i,y})\right]\Big/ y$$

$$\rightarrow \left(\sum_i \mp K_i\lambda_i\Delta c_i\right)\Big/ y \ \text{ or } \ y^2 \approx K_p t + \text{const.} \qquad (11)$$

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:

$$dy/dt \approx \sum_i K_i c_{i,y}\exp(\mp\lambda_i z_i\Delta G/2RTy)$$

$$\text{or} \ \ y^{-1} \approx \text{const.} - K_{IL} \log t \qquad (12)$$

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 ap^2 as an approximation of $\exp(p) - \exp(-p)$ in Eq. (10):

$$dy/dt \approx a\left[\sum_i K_i C_{i,y}(\lambda_i z_i \Delta G/2RT)^2\right]\Big/ y^2$$

$$\text{or} \ \ y^3 \approx K_c t + \text{const.} \qquad (13)$$

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 LaB_6. Gratifyingly, unoriented and CVD'd 110-W electrodes with negligible interelectrode losses can provide optimal TEC for applications requiring ~1000- to ~1100 K collectors[18]. Furthermore high performance W and Mo electrodes with stable or steady-state supplies of enhancing O are in the offing[74]. 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. 2: Fig. 9(a) comprises prepublished data[75]; Fig. 9(b), data obtained during the published study[76]. 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 findings[48-54,77]. For example, TECO recently heated its SiC, C, 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, C, W dome.

Interestingly, TECO uses C to more carefully adapt silicon-carbide thermal-expansion to that of W. And Chemetal[77] 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 sintered SiC exhibits an increase in strength with an increase in test temperature up to about 2800° 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 creep[80-82]. 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 O level in Na necessary to avoid embrittlement of Nb at 700° C has been estimated to be less than 10 ppm."

The preceding scare 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 ~1800 K emitters. And for these applications, satisfactory materials are few as the creep-strength curves of Fig. 10 illustrate[83].

In any event high-tempurature 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, 8W, 2Hf), ASTAR-811C (Ta, 8W, 1Re, 0.7Hf, 0.35C), Nb, 1Zr, FS-85 (Nb, 28Ta, 10W, 1Zr), TZC (Mo, 1.2Ti, 0.25Zr, 0.15C), and TZM (Mo, 0.5Ti, 0.08Zr, 0.03C).

Weight-effectiveness in space and cost-effectiveness in general drive toward minimal wall thicknesses alluded 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[37]:

> "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 α-to-γ transition for iron at 1180 K, causes no great difficulties[84]. The Ti α-to-β 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, 5Al, 2.5Sn are alpha alloys. Ti, 8Mo, 8V, 2Fe, 3Al is a beta alloy, and the most widely used Ti, 6Al, 4V is an "alpha-beta" alloy.

Like Ti, refractory metals Zr and Hf, also in periodic group IVA, undergo solid-phase transitions[43-46,84]. In contrast group VA Nb and Ta as well as group VIA 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 and MFHPs. Many other less-impressive thermophysical challenges have arisen, then fallen under the pressure of applied research.

High-Temperature TEC and MFHP's 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 complected. 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 thermophysicochemical-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 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 even greater improvements for future TEC and MFHP applications by more fully utilizing high power densities from high-temperature material interactions.

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

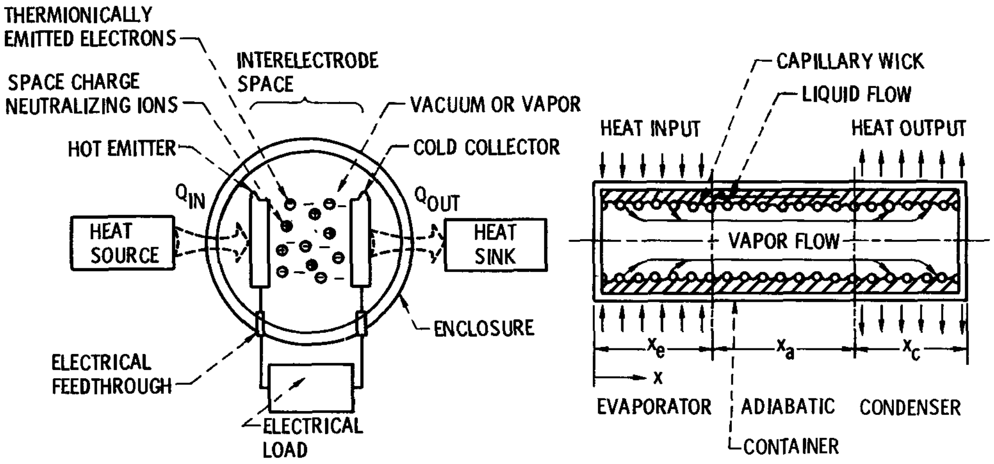
SYSTEM ELEMENT OR PRIMARY FUNCTION	HEAT-PIPE SERVICE	TEMPERATURE, K
ENERGY SOURCES		
Solar Concentrators		
Materials processing (MP) (furnaces, ovens...)	Isothermalize receivers and processors	To > 2000
Power generation (PG)(thermionic TEC, TEC topping TEC-T, high-temperature thermoelectric H-T-TE, current TE, H-T Brayton H-T-B, current B...)	Isothermalize receivers and transport thermal power (TTP)	To ~ 1850
Nuclear Reactors	Cool reactors, flatten temperature profiles, TTP, transform TP densities (TTPD), if required	
Ultimate space reactor (~MW$_e$'s) (TEC, TEC-T-B...)		To > 1850
JPL out-of-core TEC system (~0.5 MW$_e$) (TEC, TEC-T-B, H-T-TE, H-T-B...)	↓	To ~ 1675
Midpower-range (MPR) reactor (10 to 250 kW$_e$) (TEC, TE, H-T-B, B...)	↓	To ~ 1400
Minireactor (1 to 10's kW$_e$) (TE, B...)	↓	To ~ 1300
Radioisotopes (To kW$_e$'s)(TEC, H-T-TE, TE...)	Cool and isothermalize radioisotopes, TTP (TTPD)	To ~ 1500
THERMAL-TO-ELECTRIC CONVERTERS		
Thermal-Power Input		
TEC emitters	TTP, TTPD, heat, isothermalize	To > 1800
TE hot shoes	TTP, heat, isothermalize	
New materials	↓	To ~ 1600
Current materials	↓	
Best possibility	↓	~ 1300
Ready availability	↓	~ 1000

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

SYSTEM ELEMENT OR PRIMARY FUNCTION	HEAT-PIPE SERVICE	TEMPERATURE, K
B H-T heat exchanger (H-T-HE)	TTP, Act as H-T-HE	
New materials		To ~ 1400
Current materials		To ~ 1150
Potassium Rankine		To ~ 1050
Thermal-Power Rejection		
TEC collectors (depending on system power)	Isothermalize, Cool, TTP	~400 to ~1100
TE cold shoes (depending on system power)		
New materials		To ~ 950
Current materials		To ~ 800
B Heat-exchanger cooler (HEC)(system power)	Act as HEC, TTP	
New materials		~400 to ~850
Current materials		~350 to ~500
Potassium Rankine		~800
ELECTROCHEMICAL CELLS		
Fuel Cells (FC)	Cool, isothermalize, TTP	
Noble-metal catalyst		~350 to ~430
Apollo (Bacon) cell (high reject. temp. HRT)		>500
Molten carbonate (high reject. temp. HRT)		To > 920
Solid oxide (high reject. temp. HRT)		To > 1270
Electrolysis (regen. FC:Energy storage)		
Current practice		~300 to ~430
Thermal + electroyltic processing (HRT)	Heat; cool, isothermalize, TTP	
Batteries	Cool, isothermalize, TTP	
Current practice		~280
Alkali-metal, organic-electrolyte (HRT)		To > 420
Alkali-metal, solid-electrolyte (HRT)		To > 720
PHOTOVOLTAIC CELLS		
Concentrated radiation (raise low efficiencies)		To > 450
Thermally reformed radiation (raise low eff.)		To > 450
High-temperature environments		To > 450

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

SYSTEM ELEMENT OR PRIMARY FUNCTION	HEAT-PIPE SERVICE	TEMPERATURE, K
OTHER AEROSPACE APPLICATIONS		
Space radiators		To > 1100
Heat exchangers, recuperators, regenerators		To > 1850
Heat-pipe, phase-change-material Thermal capacitors		To > 1300
High-temperature structures (Ollendorf patent)		
High-power-density, high-voltage Electrical processing and electronics		To ~ 350
High-power density switching with plasma devices		T_E's to > 2000 T_C's to > 1000
Heat-pipe-cooled magnetics		
Leading-edge cooling for re-entry vehicles and hypersonic aircraft		To > 1100
Materials processing, testing, and fabrication in space		To > 2000
Tritium production ($n + Li^6 \rightarrow T + He^4 + 4.6$ MeV and $n + Li^7 \rightarrow He^4 + T + n - 2.47$ MeV) and recovery with Li heat pipes in blankets of thermonuclear reactors ($D + T \rightarrow He^4$ (3.5 MeV) + n (14.1 MeV))		> 1400



THERMIONIC-ENERGY-CONVERTER ELECTRONS

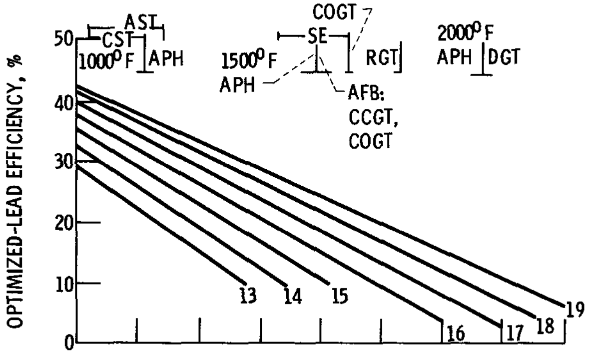
ESCAPE THE HEATED EMITTER,
PASS THROUGH THE INTERELECTRODE GAP,
ENTER THE COOLED COLLECTOR,
DEVELOP VOLTAGE ACROSS THE ELECTRODES,
FLOW BACK TO THE EMITTER EXTERNALLY,
PERFORM ELECTRICAL WORK, AND
RECYCLE CONTINUOUSLY.

THE HEAT-PIPE WORKING FLUID

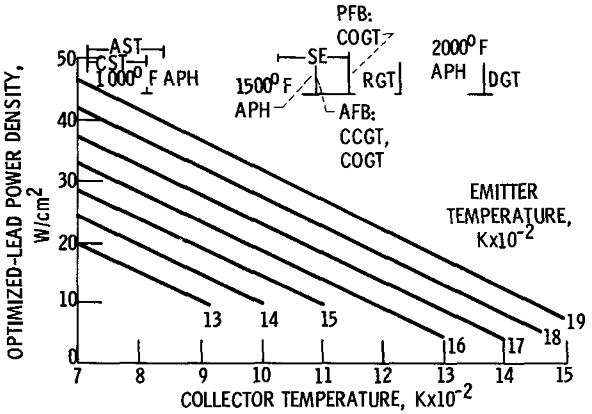
VAPORIZES IN THE HEATED "EVAPORATOR,"
FLOWS AS A VAPOR THROUGH THE "ADIABATIC SECTION,"
GIVES UP ITS HEAT OF CONDENSATION IN THE COOLED "CONDENSER,"
FLOWS AS A LIQUID BACK TO THE EVAPORATOR THROUGH THE "WICK" ARTERIES,
MOVES TO THE VAPORIZING SURFACE THROUGH THE WICK CAPILLARIES,
AND RECYCLES CONTINUOUSLY.

Figure 1. - TEC and heat-pipe cycles.

STEAM TURBINE	(ST)
CURRENT	(CST)
ADVANCED	(AST)
GAS TURBINE	(GT)
DISTILLATE-FIRED	(DGT)
RESIDUAL-FIRED	(RGT)
COAL-FIRED	(CGT)
CLOSED-CYCLE	(CCGT)
OPEN-CYCLE	(COGT)
FLUIDIZED BED	(FB)
ATMOSPHERIC	(AFB)
PRESSURIZED	(PFB)
STIRLING ENGINE	(SE)
AIR PREHEATER	(APH)



(a) THERMIONIC-ENERGY-CONVERSION EFFICIENCY.



(b) THERMIONIC-ENERGY-CONVERSION POWER DENSITY.

Figure 2. - Performance and topping temperatures for thermionic energy conversion with 30 A/cm^2, 10% back emission and negligible interelectrode losses.

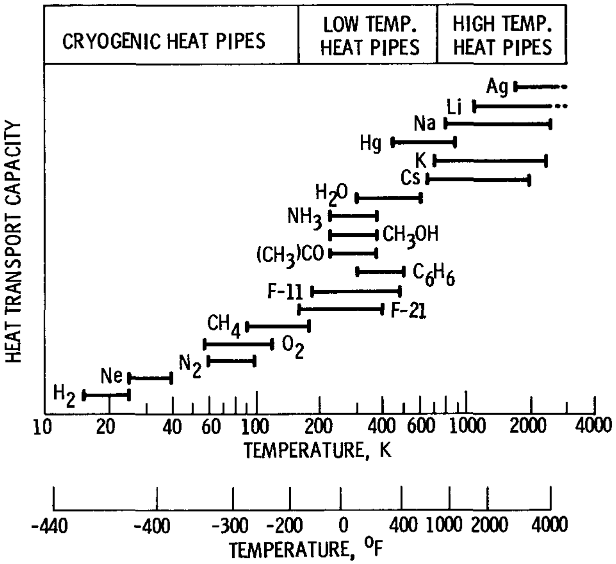
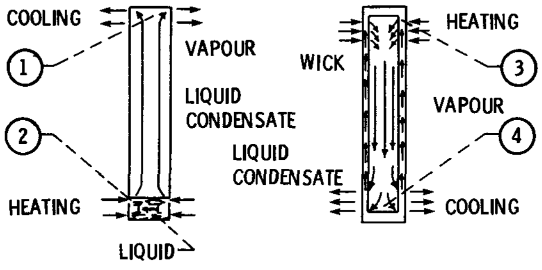


Figure 3. - Heat-pipe operating ranges.



REFLUX CAPSULE

HEAT PIPE

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 EVAPORATORS, 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-FLOW METHODS DO NOT APPROXIMATE HEAT-PIPE LIFE TESTING.

BUT A SUITABLE CYLINDRIC SCREEN CHANGES AN INEFFECTIVE CAPSULE INTO A HEAT-PIPE FOR EFFECTIVE, ECONOMICAL LIFE TESTING.

Figure 4. - Heat-pipe materials compatibility: life testing.

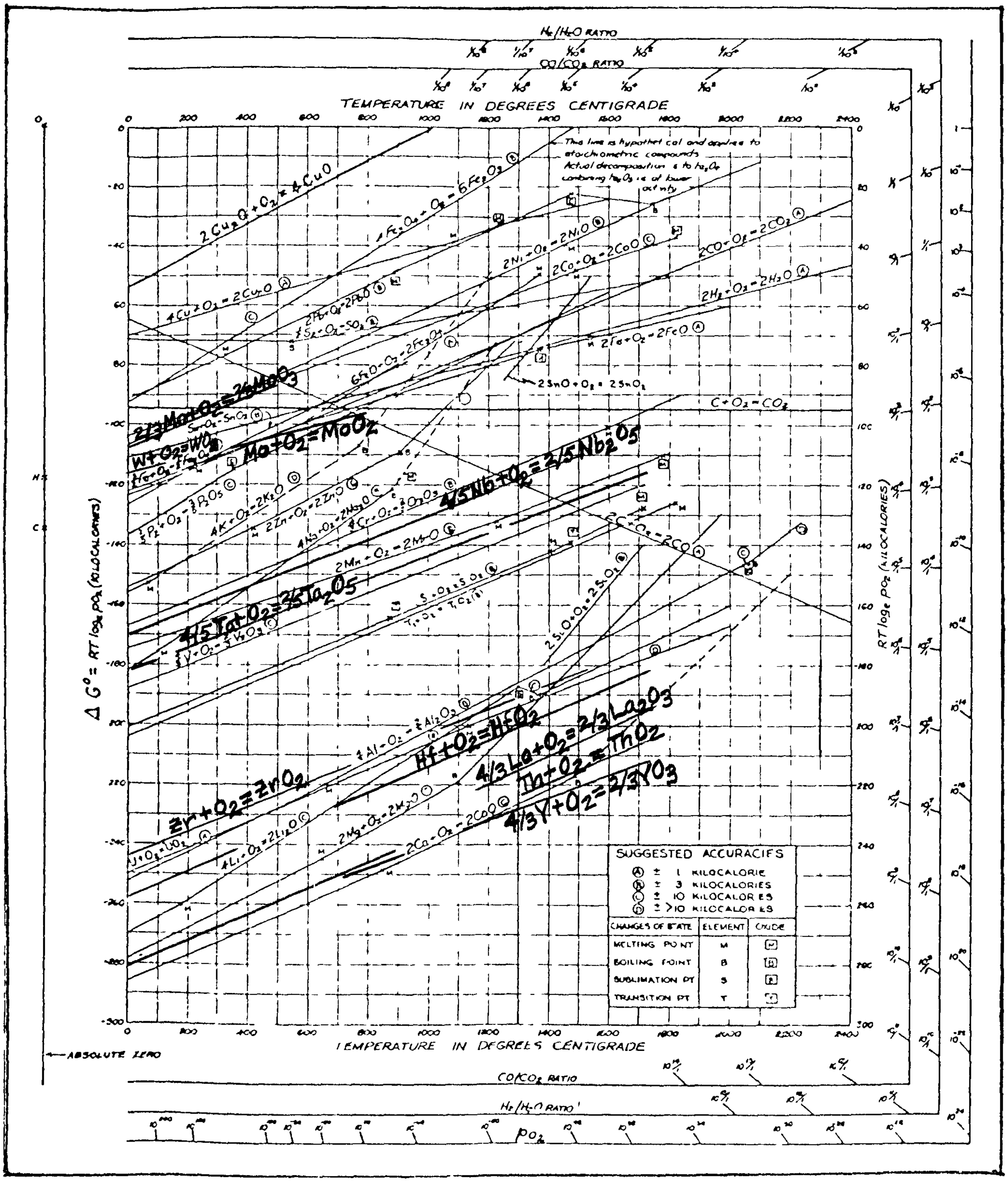


Fig. 5 Free-energy data for oxide formation (after Richardson and Jeffes, 1948)[15]

1 kcal = 4.1868 kJ; 2.303 R = 19.1546 J/mol degC;
1 atm = 101 325 kN m², 1 V equiv. = 96 606 kJ.

(Refs. 38 to 41.) (Courtesy of American Society for Metals.)

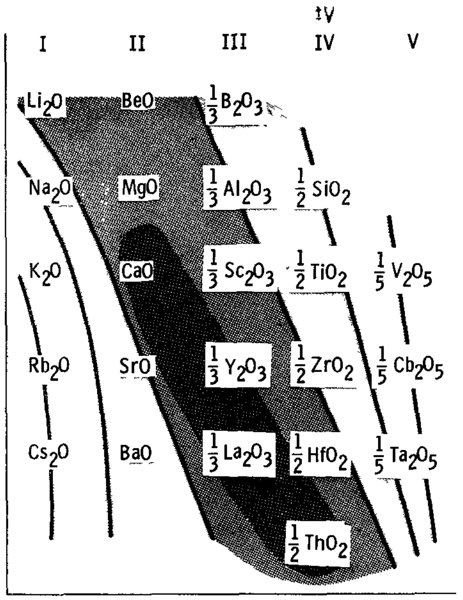


Figure 6. - Stability relationships of refractory oxides. Solid lines represent constant standard free energy of formation from the elements. The darkest area is the region of greatest stability (ref. 42).

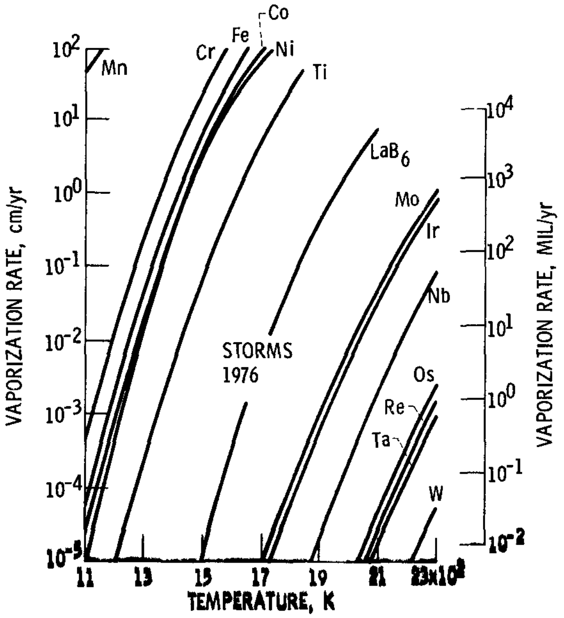
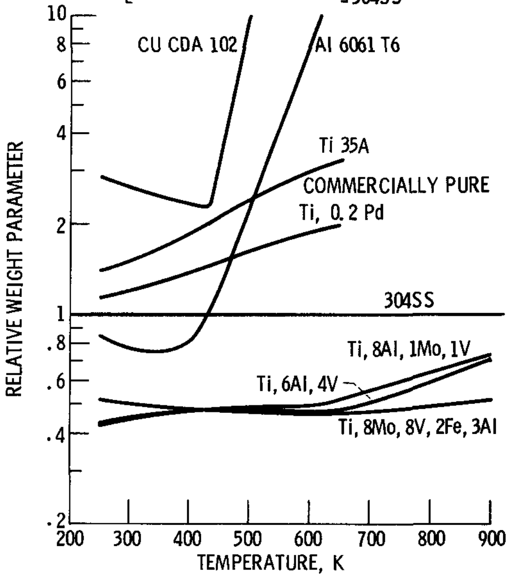


Figure 7. - Vaporization of pure metals and lanthanum hexaboride.

RELATIVE WEIGHT PARAMETER
(BASED ON ASME PRESSURE VESSEL CODE)

FOR HIGH-PRESSURE HEAT-PIPE ENVELOPES

$$\text{RWP} = \frac{\left[\dfrac{\text{DENSITY AT } T}{(\text{ULT. STRENGTH AT } T)/4}\right]_{\text{METAL}}}{\left[\dfrac{\text{DENSITY AT } T}{(\text{ULT. STRENGTH AT } T)/4}\right]_{\text{304SS}}}$$



RELATIVE WEIGHT PARAMETER

FOR LOW-PRESSURE-HEAT-PIPE ENVELOPES AND ALL WICK STRUCTURES

RWP = (METAL DENSITY AT T)/(304SS DENSITY AT T)

APPLIES WHERE ASME PRESSURE-VESSEL CODE YIELDS WALL THICKNESSES TOO THIN FOR FABRICATION, JOINING, PROCESSING, HANDLING, AND/OR OPERATION.

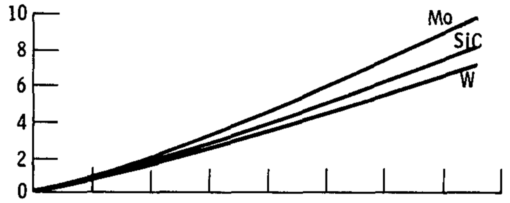
EXAMPLE: 1" - DIAM. SPACE HP AT 10 ATM. WITH A 40,000 psi (ULT' STR.) ENVELOPE.

HOOP-STRESS WALL THICKNESS (ASME P-V CODE): 7 MILLS (THINNER WALLS RESULT FOR LOWER OPERATING PRESSURES AND HIGHER ENVELOPE STRENGTHS).

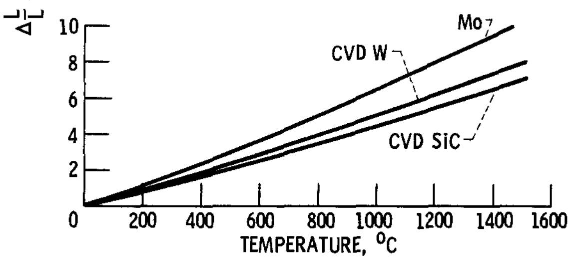
USUALLY PREFERRED WALL THICKNESS: TENS OF MILLS

	294 K (70° F)	700 K (800° F)	1033 K (1400° F)
ALUMINUM	0.33	0.34	----
COPPER	1.11	1.11	----
TITANIUM	0.56	0.57	0.58
304SS	1.0	1.0	1.0

Figure 8. - Relative weight parameters.



(a) LINEAR THERMAL EXPANSIONS FROM REF. 75.



(b) LINEAR THERMAL EXPANSIONS FROM REF. 76.

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

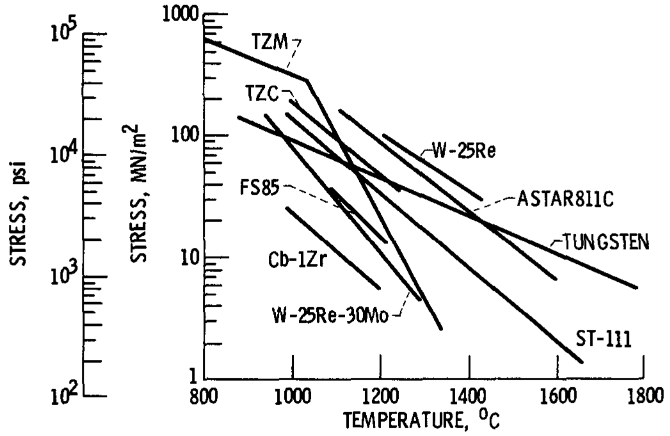


Figure 10. - Creep strength of some refractory metals and alloys for 1 percent creep in 10 000 hours.

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16. 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. 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, complected 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 thermophysicochemical stabilities dictate operating temperatures which regulate the thermoemissive 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.

17. Key Words (Suggested by Author(s))
Thermionic energy conversion (TEC); Metallic-fluid heat pipes; High temperatures; High power densities; High-temperature materials; Terrestrial and space applications

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