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**THERMOCHEMICAL CORRELATION OF MATERIAL TRANSPORT
IN AN ALKALI METAL HEAT PIPE**

by

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ABSTRACT

The use of high-power heat pipes in space power systems requires a means of life prediction. The design lifetimes required make experimental determination of life impractical. Thermochemical modeling of heat pipe corrosive failure modes has been investigated as a means of making such prediction. Results have been applied to tests of molybdenum-lithium heat pipes operating from 1400 to 1500 K. A free energy minimization routine coupled to a hydrodynamic model of the operating heat pipe has been used to give local equilibrium values of reaction products as a function of operating time. The predicted reactions for critical regions of the heat pipe were compared with limited results of post-test examinations. Corrosive damage to the heat pipe wick structure was correlated with high oxygen and nitrogen activity in the evaporator region of the heat pipe.

INTRODUCTION

The use of high-temperature, alkali metal heat pipes for heat transfer in critical applications in space power systems requires that their operational lifetime be accurately predictable. It would be possible to experimentally predict the operating lifetime of such heat pipes if it were not for the high power levels and long lifetimes required. These two factors combine to make the determination of operating life by prototypical testing prohibitive in both time and money. For a typical design lifetime of 7 years, an operating temperature of greater than 1000 K, and a heat throughput of 5 to 10 kW, the test program necessary to generate reliability predictions with a reasonable

confidence level would not be possible within typical program constraints. Therefore, life predictions and their evaluation for critical mission applications must be based on some means of test scaling that permits an accelerated test program.

Such scaling might be based on tests conducted at increased temperature, with increased mass transport or heat flow, or by means of some material substitution that would lead to increased failure rate without change in the basic failure mechanism. Any of these means of test scaling must be based on understanding the failure mechanisms which can terminate operation at design conditions.

In general, high-temperature heat pipe failure under design conditions, that is, without excessive temperature or pressure transients, will be related to the transfer of mass within the heat pipe assembly. Such mass transfer may lead to deterioration of the capillary wick structure and loss of heat pipe performance, due either to increased capillary size or decreased permeability. Concentration of transferred material locally within the heat pipe, for example in the evaporator region, may also lead to operating performance changes due to alteration of the properties of the working fluid; finally, internal mass transport may cause failure of the heat pipe containment envelope, loss of working fluid, and termination of operation. In each of these potential failure modes, the transfer of material within the heat pipe will be bounded by local thermochemical equilibrium conditions. Understanding these thermochemical mechanisms is, therefore, essential to the development of lifetime scaling methods and ultimately to the use of high-temperature heat pipes in critical space systems. The development and demonstration of such understanding is the motivation for the present effort.

Merrigan/Feber

METHOD OF APPROACH

As reported in (1), the Los Alamos National Laboratory staff has conducted extended operating tests of heat pipes at temperatures to 1500 K and with energy throughputs as high as 15 kW for periods greater than 1000 hours. This experience is unique in heat pipe life testing for the power throughput, and therefore for the flow rate of the working fluid, factors of concern in mass transfer controlled systems. In the course of these extended operating tests mass transfer was observed, leading eventually to dry-out in the evaporator region of the heat pipe. The closely controlled and known internal chemistry of the heat pipe used in this testing permitted the development of a relevant and accurate thermochemical model for the heat pipe's internal environment. The use of such thermochemical equilibrium modeling methods for the prediction of expected chemical species within heat pipes has been reported in prior Los Alamos publications (2, 3).

In the present effort these equilibrium techniques using minimization of total free energy have been applied to the various distinct operating regions of the heat pipe rather than to an overall, average internal

environment as in the prior work. As the partitioning of materials, particularly non-metallic contaminants, within the heat pipe is not known a priori, this requires an iterative procedure to determine the variation of internal chemistry with location under steady-state, constant-temperature operating conditions. The starting point for accomplishing this is an accurate determination of the initial chemical composition of the heat pipe, including working fluid, wick, and structural materials, and also the non-metallic contaminants remaining after heat pipe assembly and processing. In addition, the general phase states and thermal fluxes in the different regions of the heat pipe during design point operation are known.

For modeling, the heat pipe is divided into the evaporator, adiabatic, and condenser regions as shown in Fig. 1. Each of these regions consists of a liquid and a vapor phase in thermal equilibrium. The condenser end of the heat pipe will contain a working fluid surplus during operation, and will therefore be single phase over some length. The evaporator region may have a local area where no liquid phase of the working fluid is present. This latter situation will exist only if dry-out of the heat pipe has occurred because the local radial heat flux

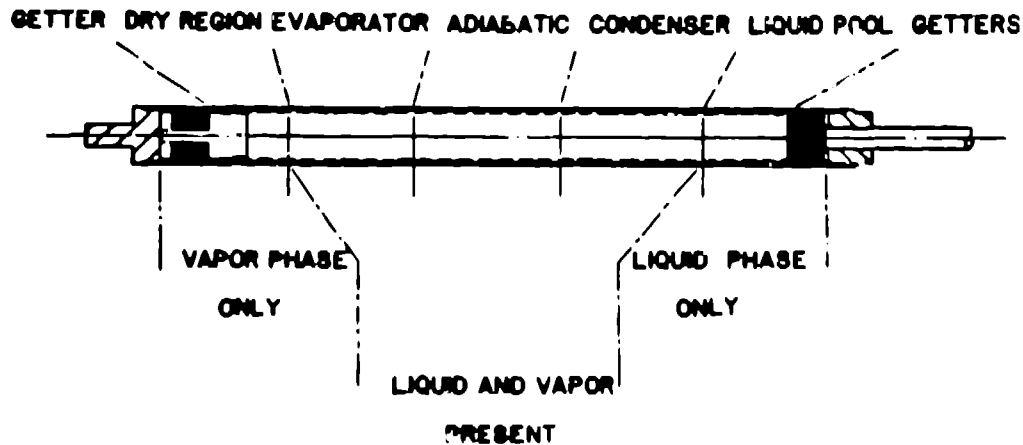


Fig. 2. Total oxygen distribution.

limits have been exceeded or under other abnormal operating conditions. This dry-out situation is of interest, although not representative of normal operating conditions, because test experience has indicated that severe mass transport of container and wick metal may occur during dry-out in some liquid metal systems. For metal mass transport modes that involve oxygen impurities, thermochemical considerations indicate that molybdenum oxides and molybdates will not form in the presence of liquid lithium even at high oxygen activity. Therefore, the most probable region for corrosion was considered to be the evaporator of the heat pipe under dry-out conditions. This is the region in which such behavior has been observed during tests, and correlation of such corrosion with predictions of the models developed was a major goal of the present effort.

DESCRIPTION OF THE THERMOCHEMICAL MODEL HPLT (HEAT PIPE LIFE TEST)

The model (HPLT) user dimensions and power typical of operating alkali metal test heat pipes. Calculations to date have been based on lithium in Mo/Ra pipes.

The model uses output from Heat Pipe Computer Program HPIPE-A, a hydrodynamic model of a heat pipe developed at the Los Alamos National Laboratory for the design and analysis of high-performance heat pipes. HPIPE-A defines vapor and liquid volumes at temperature and the rate of vaporization of the working fluid corresponding to the assumed power, wick/artery configuration, and lengths of the evaporator, adiabatic and condenser sections.

HPLT divides the total length of the heat pipe into five sub-lengths: evaporator, adiabatic, and two condenser sections plus a pool of liquid lithium at the end of the condenser sections. A dry zone at the end of the evaporator section is optional. Provision is also made for presence of a getter for impurities in any one of the sections.

The heart of HPLT is a modification of an existing computer program SOLGASMIX-PV (4), which calculates complex chemical equilibria in multi-phase systems. SOLGASMIX-PV calculates the identity and amounts of species and compositions of solutions present at equilibrium in a system containing a gas phase, a liquid solution, and multiple solid phases or solutions. Thermodynamic data are entered for species, mixtures, or solutions the user believes to be of importance at the temperature, pressure, and elemental composition of interest. Many of the data may be found in existing thermodynamic data bases; other have been generated from relevant literature sources; still others were extrapolated from lower temperatures or estimated.

HPLT assumes that chemical equilibrium is a reasonable assumption at mass flows in a heat pipe. The prediction of possible reactions of unavoidable trace elements initially present in heat pipe materials or available by diffusion through wall materials from other sources to form compounds which are potentially deleterious to heat pipe performance and lifetime will provide the basis for a correlation with test results.

Figure 1 shows the flow scheme in a heat pipe on which model calculations are based. The amount of alkali metal transported from and to each section is based on some multiple (typically 100 or 1000) of the alkali metal in the vapor phase of the adiabatic section (the shortest section). From the known rate of evaporation of alkali metal corresponding to the power throughput of the heat pipe and the amount transported per program iteration, a real time may be assigned to each iteration. Transport of impurity elements or compounds is thereby possible because the distribution coefficient between the liquid and vapor phase is not unity and formation of solids is possible. Solids are assumed not to migrate. A separate, presumably smaller, rate of transfer of alkali metal to and from the pool is specified by the user.

Likewise, if a dry region at the end of the evaporator is assumed, the user will specify the rate of circulation and evaporation of liquid alkali metal from the wet zone of the evaporator to the dry zone. That rate is subject to the constraint that the total pressure in the dry zone is equal to the total vapor pressure in the rest of the heat pipe.

Oxygen, nitrogen, silicon and carbon and the gaseous species, alkali-metal solution species, and condensed phases potentially formed by chemical reaction among themselves or with other elements in the system are included in the calculation. A total of 56 chemical species are currently considered after a screening to eliminate potential species judged to be of no importance.

Results obtained with the model depend markedly on the thermodynamics of impurity-containing species taken to be dissolved in the liquid lithium. Base line calculations included species for which reasonable extrapolations of experimental solubility and other data to 1600 K were possible. These included oxygen dissolved as Li_2O , nitrogen dissolved as Li_3N , carbon dissolved as Li_2C_2 , and silicon dissolved as $\text{Li}_{22}\text{Si}_5$.

A second round of calculations assumed the presence in solution of a ternary Li-Mo oxide or a ternary Li-Mo nitride. There is evidence for the solubility of such compounds, particularly ternary oxides, in other alkali metals, although there are no hard data for the present system.

Potential getters for oxygen include hafnium by solid solution at lower oxygen concentrations and by formation of $\text{Li}_2\text{HfO}_3(\text{s})$ at higher oxygen levels. Hafnium is also a getter for nitrogen by the formation of HfN . The transition metals are getters for silicon and carbon at anticipated impurity concentrations by the formation of silicides and carbides. All of these gettering actions are in competition with the solubility of the impurities in the liquid alkali metal. A prediction of the effect of this competition and the simultaneous gaseous transport of impurity - containing species on the possible local buildup of reaction products deleterious to heat pipe performance is the purpose of the calculation.

Calculations are usually started by assuming zero flow with the chemistry of the

entire heat pipe plus impurities at equilibrium. Elemental components are then apportioned to the sections in amounts appropriate to their volumes. Between each iteration the amount of impurities in each section is altered by the balance between the amounts of those impurities associated with the reference amount of alkali metal entering and leaving that section according to the flow schematic given in Fig. 1.

The gross features of impurity transport are essentially the same for base line calculations and for those with a ternary Mo oxide or nitride added to the liquid lithium. Typical plots for the total amounts of oxygen, nitrogen, silicon, and carbon in each section as a function of time are shown in Figs. 2 through 5. On these figures, the plotting symbols 1 through 5 refer in order

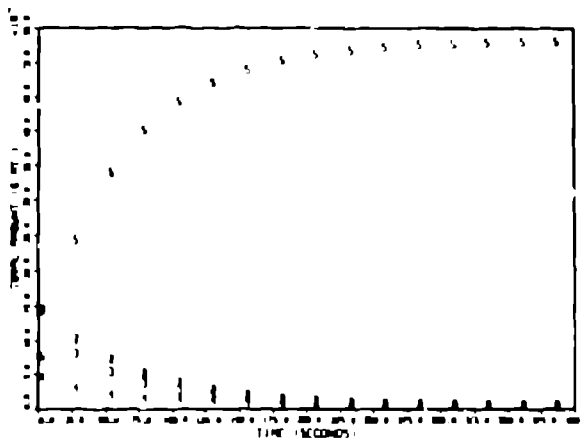


Fig. 2. Total oxygen distribution.

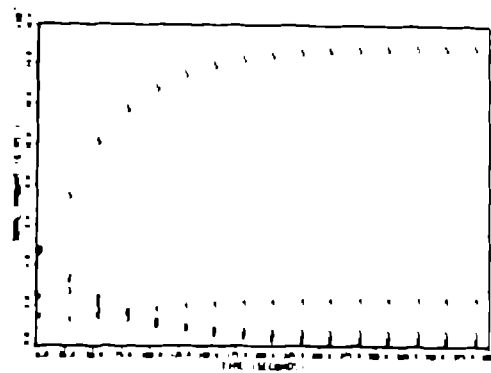


Fig. 3. Total nitrogen distribution.

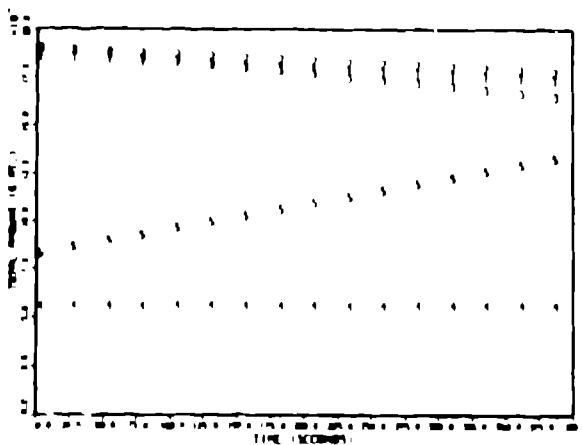


Fig. 4. Total carbon distribution.

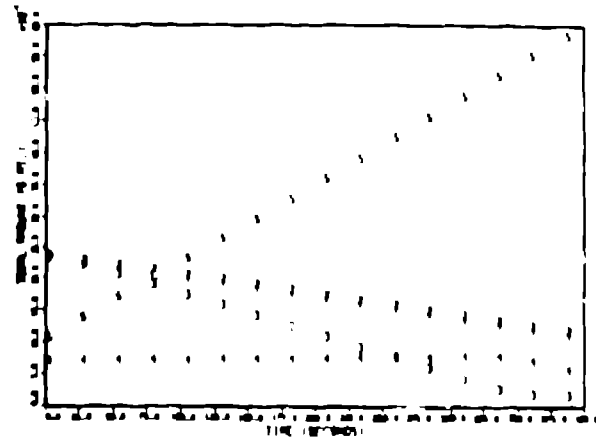


Fig. 5. Total silicon distribution.

to the total amount of impurity in the pool, two condenser zones, adiabatic zone, and evaporator. Due to the relatively low partial pressures in the gas phase of species containing the impurities, they will accumulate in the evaporator section. The rate of transport is of course decreased if the impurity forms condensed-phase compounds in other sections, as is true here for carbon and silicon. A hafnium getter in the pool is found to be of little use at modest oxygen levels because the oxygen is trapped there only as a solid solution in the hafnium and tends to be pumped out from the hafnium as total oxygen in the pool decreases.

At the power level used in the analysis, the steady-state distributions of oxygen and nitrogen are predicted to be reached in about 150 seconds. Steady-state distributions for the other impurities take longer. This rapid approach to dynamic equilibrium is the result of the assumption that the total amounts of impurities in the system are all present initially in the liquid and vapor phases of the working fluid. If these species were assumed to be distributed throughout the wick and wall materials, the approach to equilibrium would probably be controlled by diffusion of the species within the solid materials. The end result should be unchanged, although transient species concentrations would be altered by the finite release rates. Plans are to incorporate diffusion parameters in the model in the future.

The difference between base line calculations and those with additional ternary species in the liquid lithium show up in the effect on molybdenum corrosion. For the base line system, no molybdenum transport is calculated. With a ternary oxide (or nitride) added to the lithium solution, molybdenum corrosion occurs in the evaporator as oxygen (or nitrogen) is transported to that region and shifts the equilibrium involving the solution ternary. Actually a ternary nitride is the more likely candidate, as it is necessary to make the free energy of formation of a ternary oxide much more negative than is reasonable before an effect is calculated. On the other hand, entirely reasonable values for the free energy of formation of a ternary nitride in lithium solution are adequate to calculate molybdenum corrosion. Both the amount of corrosion in the evaporator and what can be a complicated pattern of a lesser amount of calculated corrosion/deposition elsewhere in the heat pipe depend on what is assumed about the thermodynamics of the ternary nitride.

With reasonable values for the free energy of formation of a ternary nitride, the effect of adding a dry region to the evaporator is to redeposit metallic molybdenum in that region as the molybdenum-

containing liquid lithium is evaporated there.

SUMMARY OF EXPERIMENTAL DEVELOPMENT

A 2-m-long 1.59-cm-diam heat pipe was fabricated of molybdenum tubing using an annular, molybdenum screen wick. The heat pipe was designed for a power throughput of 15 kW at 1500 K using lithium as a working fluid. Design length of the evaporator region of the heat pipe was 30 cm and that of the condenser was slightly over 150 cm. The condenser surface of the heat pipe was coated with plasma-sprayed zirconium diboride to increase the emissivity to about 0.6 and thereby permit radiation coupling of the heat pipe to a water-cooled ambient temperature calorimeter surface. This heat pipe was operated for a total of 1700 hours at a power level of 14 kW. A detailed operating history is given in (1). The test was halted for equipment maintenance after 514 hours, and the heat pipe was damaged during attempts to restart due, apparently, to inadequate lithium supply in the evaporator region during start-up. As a result of this incident, the heat pipe was operated at low power overnight with a dry region in the evaporator wick. Subsequently it was discovered that the wick structure was damaged in the region of the dry-out. The heat pipe was disassembled and repaired prior to continuing the test. During this repair operation, evidence of transport of material from the damaged region of the wick was discovered. Chemical and metallurgical analyses were conducted to determine the nature and extent of the material transfer.

EXPERIMENTAL DATA

The damaged area of the wick structure was located at the stagnation end of the evaporator and extended over a length of approximately 10 cm. In the repair of the heat pipe, this area was removed and the heat pipe shortened proportionally. The section of wick removed was subjected to various analyses. Scanning electron microscopy (SEM) was conducted to provide characterization of the wick structure and Auger electron spectroscopy (AES) was used to identify the chemical elements in the region of the damaged structure. These analyses showed a linear pattern of damage parallel to the centerline of the heat pipe and separation of the circumferential wires of the screen wick at the center of the damaged area. Under high magnification, the SEM photographs showed tapering of the wire strands to the central crack region (Fig. 6). AES analysis showed segregation of the wick material into its molybdenum and rhenium constituents over a distance of approximately



Fig. 6. SEM micrograph of screen at the failure position (1000x).

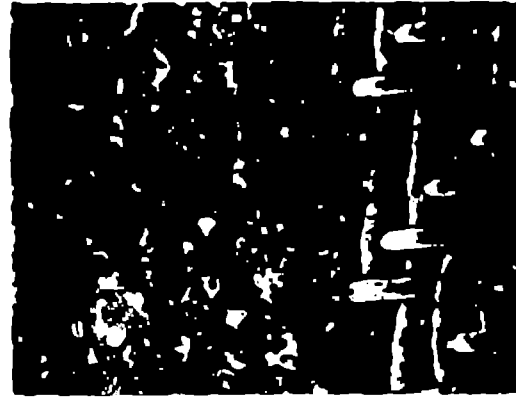


Fig. 7. SEM micrograph of screen, about 3 mm from the failure, showing Re-rich crystals, and at the left of micrograph, region containing a small amount of Fe (250x).

0.5 cm from the center of the corroded region. The SEM photographs showed crystal isomorphs in this region, suggesting deposition of rhenium and molybdenum from solution in a region near the peak corrosion area (Fig. 7). The analyses did not show abnormal levels of non-metallic contaminants in the region. However, in removing the damaged wick structure from the heat pipe, the lithium working fluid was distilled out of the heat pipe, and the heat pipe was then cut open in the atmosphere. Volatile elements on the surface of the wick would be removed by this process, and the levels of surface contaminants on the wick samples brought to equilibrium with air. As a result, the evidence of metal transport and redeposition is of more consequence than the indicated levels of non-metallic contaminant.

CORRELATION OF CORROSION PATTERNS

Internal chemistry of the test heat pipe was well characterized in pre-test examination of the materials and working fluid used. It was possible, therefore, to model the equilibrium thermochemistry of the heat pipe using the free energy minimization methods described. If a single equilibrium calculation is made treating the contents of the entire heat pipe (an average or overall analysis), a mechanism for metal transport from the wick structure involving either the liquid or vapor phase is not apparent. However, if the calculations are elaborated by dividing the heat pipe into regions

corresponding to an evaporator (containing an optional dry zone), an adiabatic zone, a condenser (sectioned into two parts), and a pool containing excess working fluid, a mechanism is indicated.

In the HPLT analysis, vapor-phase concentrations of the constituents other than lithium were found to be low, leading to concentration of non-metallic elements in the evaporator region of the heat pipe through the transport provided by the working fluid under normal operating circulation. The getter materials in the evaporator region of the heat pipe therefore reached equilibrium with evaporator concentrations of non-metals, rather than with the average values for the overall system. The result of this process was an increase in the oxygen activity in the evaporator region. With local variation in lithium evaporation rate, this process could proceed to a level of concentration that would permit the formation of lithium oxide. However, even in this extreme the models do not indicate the formation of metallic binary or ternary oxides of the wick materials. Only in the dried-out region of the heat pipe, where locally no liquid lithium is present, may oxides be formed. However, in such a region the wick material may be oxidized and the resulting oxides transferred in the vapor phase away from the dry region. Exposure of these oxides to lithium immediately adjacent to the dry region would result in reduction of the compounds to pure metals with segregation of

rhenium and molybdenum components of the wick material due to variation in the rate of reduction.

The limitation of this hypothesis lies in the need for a cyclic process to explain the build-up and reduction of oxides necessary to erode the wick structure in the manner observed. As an alternative, consideration was given to the possible formation of a ternary lithium-molybdenum-nitrogen compound having reasonable solubility in lithium. Analysis based on this assumption and using reasonable values for heat of solution is capable of explaining the corrosion patterns that were observed. The existence of a dried-out region of the heat pipe in this case would not constitute the underlying cause of corrosion, but would lead to precipitation of molybdenum and rhenium in the vicinity of the dried-out region as has been observed. This corrosion model suggests that the erosion of the wick structure as observed in these tests is a consequence of the nitrogen levels in the lithium, particularly in the evaporator region of the heat pipe, and will occur even in the absence of a evaporator dry-out. That is, it can take place in the presence of liquid lithium. If this is true, the occurrence of the phenomenon in this test heat pipe and not in other smaller test heat pipes that have been operated with similar materials for periods as long as 30,000 hours is probably a consequence of the ratio of evaporator area to condenser area in the present test heat pipe, which results in higher concentration of nitrogen contaminants in the evaporator. This chemical concentration ratio will be of crucial concern in heat pipe applications such as spacecraft radiators where high ratios of condenser to evaporator area are expected to exist.

CONCLUSIONS

The combined hydrodynamic and thermochemical modeling technique described in this paper promises to be a powerful method

of analysis for use in predicting the corrosion mechanisms in, and therefore the lifetime of, high-temperature, alkali metal heat pipes. At its present stage of development the technique is limited first of all by the lack of controlling kinetic considerations and secondly by the limited data available on the thermochemistry of some of the chemical species involved in the temperature range of interest. Despite these limitations, the HPLT model has been successful in identifying probable mechanisms of corrosion to explain the high-temperature life test results. In addition, the modeling has provided a rational means for determining the allowable levels of contaminants for high-temperature heat pipes and has demonstrated the importance of power throughput and geometric proportions on the chemical transport within a heat pipe. Extension of this work to incorporate kinetics and more accurate thermochemical properties will lead to the ultimate goal of a means of life prediction and test scaling for high-temperature heat pipes.

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