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LOS ALAMOS, NEW MEXICO

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CORROSION IN ALKALI METAL/MOLYBDENUM HEAT PIPES

Lynn B. Lundberg and Roy C. Feber, Jr.

ABSTRACT

Molybdenum/sodium (Mo/Na) and molybdenum/lithium (Mo/Li) heat pipes have been operated for long periods of time in a study of their resistance to failure by alkali metal corrosion. Some Mo/Na heat pipes have operated over 20,600 h at 1400 K without failure, while at least one similar heat pipe failed in less than 14 hours at 1435 K. Detailed post-mortem analyses which have been performed on three failed Mo/Na heat pipes all indicated impurity controlled corrosion of their evaporators. Impurities observed to be transported included carbon, oxygen, and silicon. A Mo/Li heat pipe that failed after 25,216 h of operation at 1700 K was also examined in detail. This failure was due to nickel impurities being transported to the evaporator resulting in perforation of the container tube by the formation of a low melting Mo-Ni alloy. Theoretical thermochemical calculations were conducted for these systems with the objective of corroborating the corrosion mechanisms in both types of heat pipes. The results of these calculations are in general agreement with the observed corrosion phenomena.

1. INTRODUCTION

The corrosion behavior of molybdenum/sodium (Mo/Na) and molybdenum/lithium (Mo/Li) heat pipes is being studied at the Los Alamos National Laboratory in order to evaluate the potential of these devices for long-term application as primary heat-transfer devices in space nuclear power systems. The corrosion studies described below represent an attempt to understand and elucidate the fundamental mechanisms that can cause corrosion failure in alkali-metal heat pipes using molybdenum or its alloys for containment and wick structures.

Corrosion in high-temperature, alkali-metal heat pipes is mentioned as a problem in most heat-pipe design guides^{1,2}, but even in these sources, the basic mechanisms of corrosive failure are not well defined.

The corrosion failure of high-temperature, alkali-metal heat pipes is caused by one or both of two basic mechanisms. One mechanism involves the dissolution by the alkali metal of the container and wick materials in the condenser region with redeposition of solutes in the evaporator causing eventual failure by clogging of the wick in the evaporator or by perforation of the container in the condenser area. This process results from a finite solubility of the container or wick materials in the working fluid.

The second basic mechanism is typified by evaporator perforation and usually results from the transport of some impurity element or elements to the evaporator by the working fluid. Concentration of these impurity elements in the evaporator can eventually produce corrosive products in the alkali metal that can attack the heat pipe wall. Most refractory metal/alkali metal heat pipe failures that have been reported^{3,4} are characterized by evaporator perforations resulting from impurity enhanced corrosion.

II. Mo/Na HEAT PIPE CORROSION

The experiments detailed below involved heat pipes that were less than 23 cm long with the exception of one that was nearly 2 m long. Several of the experiments were aimed at evaluating simple heat-pipe corrosion, while in others corrosion possibility was enhanced by permeating oxygen through either pure molybdenum or TZM (Mo-0.51%Ti-0.12%Cr-0.03%C), using nearly

stoichiometric UO_2 as the oxygen source. In most cases the heat pipes were driven to high input heat fluxes to make the conditions of the corrosion tests similar to those expected in the potential applications. Except for the 2-m heat pipe, the performance of the heat pipes was estimated from the observed temperatures and known surface emissivities.

The basic premise upon which these experiments were based was that failure would occur in the evaporator region from impurity-enhanced corrosion concentration of impurities. This expectation was fulfilled in the observed failures. Because the corrosion processes that developed in these test heat pipes could not be observed directly, post-mortem analysis coupled with theoretical explanations was relied on to develop corrosion models for the Mo/Na and Mo/Li heat pipes. It should be mentioned *ab initio* that we do not claim to have a complete corrosion model for these systems, but we do believe we have outlined some reasonable alternatives.

The short-specimen molybdenum heat-pipe corrosion experiments with sodium as the working fluid were directed to determining whether UO_2 contained in either pure Mo or TZM could contribute to the corrosion of the heat pipe container by permeation of oxygen through the container into the sodium. A mechanism is clearly indicated in the Gibb's free energy plots in Fig. 1, which shows that Na_2MoO_4 is significantly more stable than UO_2 . The molybdate would be expected to form at a significant rate within a Mo/Na heat pipe in contact with such a fuel if the permeation rate of oxygen through molybdenum was sufficiently high. If formation of Na_2MoO_4 occurred in the heat pipe evaporator, it might cause severe corrosion at temperatures above 962 K, where this compound is molten.

With this potential corrosion mechanism in mind, the experimental corrosion heat-pipe shown schematically in Fig. 2 was developed. As noted in the figure, UO_2 pellets sealed inside a tight-fitting, evacuated molybdenum or TZM tube were located at the center of the molybdenum heat pipe that was fitted with a wall wick of 150×150 mesh molybdenum screen. The inner tube had an outside diameter (o.d.) of 6.35 mm and a wall thickness of 0.762 mm, while the outer tube had an o.d. of 15.9 mm and a wall thickness of 0.889 mm, all of the tubing used in this study was prepared by the Metals Division of the Thermo Electron Corporation from low-carbon, arc-cast (LCA) stock; the wire for the screen wick was prepared from powder-metallurgical stock. TZM was also used as a heat-pipe container material as noted in the summary of the history of the corrosion-test heat pipes given in Table I. The material-combination shorthand in this table is: heat-pipe container/working fluid/inner container/and UO_2 , if present. The sample listed in Table I as SPAR-1 was a 2 m long, annular-wick heat pipe, built for performance testing that was disassembled and examined for signs of corrosion after test.

All the Mo/Na heat pipes discussed in this study were filled with sodium by distillation using procedures described elsewhere.⁵ The short corrosion-test heat pipes, designated MN-1, -3, -4, -6 and A in Table I, were sealed in evacuated quartz tubes for the duration of their heat cycles; the 2-m heat pipe was operated in a performance test-chamber described elsewhere.⁶ All heat pipes in this study were heated by high-frequency rf-induction in a region near one end. The short heat pipes were heated in a three-holed concentrator having a 25-mm-long inductor, while SPAR-1 was heated for 264 h of its total operating time of 362 h with a multiple-turn, 30 cm long induction coil. A 6-cm-long coil was used for the remainder of the operating time. The output power of SPAR-1 was measured continuously with a gas-gap water calorimeter, while the outputs

Fig. 1. Partial molar free energies of several compounds relevant to corrosion in Mo/Na and Mo/Li heat pipes.

of the short heat pipes were calculated from the optically measured operating temperature, assuming the molybdenum emissivity to be 0.17. The working-fluid evaporation mass fluxes listed in Table I were calculated from the known dimensions of the heat pipe evaporators with the assumption that the input heat fluxes were equal to the output heat fluxes. Post-mortem examinations have been completed on two of the three short corrosion-test heat pipes that have failed.

A. Post-Mortem Examinations on MN-1

The heat pipe with the shortest operating time to failure, MN-1, was disassembled and examined in detail. This heat pipe

Fig. 2. Mo/Na heat pipe corrosion specimen.

had been operated for 13.5 h at a constant temperature of 1435 K before it failed by evaporator perforation. Output power for the heat pipe was calculated to be 311 W. During the initial start-up of this heat pipe, a leak developed in the fill tube that may have allowed a small amount of air into the tube before it was resealed. The conjectured air leak was not confirmed on restart by the presence of a non-condensable gas at the condenser end of the heat pipe. However, the fact that an identical heat pipe, designated MN-3 in Table I, is still operating after more than 20,000 hours may indicate that the sodium in this heat pipe was contaminated by an air leak leading to an accelerated corrosion.

The hole that developed in the container-tube wall in the evaporator region of MN-1 is shown in Fig. 3. Extensive metal erosion in the evaporator tube wall is shown clearly in this photograph. A river-like pattern of metal removal was observed over the length of the evaporator in both the screen wick and the container wall surfaces that were oriented downward during the test.

Dark gray crystallites identified as pure molybdenum by x-ray diffraction techniques were found at both ends of the evaporator and attached to the screen near the hole. Screen and tube samples taken from the condenser section and a region near the

Table I. Molybdenum/Alkali Metal Heat Pipe Corrosion Test Summary.

Heat Pipe Description		Temperature (K)	Evaporation ^a Flux (g/m ² · s)	Time (h)	Status ^b
Sample I.D.	Material Combination				
MN-6	TZM/Na/Mo/UO ₂	1300	50	19,481	F
MN-4	Mo/Na/TZM	1390	66	25,030	C
MN-A	Mo/Na/Mo/UO ₂	1400	68	4,475	F
MN-3	Mo/Na/TZM/UO ₂	1400	68	20,600	C
MN-1	Mo/Na/TZM/UO ₂	1435	76	13.5	F
SPAR-1	Mo/Na	1375 ^c	244 ^c	362 ^d	D
LHP-1	Mo/Li	1700	2.4	25,216	F

^a Calculated from the estimated evaporator area and input heat flux.

^b C = Continuing as of 3/15/84; D = Discontinued for reasons other than failure; F = Failed.

^c Peak temperature and power combination operating 1 h.

^d Total time above 950 K, transferring a total of 1.5×10^6 J.

Fig. 3. Evaporator interior of heat pipe MN-1 (Mo/Na/TZM/ UO_2) after 13.5 h at 1435 K.

evaporator were chemically analyzed for carbon, oxygen and nitrogen. The tube sample from the condenser was found to contain 20 ppm carbon oxygen and <3 ppm nitrogen, while the tube sample from near the evaporator contained the same amounts of oxygen and nitrogen, but only 15 ppm carbon. The impurity concentrations in the screen wick were significantly higher. The condenser screen contained 240 ppm carbon, 160 ppm oxygen and 20 ppm nitrogen. The screen near the evaporator contained 220 ppm carbon, 260 ppm oxygen and 30 ppm nitrogen. As compared to the typical analysis of unused, vacuum-degassed screen, the carbon and nitrogen contents of the tested screen samples are high, but the oxygen contents are similar. Carbon and oxygen contents of typical molybdenum screen before exposure are given in Table II.

The TZM tube that contained the UO_2 in this experiment was superficially unaffected by the test, but a comparison of the chemical composition of unexposed TZM tubing with that used in this experiment reveals a significant increase in the carbon and oxygen content due to the exposure. The carbon content increased from 280 to 550 ppm, and the oxygen content increased from 15 ppm to 110 ppm. The carbon and oxygen are believed to have come from the UO_2 because a thin layer EDAX analysis only indicated molybdenum was observed metallographically on the inside of the TZM tube. Neither oxygen nor carbon can be

detected by EDAX. The UO_2 appeared to be slightly reduced with the stoichiometry of the exposed samples indicated as $\text{UO}_{1.94}$ by comparison with analyzed samples prepared by the same method.

B. Post-mortem Examinations on NM-A

Sample MN-A failed during restart after a shut down for radiographic examination. This sample contained UO_2 inside a pure molybdenum container tube which was in turn contained in a pure molybdenum heat pipe with sodium working fluid. The system had been operated at 1400 K for 4475 h before failure. Periodic radiographs did not indicate any signs of incipient failure. The failure occurred in the evaporator, but the hole was too small to be located precisely. Detailed post-mortem analyses revealed significant corrosion had taken place in the evaporator, but none in the condenser. The evaporator corrosion was manifested by material removal from the inside of the container wall in an area that was oriented downward during the test. The evaporator screen was embrittled as compared to the screen that had operated in the condenser of the heat pipe. Fig. 4 shows the

Fig. 4. Evaporator interior of heat pipe MN-A (Mo/Na/Mo/ UO_2) after 4475 h at 1400 K.

Table II. Distribution of Impurities in MN-A (Mo/Na/Mo/ UO_2) Heat Pipe Screen.

Element	Concentration (wppm)*				
	Secondary Condenser	Evaporator	Primary Condenser Next to Evaporator	Far End	Unused Screen
O	960	380	130	110	220
C	130	120	370	90	85
Si	150	300	60	60	30
Na	900	450	<45	45	<45
Mg	4.5	9	6	12	6
Al	15	20	15	15	5
Ca	1.5	150	<1.5	1.5	7
Ti	7.5	7.5	<15	<15	<15
Cr	45	100	60	60	35
Mn	3	7.5	2	2	<2
Fe	120	180	90	90	130
Ni	120	200	40	40	160
Cu	6	6	<4.5	4.5	6
Sr	<1.5	1.5	<1.5	<1.5	<1.5
Bi	<4.5	15	<4.5	<4.5	<4.5

*Concentrations listed are less than the indicated detection limit.

Fig. 5. ESCA (2000 eV) scan data from black nodules found in the evaporator of MN-A after argon ion-milling.

inside of the evaporator of this heat pipe after residual sodium was removed with pure ethanol. Besides the wall erosion, black, glassy nodules can be seen on the surfaces.

These black nodules were analyzed with electron microprobe and Auger-ESCA surface analysis to determine their elemental composition. Scans were performed on several of the nodules seen in Fig. 4 with similar results. They contained oxygen, sodium and silicon with minor amounts of carbon, aluminum, calcium and barium. A typical 2000 eV ESCA scan of a black nodule after argon ion-milling is given in Fig. 5. The peaks for Si, C, O and Na are clearly seen. Surface charge effects were observed during the Auger-ESCA examination of the nodules, indicating they were insulators. Nickel was found along with the expected molybdenum next to one of the black nodules. A secondary-electron micrograph and the dimensional x-ray dot maps produced by the electron microprobe from a typical black nodule and the surrounding area are given in Fig. 6. The x-ray dot maps in Figs. 6(b)-6(d), indicate the major constituents to be Na, O, and Si, while as indicated in Figs. 6(e)-6(g) lower concentrations of C, Ca, and Al were also detected. Ba was also detected in the black nodule seen in Fig. 6(a). As indicated in Fig. 6(h), molybdenum was confirmed as the major constituent surrounding the nodule, but, as indicated in Fig. 6(i), the surface was contaminated with nickel. Auger-ESCA scanning disclosed nickel along with Si, C, O, and Na, under a piece of screen that was found partially attached to the inside of the evaporator wall.

Crater-like features were found on the inside surface of the molybdenum container adjacent to a river-like erosion pattern at the entrance to the evaporator. The rim and the floor of a crater were scanned with Auger-ESCA. Before ion-milling, Mo, C, O, and Na were found in both locations. These elements persisted after more than 90 min of surface ion-milling with a 25 mA current of 5 kV argon ions corresponding to a milling depth of about 50 μm . Bulk chemical analysis of the molybdenum-screen wick from this corrosion-test heat pipe was consistent with the microprobe analyses. Table II provides a list of elements found concentrated in the evaporator after the test. These data also indicate concentration of oxygen, carbon and sodium in the secondary condenser. Stripping of impurities from the condenser is also indicated by comparison of the concentrations in the various locations.

The molybdenum tube that contained the UO_2 during the experiment showed no obvious signs of attack by either the sodium or UO_2 . The grain size of the molybdenum in the UO_2 containment tube was only about half that of the heat pipe container tube. The smallest grains in the container tube were found in the secondary condenser where they were about 250 μm across. The re-distribution of interstitial impurity contamination along the heat-pipe container during the test resulted in a reduced grain size in the evaporator and secondary condenser

when compared to the primary condenser. Oxygen passing through the inner Mo tube from the UO_2 to the sodium working fluid during heat pipe operation might have caused the reduced grain size in the UO_2 to the sodium working fluid during heat pipe operation might have caused the reduced grain size in the UO_2 container tube. The UO_2 was measured to be $\text{UO}_{1.993}$ at the end of this experiment which is a lower O/U ratio than observed for the UO_2 in sample MN-1 and is consistent with expectations. No metallic uranium was detected in a metallographic analysis of the UO_2 .

C. Post-mortem Examinations on SPAR-1

SPAR-1 was operated at varying temperature and power, and, as indicated in Table I, had transferred a total of 1.5 GJ of heat energy at temperatures above 950 K during testing. This heat pipe contained getter materials located in the evaporator end. The getter consisted of a loose stack of hafnium foils placed between the closed end of the screen-tube wick and the end-cap.

Although the total energy throughput for this heat pipe was less than for most other tests, the post-mortem examinations indicated some noticeable effects of operation. Minor corrosion of the screen-tube wick was observed in the evaporator section as evidenced by a black deposit on the inside of the screen and removal and redeposition of molybdenum from the screen wires in the same area. Chemical analyses of screen-tube wick sections from various regions of the heat pipe indicated significant redistribution of carbon and oxygen. Figure 7 illustrates the after-test carbon, oxygen, and nitrogen distribution in the screen-tube wick. Carbon and oxygen were transferred both to the evaporator and to the region beyond the condenser that contained the surplus liquid during heat-pipe operation.

Auger analysis was performed on the inside surfaces of screen-tube samples taken from the regions indicated for bulk chemical analysis in Fig. 7. Three samples from the evaporator section were surface analyzed, including one with "crystallites" on the inside surface and two with inside surface discolorations. In all three cases, Mo, C, O, Na, and Si were detected in both the pre- and post-sputter scans. Al was also detected on the surface of one of the samples with surface discoloration. Auger analysis of surface deposits on the inside of a screen-tube section taken from the liquid pool region at the condenser-end indicated the presence of C, O, and Na as well as Mo. When the surface was ion milled, the amounts of O and Na were reduced, but the amounts of C and Mo were not. These elements were also detected on the inside surface of a screen-tube section taken from the center of the condenser, but all except the molybdenum and sodium tended to disappear as the surface was ion-milled away, which indicates that the other elements were probably only surface contaminants.

Auger analysis was performed on the inside surface of sections of container tube taken from the evaporator and condenser regions of the heat pipe. Mo, C, O, Na and Si were detected on the inside of the container-tube section from the evaporator, but only the molybdenum persisted after ion-milling to deeper levels. These same elements were detected on the inside surface of the container-tube section from the condenser. However, in this case the silicon (and molybdenum) contents increased to a relatively high level with deeper ion-milling, but the C, O and Na concentrations decreased. This might indicate the source of the silicon in the observed deposits to be either a deep surface or bulk contamination on the inside of the container tube.

D. Discussion of Mo/Na Heat Pipe Corrosion

It is clear from the data that Mo/Na heat pipes can fail as a result of impurity transport to the evaporator with concentration

(a)

(b)

(c)

(d)

(e)

(f)

Fig. 6. Secondary electron micrograph (a) and x-ray dot maps (b thru f) from a black nodule found in heat pipe MN-A.

Fig. 6 (cont)

to levels at which the impurities are corrosive. The impurities that were observed to concentrate significantly in the evaporator in these tests include O, C, Si, Ca, Cr, Fe, and Ni. (See Table II and Fig. 7.) Nitrogen concentration in the evaporator was never observed. Carbon and oxygen were also seen to concentrate at the ends of the heat pipe, but no evidence of corrosion was observed in these locations. The major source of the concentrated impurities in heat pipes that have operated for long times is probably the screen wick in the condenser. Reduced impurity levels were always observed at this location in the the screen, but not in the container tube. This may be related to the high surface to volume ratio of the fine screen material. The impurity source in the heat pipes that failed in short times was probably sodium that was impure as charged.

The specific corrosive compound or compounds that caused failure of the Mo/Na heat pipes have not been isolated, but evidence for the mechanics of the corrosion process has been disclosed. The corrosion appears to involve the formation in the evaporator of a compound between molybdenum, selected impurities and sodium. When the compound is transported to a region where it contacts relatively pure sodium returning to the

evaporator, it is reduced to metallic molybdenum and an impurity compound which eventually returns to the evaporator to continue the corrosion loop or cycle. It is not entirely clear from the experiments whether the Mo-containing compound is transported through the vapor phase, as a separate condensed phase, or as Na-soluble species. It is also uncertain whether a corrosion cycle is set up under steady, normal heat pipe flow conditions, or if the impurity concentrations required are reached only under off-design or transient situations such as a dry-out.

Oxygen permeation through molybdenum from UO_2 as a source of corrosion in Mo/Na heat pipes is suggested but not confirmed by the data. Post-mortem analysis of the UO_2 from the TZM/Na/Mo/ UO_2 sample (MN-6) that failed after 19,481 h at 1300 K may shed light on this point. In addition to the possibility the cycle involving compounds containing Na, Mo, and O, a corrosion cycle involving silicon is suggested by the nonmetallic, black, glassy nodules observed in the evaporator of sample MN-A. These nodules were shown by microanalyses to contain mostly Si, Na and O, which suggests that they are silicates. Furthermore, Na_2SiO_3 and Na_2SiO_4 are known to be stable in liquid sodium at 873 K.¹⁰ However, more experimental

Fig. 7. Impurity Distribution in the screen tube wick from SPAR-1.

work will be required to establish whether these nodules are directly involved in the corrosion process.

Complex chemical equilibrium calculations have been used to evaluate possible mechanisms for the observed Mo/Na corrosion. The system was modeled to include a gas phase, a liquid-Na phase containing dissolved impurities, and other condensed phases formed from the bulk and impurity element components. A version of the computer program SOLGASMIX-PV¹¹ was used to solve the complex chemical equilibrium problem. Standard free energies of formation of the possible chemical species as a function of temperature and the initial amounts of all elements assumed to be in the system were specified as program input. A free-energy minimization method is used in the program to calculate the identities and amounts of species present at equilibrium between a gas, a liquid alkali-metal solution, and condensed phases of invariant composition.

A major task in the analysis was the compilation of a set of mutually consistent free energies of formation. The JANAF Tables¹² were used as a starting point, but it was necessary to recalculate some of these Tables using more recent experimental data and to supplement them with species not found therein. In many cases temperatures of interest were well above those of the experimental measurements on which the standard free energies of formation are based. The required extrapolation introduces uncertainties, as does the possibility that some important high-temperature species have been omitted either because they have not been detected experimentally or because the available thermodynamic data are judged to be insufficient to derive meaningful values for their free energies of formation.

1. Base Calculation. The major impurities that were present in a Mo/Na heat pipes included C, O, N, and Si. For calculational purposes, it was assumed that only these impurities were present in a 2-m-long Mo/Na heat pipe with a 15.9-mm o.d. and a 0.05 mm diameter wire and positioned against the inner surface of the Mo tube. The O, N, and C contents of the molybdenum were taken to be 100, 30, and 50 ppm, respectively and the sodium charge 85 g. The contributions to the total impurities due to contaminants in the sodium charge were considered negligible. The assumed impurities due to contaminants in the sodium charge were considered negligible. The assumed impurity levels correspond to 0.0015 g-atom O/mole of Na (1045 appm), 0.0005 g-atom N/mole of Na (305 appm), and 0.001 g-atom C/mole of Na (520 appm).

2. Solubilities of Selected Impurities in Liquid Sodium. Data exist for the solubility of oxygen in liquid Na to 850 K¹³ (solution species: Na_2O_2) and for the solubility of carbon to about 1100

K^{14,17} (solution species: Na_2C_2). Solubilities of these impurities were extrapolated to 1500 K in accordance with known or assumed phase diagrams. Nitrogen and silicon have negligibly small solubilities in otherwise pure sodium¹⁸. However, there are data for the enhanced solubility of carbon under an overpressure of nitrogen at temperatures to about 1000 K, presumably due to the formation of NaCN in liquid Na^{17,18}, and for the enhanced solubility of carbon in the presence of oxygen at temperatures of about 1000 K, presumably due to the formation of Na_2CO_3 in solution.¹⁷ As the solubilities of NaCN and Na_2CO_3 in liquid Na were not judged to directly influence the mechanisms for possible mass transport of Mo and reliable extrapolation of existing solubility data to temperatures of interest was particularly uncertain, such extrapolation was not attempted.

In contrast with many other transition metals, Mo is stated to show no corrosion in liquid Na saturated with oxygen at 873 K (>3000 appm O).¹⁹ As a first approximation, in the absence of any conflicting data the solubility of Mo in liquid Na, either as the metal or as a ternary oxide, was assumed to be negligible.

3. Molybdenum Species in the Calculation. It was assumed that mass transport of Mo under the near-isothermal conditions postulated and due to O, N, C, or Si impurities would occur by reaction of Mo with an impurity to form a mobile gaseous or condensed-phase reaction product. The reaction products included in the calculations were: gaseous phases - MoO , MoO_2 , MoO_3 , NaMoO_3 , Na_2MoO_4 , Na_2MoO_5 ; condensed phases - MoO_2 , Na_2MoO_4 , Mo_2C , Mo_2N , Mo_3Si .

4. Summary of Calculational Results. With the base-line C, O and N impurity concentrations, Mo_2C (mp=2703 K) was the only Mo-containing condensed phase calculated to form at 1400 K, the nominal operating temperature of the model heat pipe. If the sodium was saturated with oxygen, Na_2MoO_4 (mp=962 K) was calculated to form. NaMoO_3 might also form, but the thermodynamic data for this compound are not sufficient to be positive. The amount of oxygen required for saturation of the sodium at 1400 K is some 100 times the base-line concentration, but this is a credible eventuality in the evaporator if there is sufficient oxygen in the system that is free to be dissolved by the condensing sodium. This could cause a progressive increase in the local oxygen concentration until saturation was achieved and Na_2MoO_4 (l) separated out locally. When the latter contacts the returning "clean" liquid Na, the molybdate will decompose liberating Mo and releasing oxygen to the sodium. The resulting cyclic process could eventually lead to perforation of the evaporator. This proposed corrosion process is shown schematically in Fig. 8. Below 1200 K, Na_2O (mp=1405 K) is the condensed phase calculated to form when the system is saturated with oxygen, a result that agrees with the observations of Kef. 19 regarding the lack of sodium corrosion of Mo at 873 K.

There also exists a possibility for mass transport of molybdenum through the vapor phase. As the oxygen content of the liquid Na increases, the total partial pressures of the gaseous sodium molybdates increases dramatically, although the maximum magnitude of the pressure is relatively modest. The calculated extreme values of that partial pressure and the corresponding partial pressure of Na_2O and MoO in atmospheres at 1400 K for the baseline oxygen concentration are: $\text{Na}_2\text{O} = 5 \times 10^{-9}$, $\text{MoO} = 4 \times 10^{-16}$, $\text{Na}_2\text{MoO}_3 + \text{Na}_2\text{MoO}_4 = 7 \times 10^{-14}$; while for the oxygen saturated system the calculated partial pressures are, in the same order: 6×10^{-7} , 8×10^{-16} , 4×10^{-7} .

For calculations of the predicted fate of a silicon impurity at 1400 K, the condensed-phase species Na_2SiO_3 (mp=1362 K), Na_4SiO_4 (mp=1393 K), Mo_2Si (mp=2298 K), and SiO_2 (mp=1696±50 K) were included. If Mo_2Si were not included as a possible reaction product, corresponding to the unavailability of a molybdenum surface, the Si-containing species formed would

Fig. 8. Schematic of a proposed oxygen driven corrosion mechanism in Mo/Na heat pipes.

depend markedly on the ratio of ppm O to ppm Si, R , in the multiphase system. For $R < 1.7$, a mixture of elemental Si ($mp = 1685$ K) and Na_2SiO_3 is calculated to form, and for a short range around $R = 1.7$, Na_2SiO_3 is the only product predicted. For $1.7 < R < 2.4$, a mixture of Na_2SiO_3 and Na_2SiO_4 results. For $R > 2.4$, Na_2SiO_4 is calculated to be the sole product. The exact value of R for these boundaries depends somewhat on the total impurity content. If Mo_2Si were included as a possible condensed phase it and Na_2SiO_4 would be the only Si-containing products calculated to form. For R less than about 2.5, a mixture of Mo_2Si and Na_2SiO_4 would be produced. For $R > 2.5$, the sole Si-containing product is Na_2SiO_4 . These calculations extend the predicted temperature at which the sodium silicates are stable to liquid Na from an experimentally observed 873 K¹⁰ to at least 1400 K and support a conclusion that the glassy nodules seen in sample MN-A were sodium silicates.

If an interruption of liquid Na flow were coupled with a temperature excursion such as a simple shutdown, additional mechanisms for molybdenum transport would be possible. For example, solid Na_2O separating out locally at temperatures below 1200 K could react with molybdenum at temperatures above 1200 K to form the mobile sodium molybdate.

The above discussion of Mo/Na heat pipe corrosion has been largely restricted to possible mechanism involving an oxygen impurity. Furthermore, the known compounds, $NaMoO_3$ and Na_2MoO_4 ,²⁰ were not considered in the calculations. It is difficult to assess the effects of carbon or silicon on Mo transport beyond noting that if any Mo_2C or Mo_2Si formed were dislodged from the molybdenum surfaces, transport of that material to a region containing relatively pure sodium could in principle result in redeposition of pure molybdenum. However, this does not seem to be in agreement with the location of the observed gross corrosion in the heat-pipe tests. Nitrogen impurities in liquid Na are not judged to be important for transport of molybdenum. As noted above, deposits containing the elements Al and Si have been identified in post-mortems of Mo/Na heat pipe tests. The implication of these elements for molybdenum transport are currently under study.

II. Mo/Li HEAT PIPE CORROSION

A. Experimental Details

A Mo/Li heat pipe was operated at 1700 K for 25,216 h before it failed. The LCAC molybdenum heat-pipe container tube was 165 mm long with an o.d. of 25.4 mm, and a wall thickness of

1.78 mm. A sketch of the heat pipe is presented as Fig. 9. The wick consisted of two layers of 150×150 mesh molybdenum screen pushed tightly against the inside surface of the tube. Pieces of hafnium foil, a total of 2 g, were held against the evaporator end cap with two layers of the wick screen as illustrated in Fig. 9. The hafnium was included to act as a getter for O, C and N. As indicated in Fig. 1, hafnium can be expected to remove oxygen from lithium to below 10 ppm. The molybdenum test strips indicated in Fig. 9 were doped, HT-grade molybdenum included to determine its lithium compatibility.

The filling procedure differed considerably from that used for the Mo/Na heat pipes. A quantity of solid lithium sufficient to fill the wick plus some excess was placed inside the container tube which had one end-cap electron-beam welded onto it. The second closure end-cap was then inserted into the open end of the container tube, and the heat pipe was operated in a vacuum with this end-cap loosely in place to drive out the non-condensable gases and make a temporary vacuum-tight lithium seal. Final sealing was accomplished by electron beam welding the end-cap in place. The electron beam of the welder was capable of boiling the lithium out of the joint without interfering with the fusion welding of the molybdenum end cap to the container tube.

The completed heat pipe was sealed in an evacuated quartz tube and heated by high frequency rf-induction with a water-cooled, wound copper inductor coil that extended approximately 5 cm along the length of the heat pipe near the end that contained the getter. The heat pipe was operated in a horizontal position with one quadrant of the tube always oriented downward. The temperature of the pipe was measured optically, and an optical sensor controlled an interlock system that would shut down the rf-generator in the event of either an over- or under-temperature condition. The total output power of the heat pipe at 1700 K was calculated to be 1056 W which, as indicated in Table I, represents an approximate lithium evaporation flux of $2.4 \text{ g/m}^2 \cdot \text{s}$. Radiographs of the entire heat pipe were taken periodically during its lifetime and did not indicate any noticeable attack of the internal surfaces of the container tube; however, these radiographs did indicate a partial collapse of the wick into the vapor passage on the side of the tube that was in the downward position during operation. Another noticeable change in the pipe over the course of the test was the development of metal grains large enough to be easily visible to the naked eye. Periodic diametral measurements were taken on the container tube, and the observed small increases were close to that predicted from uniaxial creep data for pure molybdenum²¹ using the Von Mises effective stress for the heat-pipe creep stress. During the total 25,216 h of operation at 1700 K the heat pipe underwent at least 233 thermal cycles between room temperature and 1700 K. Failure occurred through development of two small holes in the evaporator. Lithium loss from the holes caused the optical sensor to detect a

Fig. 9. Mo/Li heat pipe corrosion specimen.

malfunction and turn off the rf-generator. The quartz envelope was not broken by the heat pipe failure.

During disassembly, the heat pipe was found to be mostly empty of the lithium, so post-test chemical analysis of the lithium working fluid could not be performed. Visual examination of the various sections of the heat pipe were conducted after reacting the residual lithium with water. Although the failure holes were obvious on the outside of the pipe, they could not be unambiguously located on the inside of the container tube.

Seven metallographic samples were taken from various regions of the heat pipe. One of them included the hole. After polishing, the larger of the two holes was exposed in cross-section, and the structures along the edge of the hole's track were observed. The central region of the hole can be seen in the optical photomicrograph in Fig. 10(a). The four areas marked A thru D in this photomicrograph were analyzed with an electron microprobe, and an ion microprobe was used to analyze areas C and D. Electron microprobe analysis of the structures in area A, shown in the back-scattered electron micrograph in Fig. 10(b), indicated that position 1, the darker structure, contained both Mo and Ni, while position 2, the lighter structure, contained mostly Mo and a small amount of Ni. Similar analyses were obtained on the structure in area B in Fig. 10(a). Because there is a peritectic in the Mo-Ni binary phase system with a melting temperature of 1635 K²², it is probable that the structure at position 1 in Fig. 10(b) is the remnant of nickel-rich liquid, while the structure in position 2 is a molybdenum-rich Mo-Ni solid solution that is being dissolved by the nickel-rich liquid. Area C, which is shown at higher magnification in Fig. 10(c), was determined by the electron microprobe to contain Mo, Ni, Fe and Cr at position 1, while position 2 was determined to contain only molybdenum. The ion microprobe indicated that lithium and oxygen were also present at position 1. Area D contained the two distinct structures seen in Fig. 10(d). The electron microprobe indicated that position 1 and 2 in the larger structure seen in Fig. 9(d) contained Mo, Ni, Fe and Cr, and the ion microprobe revealed that this structure also contained oxygen and lithium. An enlargement of the smaller structure in Fig. 10(d) is seen in Fig. 10(e), and the electron microprobe revealed that this structure had a somewhat different composition than had previously been observed. Positions 3 and 4 contained trace amounts of Fe, Cr and Si in addition to the major constituents Mo and Ni. Position 5 at the edge of this structure was also found to contain both Mo and Ni.

The perforation of the heat pipe wall probably initiated as a result of grain boundary attack. Grain boundary penetration was observed in the vicinity of the hole on the inside of the heat pipe in the evaporator along with an occasional string of grain boundary precipitates near the inside surface of the tube.

A surface layer ripple structure was found on the inside of the part of the container tube that had been on the down-side of the evaporator during operation. A photomicrograph of the cross-section of this structure is seen in Fig. 11. This surface layer was analyzed with the electron microprobe, and it was found to be rich in hafnium. Hafnium was also found to have diffused an additional 10 to 20 μm into the heat pipe wall, and in some areas near the inside of the tube wall, hafnium-rich grain boundary precipitates were found at greater depths. The hafnium had been transported from the getter foils during the test. No remnant of the foils was found in their original location after the test; however, single crystals of hafnium carbide were collected off the inside surface of the molybdenum screen near the original location. Hafnium was also detected on the surface of the HT-molybdenum strip that had resided in the evaporator during the test.

Chemical analyses of container-tube sections taken from various regions of the heat pipe suggest that there had been some redistribution of carbon and oxygen within the heat pipe. The nitrogen content of the tube specimens was always below the detection limit, 10 ppm. Both the carbon content and the oxygen

content of the tube near the getter packet were very low, 5 ppm and <5 ppm, respectively, while in the center of the evaporator carbon had risen to 15 ppm and oxygen to 20 ppm. Tube sections that had operated next to the evaporator in the primary condenser were found to contain 20 ppm C and 10 ppm O for the sample that had operated on the top and 10 ppm C and 45 ppm O for the sample that had operated on the bottom. The oxygen concentration of the screen that had operated on the bottom at the evaporator end of the condenser was determined to be 110 ppm. A sample of tubing that had operated at the end of the primary condenser was found to contain 5 ppm carbon and 30 ppm oxygen. The carbon and oxygen contents of these various tubing samples suggest that the pattern of transport to the evaporator and the extreme end of the condenser seen previously for Mo/Na heat pipes is repeated in this Mo/Li heat pipe. This is further supported by the fact that the HT-molybdenum strips that operated in the evaporator were determined to contain 40 ppm carbon, 840 ppm oxygen and 12 ppm nitrogen. These strips were contaminated with hafnium which might have enhanced the levels of C, O, and N found by bulk chemical analysis.

B. Discussion of Mo/Li Heat Pipe Corrosion

A possible mechanism for the failure of the heat pipe is indicated by the observations. The stainless steel component impurities, Fe, Ni, and Cr, were concentrated in the evaporator of the heat pipe as a result of normal operation, until locally the nickel concentration reached a level in excess of 1.8 at.% whereupon a liquid phase formed which eventually penetrated the heat pipe wall. Because other elements, such as Fe, Cr, Si and O, were found in the vicinity of the hole, the actual failure mechanism is probably much more complex than that just hypothesized, but as predicted by Katsuta and Furukawa²² and indicated by the experimental data, nickel in liquid lithium does affect the compatibility of molybdenum with lithium. These authors observed nickel contamination of molybdenum after only 100 h at 873 K in lithium that was contained in a stainless steel vessel. Because the lithium in this experiment had been processed and stored in stainless steel containers and not distilled into the heat pipe, it is reasonable to presume that the starting lithium was contaminated with stainless-steel components with nickel expected as the most abundant metal impurity due to its high solubility in lithium. The solubility of Ni in liquid Li is known to be relatively high even at 1100 K and to increase sharply with nitrogen content over the range 150-220 wppm.²⁴

Given the presence of nickel as an impurity in the Mo/Li heat pipe, it is possible to rationalize the transport of the hafnium getter from its original location on the basis of the Hf-Ni phase diagram.⁴³ This indicates a number of peritectic or eutectic compositions with melting temperatures ranging from 1425 K to 1625 K. The high solubility of nickel in liquid Li and the complicated thermal history of the heat pipe probably assure the mobility of the nickel required to produce transport of both molybdenum and hafnium. The redeposition of some of the hafnium as HfC may not be indicative of the transport mechanism. If redeposition as metallic hafnium were to occur prior to or simultaneous with release of carbon from the molybdenum wick or container by extraction into the liquid Li, HfC would be formed at the site of the redeposition.

Although appeal to the effect of O, N, or C impurities does not appear necessary to explain the failure of the Mo/Li heat pipe described here, it is desirable to consider what these effects might be, especially with regard to the transport of the impurities to the evaporator. Whereas corrosion of transition metals by liquid Na is largely attributed to reaction with Na_2O dissolved in the alkali metal to form ternary oxides, corrosion in liquid Li is more commonly attributed to reaction with dissolved nitrogen (present in solution as Li_3N) to form ternary nitrides. Although the

(a)

(b)

(c)

(d)

(e)

Fig. 10 Microstructures seen in the vicinity of the leakage hole in the MO/Li life test heat pic. (a) Hole cross-section, inside of tube to the left; (b) area A in (a); (c) area C in (a); (d) area D in (a); (e) area D in (a) area to the left positions 1 and 2 in (d).

Fig. 11. Cross-section of the inside surface of the bottom of the evaporator in the Mo/Li heat pipe.

solubility of oxygen in liquid Li is less than in liquid Na,²⁶ the former is still significant. However, the very high stability of Li_2O relative to that of Na_2O makes the former relatively unreactive to the transition metals. Alternatively, liquid Li will reduce oxides of most transition metals to the metal. Hafnium is an exception, which makes it of some use as an oxygen getter in lithium system. Gettering of oxygen by hafnium in lithium system is calculated to proceed by the formation of Li_2HfO_4 (mp=1925 K) rather than HfO_2 . Complex chemical equilibrium calculations which include gaseous and condensed-phase lithium molybdates in the data base indicate no corrosion of Mo by oxygen when in contact with liquid Li at temperatures to 1000 K. Oxygen saturation leads to the formation of Li_2O (mp=1843 K). Due to absence of experimental data, these calculations did not include effects of the solubility of lithium molybdate in liquid Li. The only situation calculated to result in the formation of compounds such as Li_2MoO_4 (mp=974 K) or LiMoO_3 in off-normal operation such as an evaporator dryout that could result in the exposure of Li_2O containing a slight amount of additional oxygen to Mo in the absence of liquid Li. As an interesting sidelight, it is calculated with data from recent studies of gaseous species over Li_2O at high temperatures^{27,28} that at conditions in a Mo/Li heat pipe, $\text{Li}_2\text{O(g)}$ will have the highest partial pressure of the gaseous lithium oxides.

The solubility of Li_3N (mp=1086 K) in liquid Li is large,^{29,30} and because the compound is relatively unstable, the solution is expected to be reactive to the transition metals. Unfortunately, virtually no thermodynamic or solubility data exist for the transition metal ternary nitrides. For purposes of the present calculations in the Mo, Hf/Li/N system, thermodynamic data to 1700 K were estimated for the condensed phases Li_3HfN_3 and Li_3MoN_3 . These phases have been synthesized,^{31,32} but no thermodynamic data are available. Although attempts to prepare a ternary nitride of Mo with a Li/Mo ratio less than 9 to 1 have been unsuccessful, estimated thermodynamic data for the hypothetical compound Li_3MoN_3 have been included. Data for the binary nitrides of hafnium and molybdenum were taken from the literature.

Hafnium is calculated to be a good getter for nitrogen at 1500 K at the base-line nitrogen concentration by the formation of HfN , which forms in preference to Li_3HfN_3 . In the absence of Hf, a condensed-phase nitride containing Mo does not form at base-line nitrogen concentrations. If nitrogen is added to the calcula-

tion in unrealistically high concentrations, Li_3MoN_3 is calculated to form, but not Li_2MoN_2 . Because of the high nitrogen concentrations required this is not a significant result, although if such a compound were soluble in liquid Li, a more reasonable mechanism for possible Mo transport would exist at more modest nitrogen levels. There exist fragmentary data for the solubility of Mo in liquid Li as a function of nitrogen content at 1300 K,³³ but more data are needed before reliable calculations can be predictive.

IV. CONCLUSIONS

The corrosion observed in both the Mo/Na and Mo/Li heat pipes was related to impurity effects and occurred in the evaporator. Because of this corrosion mechanism, great variability of heat pipe lifetimes was seen. The impurities may have been residual in the alkali metal or in the heat-pipe container or wick, but their rate of transport to the evaporator probably governed the heat pipe lifetime. Impurities such as oxygen, carbon, and silicon can collect in the evaporators of Mo/Na heat pipes forming compounds such as Na_2MoO_4 , Na_2O , and Na_4SiO_4 , which may cause heat pipe corrosion. These impurities plus nitrogen and nickel are seen to be important in the corrosion of Mo/Li heat pipes. Due to the complexity of the corrosion processes in both types of heat pipes much more experimental and theoretical work is required to elucidate them. It is essential that experimental and theoretical work proceed concurrently because neither alone can satisfactorily establish cause and effect relationship in alkali metal heat pipe corrosion.

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