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DMIC review of recent developments
Liquid Metals
F. M. Simons • June 2[illegible], 19[illegible]

GENERAL

Research on molten metals as heat-transfer media and thermodynamic working fluids is continuing at a number of sites. Major emphasis today is on sodium as the coolant for fast-breeder power-producing nuclear reactors. However, other applications and other liquid metals are still receiving attention (e.g., lithium for cooling rocket nozzles; Rankine-cycle space power systems involving potassium, lithium, mercury, and NaK; magnetohydrodynamic generators with cesium-seeded plasma; and thermionic generators with lithium-heated cathodes and cesium space-charge neutralization).

LITERATURE REVIEWS

A critical review of the literature on the solubilities of transition metals in molten alkali and alkaline-earth metals has been published by Lawrence Radiation Laboratory.(1) This valuable compilation summarizes the data graphically on each of the numerous systems studied. Solvents covered are lithium, sodium, potassium, rubidium, cesium, magnesium, calcium, lanthanum, and cerium. Solutes include iron, nickel, chromium, cobalt, manganese, titanium, tantalum, molybdenum, vanadium, tungsten, uranium, and zirconium.

A detailed review of liquid-metal embrittlement phenomena has been published by Martin-Marietta.(2) The reviewers believe that chemisorption of the liquid metal reduces the atomic-bond strength at regions of stress concentration in the solid metal. They disagree with Robertson's concept that embrittlement results from stress-enhanced dissolution and subsequent diffusion of the liquid metal at a crack tip.(3) The review discusses the effects of chemical composition, temperature, prestrain, and rate of loading on severity of embrittlement, and concludes that there are still substantial gaps in our understanding of the phenomena.

A state-of-the-art review of the compatibility of construction materials with alkali metals for space nuclear power systems has been published by workers at Oak Ridge.(4) Because operating temperatures must be as high as feasible, refractory metals appear to be the most promising construction-material candidates. Lithium, potassium, and cesium are the fluids which have been given most attention as heat-transfer and working media for high-performance space nuclear reactors utilizing Rankine-cycle conversion. Interactions among the myriad corrosion-governing parameters (e.g., temperature, temperature gradient, surface-to-volume ratios, purity of materials, flow conditions, presence of dissimilar materials, metallurgical condition of the container) make the corrosion behavior in any conceptual system difficult to predict quantitatively. About a decade of laboratory work, ranging from static, isothermal capsule experiments to highly sophisticated pumped-loop tests has demonstrated the following:

(1) Reliable systems utilizing potassium or cesium up to 2000 F can be constructed of first-generation columbium-base alloys like Cb-1Zr, and to 2200 F with advanced columbium-base alloys like D-43 (10W-1Zr), C-129 (10W-10Hf), and FS-85 (28Ta-10W-1Zr).

(2) Columbium-base alloys can be used at even higher temperatures in lithium systems.

(3) Tantalum-base alloys like Ta-10W and T-111 (8W-2Hf) appear satisfactory for potassium or cesium to at least 2200 F, and probably a few hundred degrees higher with lithium.

CORROSION BY SODIUM AND NaK

The corrosion of TIG welds in SNAP-8 tantalum tubing containing 55 to 520 ppm oxygen by eutectic NaK containing about 10 ppm oxygen was investigated at General Electric.(5) Specimens were exposed in tantalum capsules for either 100 hr at 1200 F or 1000 hr for 1350 F. Metallography showed no evidence of attack in specimens containing 220 ppm oxygen or less, although all the 1350 F specimens suffered modest weight losses (presumably because of oxygen gettering by the NaK).

Specimens with 270 ppm oxygen suffered 2 to 4 mils penetration in the heat-affected zone, while those with 520 ppm oxygen were much more severely attacked. Of these, curiously, the ones tested at 1200 F for 100 hr were completely penetrated (20 mils), while those tested at 1350 F for 1000 hr were attacked to a depth of only about 8 mils.

The phenomenon of reduced corrosion at increased temperatures and exposure times is explained by the researchers as follows. Oxygen in the tantalum can diffuse to the surface and dissolve in the NaK much faster at 1350 than at 1200 F. In fact, at 1350 F this diffusion and dissolution occur so fast that the oxygen concentration in the tantalum region where corrosion is advancing along grain boundaries and crystallographic planes can be reduced to below the corrosion threshold and thereby retard the penetration into the specimen. This concept is consistent with the observed reductions in oxygen content of all tantalum specimens following exposure to NaK.

with the greatest reductions occurring after the 1300 F exposure.

The large grain size and long transverse grain boundaries in the fusion zone of high-oxygen specimens account for the deeper corrosive attack noted there, as compared with attack in the heat-affected zone. Corrosion in both the fusion and heat-affected zones of specimens containing 270 ppm oxygen was more severe than in the base metal. Contamination of the TIG atmosphere (helium) with up to 150 ppm of air during welding had no observable effect on the weld's corrosion resistance to NaK.

The conclusion from this study is that welded and unwelded tantalum in the SNAP-8 boiler will not be attacked by the NaK unless the tantalum contains 270 ppm oxygen or higher--a circumstance which is unlikely to develop accidentally, by virtue of the inaccessibility of the tantalum-NaK interface to oxygen.

A sodium thermal-convection loop constructed of Cb-1Zr was operated in a vacuum environment by General Electric for 1000 hr at a peak temperature of 3480 F and a ΔT of 980 F to check out components in preparation for subsequent tests on forced-convection systems.(6) Posttest metallographic examination of tubing specimens from all regions of the loop revealed no evidence of corrosion of either the base material or weldments. Chemical analyses of the tubing indicated that the nitrogen and carbon contents were unaffected by the exposure but that the oxygen level had dropped in the hottest regions of the loop and increased in the cooler zones. An unexpectedly high hydrogen level and consequent embrittlement of tubing was traced to the posttest alcohol-cleaning technique used.

Encouraged by these results, General Electric workers constructed a forced-circulation Cb-1Zr loop, and ran it for 2650 hr with a maximum temperature of 2065 F and a ΔT of 100 F.(7) As with the thermal-convection loop, detailed chemical and metallurgical examinations of the loop tubing revealed no evidence of significant contamination or corrosion from either the sodium or the vacuum-chamber environment. Again, however, there was a transfer of oxygen from the high- to the low-temperature sections of the loop tubing.

Impurities are known to have an important effect on the corrosion and mechanical properties of refractory metals, but the mechanisms have not been defined. Results of studies of the kinetics in the tantalum-oxygen-sodium and columbium-oxygen-sodium systems carried out by Argonne should be very useful in establishing a predictive capability.(8) Starting with literature values for the solubilities of oxygen in sodium, tantalum, and columbium, the investigators derived the parabolic rate constants for oxygen-solution in tantalum and columbium in the presence of low-oxygen (1 to 20 ppm) sodium. They also predicted the conditions of temperature and oxygen content of sodium over which the phases tantalum and Ta_2O_5 and columbium, CbO, and CbO_2 are thermodynamically stable in sodium. Calculated distribution coefficients (equilibrium ratio of oxygen concentration in refractory metal to oxygen concentration in sodium) are shown in Figure 1. Apparently, tantalum does not give up its oxygen to sodium nearly as readily as it does to potassium, according to the NASA-Lewis observations discussed under "Corrosion by Potassium".(9)

CORROSION BY POTASSIUM

Workers at Lewis Research Center succeeded in isolating and identifying the hygroscopic crystalline solid resulting from a 96-hr treatment at 1800 F of a 1-g coil of oxygen-doped (3800 ppm) 0.025-cm tantalum wire in a tantalum capsule containing 0.9 g of potassium.(9) The tantalum wire was completely deoxidized, and the corrosion product was found by X-ray and chemical analyses to be K_3TaO_4. The dissolution appears to be governed by the equation

$$3K + Ta + 4O_{(Ta)} \rightarrow K_3TaO_{4(K)}$$

which suggests that the extent of corrosion in the tantalum-oxygen-potassium system can be predicted if the total amount of interstitial oxygen in the tantalum is known. This is consistent with results of Oak Ridge studies, which showed that tantalum would give up oxygen to potassium at 600 C (1110 F) even when the initial oxygen in the potassium was very high (to 3300 ppm) and that in the tantalum was quite low (50 ppm).(10)

Alloys of columbium that contain strong oxide formers like zirconium or yttrium have shown excellent resistance to boiling potassium at temperatures up to 1300 C (2370 F) for times as long as 5000 hr. Subsequent comparable studies revealed that without such oxide formers, columbium is heavily attacked by 1200 C (2190 F) refluxing potassium and that the severity of the attack increases with increasing oxygen content of the potassium.(10) This sensitivity to the oxygen content of the potassium is much more pronounced in boiling-refluxing systems than in nonboiling potassium systems. For example, additions of up to 2400 ppm of oxygen to the potassium in an all-liquid (nonboiling) system caused only slight increases in attack of the columbium. The Oak Ridge researchers hypothesize that the difference stems from increased local concentrations of oxygen as a result of distillation effects in the boiling process. While columbium does not normally getter oxygen from potassium, these local-enrichment effects are believed to drive the oxygen into the columbium and cause gross attack. The usual behavior in the columbium-oxygen-potassium system is for oxygen to migrate from the columbium to the potassium at a rate governed by the diffusivity of oxygen in columbium.

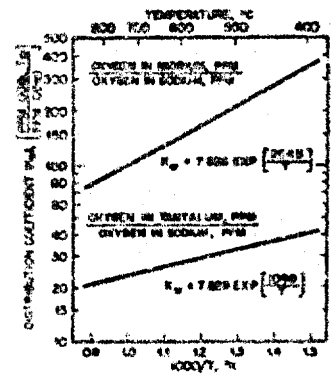


FIGURE 1. DISTRIBUTION COEFFICIENTS OF OXYGEN BETWEEN TANTALUM AND SODIUM, AND COLUMBIUM AND SODIUM(8)

DiStefano has summarized the Oak Ridge results of over 67,000 hr of testing of the refractory alloys Cb-1Zr, D-43 (Cb-10W-1Zr), T-111 (Ta-8W-2Hf), TZM (Mo-0.5Ti-0.1Zr), and C-129Y (Cb-10W-10Hf-0.1Y) in boiling-refluxing potassium at 1100 to 1400 C (2010 to 2550 F).(11) (Note that all of these alloys contain an active gettering element.) No serious corrosion interactions were observed in any of the tests, the weight changes of insert specimens being directly related to migration of oxygen. Similar tests on Cb-1Zr with 1200 C (2190 F) refluxing sodium, rubidium, and cesium failed to show any significant differences in the corrosiveness of the various alkali metals, there being essentially no attack in each case.

Table 1 summarizes results of the Atomics International experimental solubility program involving refractory metals and alloys in potassium or lithium.(12) The addition of up to 2 weight percent of a gettering element (zirconium, hafnium, or titanium) to tantalum and columbium dramatically reduces the apparent solubility of the metal in potassium or lithium. All solutes except rhenium are more soluble in potassium than in lithium.

At United Nuclear, molten potassium with controlled additions of up to 200 ppm oxygen was circulated between 1200 and 1600 F in Type 316 stainless steel loops containing strings of Cb-1Zr and stainless steel test specimens in the heater legs.(13) The oxygen additions were apparently gettered rapidly by the Cb-1Zr, as they had no observable effect on the stainless steel corrosion rates but caused a pronounced increase in the initial rate of Cb-1Zr surface removal. However, there were no identifiable oxide films or microstructural changes in the Cb-1Zr specimens, which remained ductile. The initially high corrosion-weight-loss rates in the Cb-1Zr decayed with time and returned essentially to normal rates (<0.1 mil/year) in about 2500 hr if no further oxygen was added. Increasing the potassium flow velocity by a factor of 18 had no obvious effect on the weight-loss rate of the Cb-1Zr.

Six alloys (Type 318 stainless steel, HS-25, Hastelloys C, N, and X, and René 41) were evaluated at Lewis Research Center for ability to withstand 1800 F boiling potassium well enough for use in hardware for ground testing space-power-system components.(14) Capsules machined from rod stock of the test alloys were exposed to 1800 F boiling-refluxing potassium and examined metallographically. All of the materials showed some evidence of corrosion. However, only the Type 318 stainless steel exhibited severe enough attack to be eliminated from further consideration. An interesting sidelight of this work is that the potassium, which contained no more than 20 ppm oxygen initially, showed up to 500 ppm oxygen after the test. The source of the oxygen is unknown, but the greatest pickup occurred in the capsules that were attacked the most. The materials could be arbitrarily ranked into three groups. Most resistant were René 41 and HS-25; next were Hastelloys N, C, and X (in that order); and finally, Type 318 stainless steel.

A Type 316 stainless steel, gas-fired loop and potassium vapor-turbine test facility was constructed by General Electric. Testing of candidate refractory turbine alloys was done by inserting sample blades and stationary inserts in the turbine second stage and running a 2100-hr endurance test with turbine-inlet potassium vapor at 1500 F.(15)

TABLE 1. SOLUBILITIES OF METALS IN POTASSIUM AND LITHIUM(12)

Solute	Solubility in Potassium		Solubility in Lithium	
	wppm	Temperature Range,(a) C	wppm	Temperature Range,(a) C
Ta from T-111(b)	$\log S\ (wppm) = 2.099 - \frac{4099}{T(K)}$	1200-1600	0-2	1200-1600
Ta from ASTAR-811C(b)	6-10	1200-1600	0-3	1200-1600
Ta from Ta-0.5Zr	500-3000	1200-1600	--	--
Cb from Cb-1Zr	~6	1200-1400	--	--
Cb from Cb-0.5Zr	10-15	1200-1600	--	--
Mo from Mo-0.5Zr	~100	1200-1400	--	--
Mo from TZM(a)	~12	1400	--	--
Hf from ASTAR-811C(b)	--	--	4-10	1200-1600
Hf (zone refined)	~100	1200-1400	6	1200-1400
Zr (zone refined)	60-100	900-1200	--	--
W (vapor deposited)	40-80	1200-1600	0-3	1200-1600
Re	<1	1200-1600	0-2	1200-1600
Mo	--	--	2-15	1200-1600

(a) 900 C = 1652 F, 1200 C = 2192 F, 1400 C = 2552 F, 1600 C = 2912 F.
(b) T-111 = Ta-8W-2Hf; ASTAR-811C = Ta-8W-1Hf-1Re-0.025C; TZM = Mo-0.5Ti-0.07Zr.

Minimal deterioration of the stainless steel turbine parts and the sample rotor blades of U-700, TZM, and TZC occurred. Average weight losses of the U-700 blades after the 2100-hr run were 0.3 percent (Stage 1) and 0.02 percent (Stage 2), and the TZM and TZC blades in Stage 2 lost about 0.1 percent in weight.

In view of these encouraging results, the turbine was tested for an additional 3000 hr, with the following conclusions:(16)

(1) The oxygen and carbon levels in the potassium, which were low at the outset, were reduced even further as the test progressed. This may be part of the reason that blade corrosion was less in the 3000-hr test than in the 2100-hr test.

(2) The room-temperature ductility of the U-700 blades in the first stage was reduced because of sigma-phase formation, and the room-temperature ductilities of the refractory alloys were in some instances likewise lowered.

(3) Some erosion of the René 41 blade clips and of the Type 316 stainless steel shrouds in both stages was noted, although even the worst erosion (second stage) was not considered serious.

(4) The observed mass-transfer and alloy-depletion effects were also not considered serious, being generally less than 1 mil deep.

(5) There was no damage to the turbine which compromised its safety or reliability.

Oak Ridge has completed a 3000-hr test of a Cb-1Zr boiling-potassium forced-circulation loop containing three stages of nozzles and simulated turbine blades subjected to 97 to 83 percent quality potassium vapor at 1015 to 680 C (1860 to 1256 F).(17) The only surface change found in the entire loop was a roughening of the leading edge of the second-stage blade specimen to a depth of 1 mil where it had been impinged upon by 3080 ft/sec vapor of 83 percent quality. The Cb-1Zr alloy had gettered oxygen from the potassium--particularly in the hotter loop regions. A chromium-rich layer found on the second-stage blade was attributed to chromium leached from the stainless steel pump cell. This suggests that stainless steel components should have been avoided altogether, since even this very limited surface area of low-temperature stainless caused noticeable chromium transport. The creep resistance of Cb-1Zr is marginal for service near 1100 C (2010 F), as evidenced by a significant increase in diameter of the tubing at the dryer section of the loop.

CORROSION BY LITHIUM

The results of short-time tensile tests of Soviet-developed experimental alloys for service in molten lithium are shown in Figure 2.[18] Sheet tensile specimens were encapsulated in a columbium tube containing filtered lithium (100 ppm oxygen and 190 ppm nitrogen), soaked at 1000 C (1830 F) for the times shown, then tensile tested in an argon atmosphere. The results (solid curves) were compared with those for identical control specimens (dashed curves) which had been given similar heat treatments in argon without lithium present. The lithium apparently had a negligible influence on the strength and ductility of PH-3, PH-5, and PH-6, and only a slight weakening effect on PH-2.

The Jet Propulsion Laboratory has been studying a magnetohydrodynamic (MHD) power system in which liquid lithium is accelerated by cesium vapor in a two-phase nozzle, separated from the cesium, decelerated in an MHD generator, and finally forced by its remaining dynamic head through a heat source and back to the nozzle. There were indications that materials which had withstood static lithium at 1090 C (1995 F) were badly eroded after 100 hr under a 150-ft/sec 1090 C lithium jet. The alloy Cb-1Zr was least affected.

Follow-up experiments corroborated these observations quantitatively.[19] Two materials, Cb-1Zr alloy and yttrium oxide, were subjected to the lithium stream. After 109 hr at 1143 C (2090 F), the yttria specimens were completely dissolved. The maximum depth of material removed from the columbium alloy after an additional 391 hr at 1090 C was 7 μ. This value corresponds to the depth calculated from turbulent mass-transfer relations for simple dissolution if the temperature coefficient of solubility is taken to be 1.2×10^{-9} g Cb/(g Li)(C).

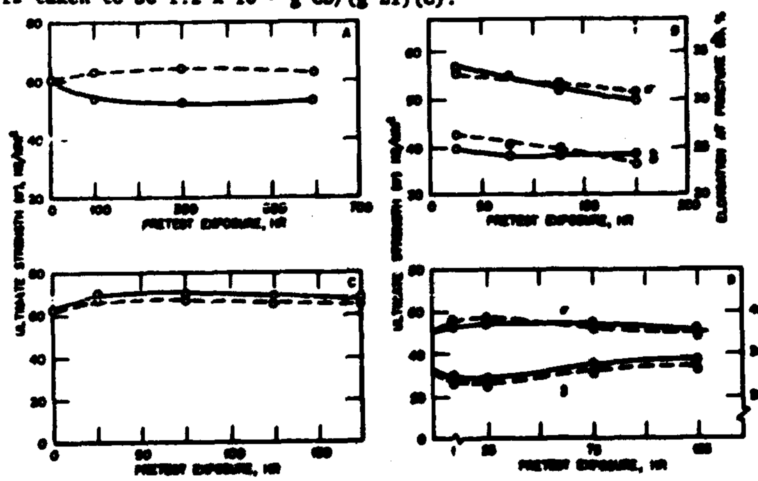
The feasibility of evaporatively cooling refractory rocket-nozzle-throat liners was demonstrated at Aerojet-General by test firing a 2.7-in.-diam lithium-cooled liner for 60 seconds at 670 psia chamber pressure, 6500 F flame temperature, and highly aluminized solid propellant, with no apparent erosion.[20] The flame-side throat temperature of the T-222 alloy, 0.130-in.-thick liner was designed to stabilize at 4360 F.

Soluble corrosion inhibitors for lithium-refractory metal systems have been investigated at Argonne. Corrosion of tantalum by lithium has been found to be inhibited by additions of silicon or iridium.[21] For silicon, the protective layer was identified as Ta_2Si. With 1.0 and 1.5 atomic percent iridium additions to lithium in high-purity tantalum capsules, a 50-μ protective layer was found after a 9-day exposure at 1200 C (2190 F). The layer consisted of three phases: Ta_3Ir next to the tantalum, $TaIr_3$ on the outside, and TaIr in between.

Examination of 82 insert specimens from a T-222 (Ta-10.2W-2.3Hf-0.014C) thermal-convection loop after 3000 hr of lithium circulation at 1350 to 1140 C (2460 to 2085 F) and 2.5 ft/sec disclosed very small hot-zone weight losses (0.8 mg/cm², max) over about two thirds of the loop and minimal cold-zone weight gains (2.0 mg/cm², max) over the remaining third.[22] A significant transfer of hafnium from the hotter to the cooler regions was noted; surfaces near the heater entrance analyzed as much as 60 weight percent hafnium.

A Cornell University dissertation on the penetration of grain boundaries of columbium by lithium at 800 to 1050 C (1470 to 1920 F) also includes a quantitative model for the process.[23] The columbium specimens consisted of oriented bicrystals, each containing a simple tilt grain boundary at an angle of 6, 16, or 33 degrees, and 0 to 2400 ppm of oxygen. The following observations were reported:

(1) Specimens without oxygen showed no reaction with lithium; the reaction rate increased with increasing oxygen content.



Curve	Alloy	Nominal composition, wt.% [illegible]			Interstitials, wt.%		
		W	Mo	Zr	O	N	C
A	PH-[illegible]	7 to 10			[illegible]	[illegible]	[illegible]
B	PH-[illegible]	4.5 to 6		1 to 1.5	[illegible]	[illegible]	[illegible]
C	PH-[illegible]	9 to 11		1 to 1.5	[illegible]		[illegible]
D	PH-[illegible]	4.5 to 6	4.5 to 6	1 to 1.5	[illegible]		[illegible]

FIGURE 2. EFFECT OF EXPOSURE TO MOLTEN LITHIUM ON THE 1000 C TENSILE PROPERTIES OF EXPERIMENTAL COLUMBIUM-BASE ALLOYS[18]

Solid Curves: specimens soaked in lithium at 1000 C.

Dashed Curves: specimens heated in argon at 1000 C.

(2) Specimens of all three orientations suffered surface attack, but only the 16 and 33 degree specimens showed preferential attack in the grain boundaries. In the latter, the depth of grain-boundary penetration increased as the square root of exposure time.

(3) The rate constant, k, for grain-boundary attack, according to X (depth of penetration) = $kt^{1/2}$, had an activation energy of ~70 kcal/mole.

(4) Penetration was anisotropic, the rate parallel with the common <110> being larger than the rate perpendicular to it.

(5) The corrosion process appeared to be controlled by solid-state grain-boundary diffusion.

The effect of oxygen contamination of T-111 and T-222 TIG-welded specimens on their corrosion resistance to lithium was determined at Oak Ridge in 100-hr exposures at 750 and 1200 C (1382 and 2192 F).[10] No attack of the weld or heat-affected zones was observed in samples containing up to 540 ppm oxygen. However, the base metal was attacked to a depth of 10 mils unless it had been heat treated for 2 hr at 1300 C (2372 F) after welding. This was explained by the fact that the weld heat was sufficient to homogenize the oxygen concentration and cause precipitation of HfO_2 in the weld and in the heat-affected zone, but not in the base metal. Unless the base metal was annealed, the large concentration of oxygen near the surface rendered it susceptible to heavy attack.

Workers at the Lawrence Radiation Laboratory have devised a pumped-capsule apparatus for dynamic corrosion testing of materials by high-temperature molten metals.[24] They demonstrated its feasibility by circulating liquid lithium at about 1500 C (2730 F) (hot end) and 1250 C (2280 F) (cold end) at about 1 ft/sec for close to 700 hr and found little corrosion damage to the W-30 at.% Mo-30 at.% Re capsule parts. The pumped capsule consists of a closed tube containing a splitter plate which separates the bore into two semicircular channels. The two channels join at both ends of the tube to form a complete loop. The molten metal is circulated by a d-c electromagnetic Faraday conduction pump. Heating one end of the tube and cooling the other simulates a polythermal coolant loop.

CORROSION BY MERCURY

To gain a better understanding of the mechanism and kinetics of corrosion of materials used in mercury Rankine-cycle systems, 108 refluxing-mercury capsule tests were run at Lewis Research Center on the cobalt-base alloys HS-25 and H-8187 and the iron-base alloys SICROMO-9M, AM-350, and AM-355.[25] Exposure times up to 5000 hr and temperatures between 1000 and 1300 F were employed.

Three types of attack were observed. The AM alloys suffered uniform surface dissolution and surface depletion of manganese, chromium, and nickel. The HS-25 and H-8187 showed leached-out porous corrosion zones, depleted in nickel, chromium, and cobalt and enriched in tungsten. The SICROMO-9M had a channel-like, grain-boundary-penetrated corrosion zone with no compositional change. As can be seen in Figure 3, all except the AM alloys underwent changes in mechanisms of corrosion with time. In the linear regimes, boundary-layer diffusion is the probable rate-controlling step, whereas in the parabolic regimes it is more likely liquid diffusion.

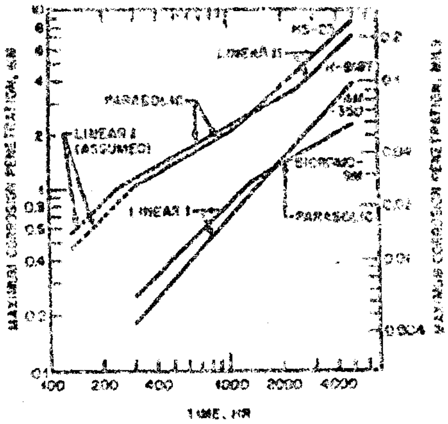


FIGURE 3. CORROSION RATE OF TEST ALLOYS BY REFLUXING MERCURY AT 1100 F[25]

In the SNAP-2 version of the Mercury Rankine Power Conversion Program, reactor-heated NaK is pumped through a NaK-to-mercury boiler and the mercury vapor drives a turbogenerator unit. The extensive mercury-corrosion tests conducted under this program have been summarized in several topical reports by TRW Equipment Laboratories.[26,27] In addition to over 1 million hours of capsule and loop testing, more than 30,000 hours of boiler-test operation was accumulated. Figure 4 shows a representative mass-transfer pattern in one of the HS-25 test boiler tubes after 2200 hours of operation. This was the result of selective leaching of various elements from the HS-25. The deposits are predominantly cobalt (95 weight percent), with some iron; the leached zone is depleted in nickel, chromium, and cobalt, and somewhat enriched in tungsten.

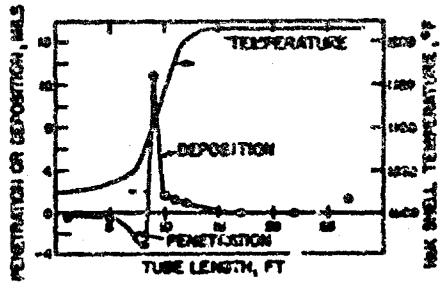


FIGURE 4. CORROSION-TEMPERATURE CORRELATION FOR NaK-HEATED HS-25 MERCURY BOILER TUBE[26]

The corrosion products carried by the mercury pose a major system-design problem because of their tendency to deposit in critical areas like mercury-lubricated sleeve-bearing surfaces, lubricant-line filters, the mercury pump, and the turbine nozzles and vanes. These corrosion products have been identified as ferrites, possessing a spinel structure of either the gamma Me_2C_3 or Me_3C_4 type. Their effects can be minimized by operating the boiler and condenser for at least 200 hr, then flushing with clean mercury and recharging before operating the turboalternater unit. This preconditioning eliminates the bulk of the corrosion products; their concentration drops to a steady-state of around 0.01 ppm in the liquid after reaching a much higher value in the first

100 to 200 hr. Since the major source of corrosion products is the boiler, maintaining a high-vapor quality (over 95 percent) at the exit will minimize carry-over.

A great deal of effort has gone into the evaluation of 9Cr-1Mo steel as the construction material for the mercury boiler in the SNAP-8 space power system. A report has been issued by Aerojet-General summarizing earlier capsule and loop-test findings and describing both an analytical method used to predict corrosion behavior and a final set of loop experiments to confirm the analysis.(28) This work led to the following conclusions:

(1) Corrosion of 9Cr-1Mo steel by flowing mercury is by dissolution of the alloy constituents in the mercury.

(2) The corrosion rate is velocity dependent, suggesting that the rate-controlling step is diffusion transport of solute molecules through the laminar sublayer adjacent to the wall.

(3) Corrosion rates can be calculated by a mass-transfer equation which indicates that under the fully wetted condition required for good heat transfer, 9Cr-1Mo steel is not suitable for 10,000-hr service in the SNAP-8 boiler.

(4) Materials like tantalum and columbium, which are essentially insoluble in mercury, are preferable to 9Cr-1Mo steel.

CAVITATION IN LIQUID METALS

The problems of cavitation in liquid metals were reviewed in a paper by Hammitt, with particular emphasis on their application to the sodium-cooled fast breeder reactor and cavitation similitude between water and sodium.(29)

As a guide to the selection of construction materials for the low-pressure components of a potassium-vapor Rankine-cycle system, Hydronautics studied cavitation damage of candidate materials in potassium up to 705 C (1380 F). The materials were Type 316 stainless steel, TZC, T-111, Cb-132M, and TiC-10Cb.(30) The TiC cermet was by far the most erosion resistant at 600 F. However, at 1000 F, it showed the poorest resistance and T-111 was best.

REFERENCES

(1) Anthrop, D. F., "The Solubilities of Transition Metals in Liquid Alkali and Alkaline Earth Metals, Lanthanum and Cerium: A Critical Review of the Literature", Report UCRL-50315, Lawrence Radiation Laboratory, University of California, Livermore, Calif., Contract W-7405-eng-48 (September 20, 1967). (Available from the Clearinghouse for Federal Scientific and Technical Information for $3.00).

(2) Westwood, A.R.C., Preece, C. M., and Kamdar, M. H., "Adsorption-Induced Brittle Fracture in Liquid-Metal Environments", Report RIAS-TR-67-8C (AD 658210), Research Institute for Advanced Studies, Martin Marietta Corporation, Baltimore, Md., Contract DA-19-001-AMC-1109(X) (May 1967).

(3) Robertson, W. M., "Propagation of a Crack Filled with Liquid Metal", Trans. Met. Soc., AIME, 236, 1478-1482 (October 1966).

(4) Hermes, W. O., and Litman, A. P., "Compatibility of Materials With Alkali Metals for Space Nuclear Power Systems", Nucl. Applic., 5 (3), 156-172 (September 1968).

(5) Harrison, R. W., "SNAP-8 Refractory Boiler Development, Corrosion of Oxygen Contaminated Tantalum in NaK", Topical Report 1, Report GESP-128, General Electric Nuclear Systems Programs, Space Systems, General Electric Company, Cincinnati, O., Contract NAS 3-10610 (January 14, 1969).

(6) Hoffman, E. E., and Holowach, J., "Cb-1Zr Sodium Thermal Convection Loop, Potassium Corrosion Test Loop Development", Topical Report No. 5, Report R67SD3014, Missile and Space Div., General Electric Company, Cincinnati, O., Contract NAS 3-2547 (June 15, 1967).

(7) Hoffman, E. E., and Holowach, J., "Cb-1Zr Pumped Sodium Loop, Potassium Corrosion Test Loop Development", Topical Report No. 6, Report R67SD3015, Missile and Space Div., General Electric Company, Cincinnati, O., Contract NAS 3-2547 (December 30, 1967).

(8) Kassner, T. F., and Smith, D. L., "Calculations on the Kinetics of Oxygen Solution in Tantalum and Niobium in a Liquid-Sodium Environment", Report ANL-7345, Argonne National Laboratory, Argonne, Ill., Contract W-31-109-eng-38 (September 1967).

(9) Hickman, Jr., C. W., "Corrosion Product of the Tantalum-Interstitial Oxygen-Potassium System at 1800 F (1255 K)", Report NASA TN D-4213 (N68-11511), NASA, Lewis Research Center, Cleveland, O. (December 1967).

(10) Preliminary information from Oak Ridge National Laboratory, Oak Ridge, Tenn., on USAEC Contract W-7405-eng-26.

(11) DiStefano, J. R., "Refluxing Capsule Experiments with Refractory Metals", Report ORNL-4323, Oak Ridge National Laboratory, Oak Ridge, Tenn., Contract W-7405-eng-26 (January 1969).

(12) Eichelberger, R. L., et al, "Solubility Studies of Refractory Metals and Alloys in Potassium and in Lithium", Report AI-68-110, Atomics International, Canoga Park, Calif., Contract NAS 3-4163 (February 28, 1969).

(13) Goldmann, K., and McKee, J. M., "Oxygen Effects in a Type 316 Stainless Steel, Nb-1%Zr, Liquid Potassium System", Nucl. Applic., 6 (4), 321-331 (April 1969).

(14) Sinclair, J. H., "Compatibility of Several Iron-, Cobalt-, and Nickel-Base Alloys with Refluxing Potassium at 1900 F", Report NASA TM X-1617 (N68-30065), NASA, Lewis Research Center, Cleveland, O. (March 11, 1968).

(15) Nichols, H. E., and Fink, K. W., "Two-Stage Potassium Test Turbine, Vol. II, Mechanical Design and Development", Report NASA CR-923, Missile and Space Div., General Electric Company, Cincinnati, O., Contract NAS 5-1143 (February 1968).

(16) Schnetzer, E. (Ed.), "5000-Hour Test--Two-Stage Potassium Turbine, Final Report", Report NASA CR-72273, Missile and Space Div., General Electric Company, Cincinnati, O., Contract NAS 3-3143 (July 1967).

(17) Jansen, D. H., et al, "Niobium-1% Zirconium Boiling-Potassium Forced-Circulation Loop Test", Report ORNL-4291, Oak Ridge National Laboratory, Oak Ridge, Tenn., Contract W-7405-eng-26 (December 1968).

(18) Savitskiy, Ye.M., et al, "Niobium-Based Alloys and Their Properties", Translation JPRS-4312 [from At.Energ. (USSR), 23 (7), 32-37 (July 1967)].

(19) Hays, L. G., "Corrosion of Nb-1% Zr Alloy and Yttria by Lithium at High Flow Velocities", Report JPL TR 32-1233 (N68-15617), Jet Propulsion Laboratory, California Institute of Technology, Pasadena, Calif., Contract NAS 7-100 (December 1, 1967).

(20) Baker, Jr., W. H., "Demonstration of a Submerged Cooled Nozzle", Final Report AFRPL TR 68-189, Aerojet-General Corporation, Sacramento, Calif., Contract AF 04(611)-10934 (November 1968).

(21) "Reactor Development Program Progress Report, February, 1968", Report ANL-7427, Argonne National Laboratory, Argonne, Ill., Contract W-31-109-eng-38 (March 26, 1968).

(22) Preliminary information from Oak Ridge National Laboratory, Oak Ridge, Tenn. on USAEC Contract W-7405-eng-26.

(23) Brehm, W. F., et al, "Grain Boundary Penetration of Niobium (Columbium) by Lithium", Trans. Met. Soc., AIME, 242, 1205-1210 (July 1968).

(24) Johnson, C. E., "Fast Reactor Systems for Space Power", Report CONF-680419, Proceedings of the National Topical Meeting on Fast Reactor Systems, Materials, and Components, Cincinnati, O., pp 41-60, April 2-4, 1968.

(25) Rosenblum, L., et al, "Mechanism and Kinetics of Corrosion of Selected Iron and Cobalt Alloys in Refluxing Mercury", Report NASA TN D-4450, NASA, Lewis Research Center, Cleveland, O., (October 24, 1967).

(26) Ziobro, R. J., and Koestel, A. S., "Mercury Boiler Development on the SNAP-2/MRPC Program", Topical Report No. 34, Report TRW-490-32, TRW Equipment Laboratories, Cleveland, O., Contract AT(04-3)-490 (June 1964).

(27) Schulze, R. C., and Varga, F. J., "Corrosion Products in the SNAP-2/MRPC CRU V Test System", Topical Report No. 35, Report TRW-490-33, TRW Equipment Laboratories, Cleveland, O., Contract AT(04-3)-490 (June 1968).

(28) Farwell, B. E., et al, "9Cr-1Mo Steel as a Mercury Containment Material for the SNAP-8 Boiler", Report NASA CR-72503 (Aerojet 3661), Aerojet-General Corporation, Azusa, Calif., Contract NAS 5-417 (January 1968).

(29) Hammitt, F. G., "Cavitation Phenomena in Liquid Metals", Report 01357-1-T (USAEC File No. NP-17259), University of Michigan, Ann Arbor, Mich. (December 1967).

(30) Thiruvengadam, A., et al, "Cavitation Damage in Liquid Metals (Potassium Studies)", Report TR-607-Final, Hydronautics, Inc., Laurel, Md., Contract NAS 3-8506 (April 1968).

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R. W. Endebrock, Editor