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C-92b, M-3679
Systems for Nuclear
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Lawrence Radiation Laboratory
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UCRL-50004-67-1

ADVANCED SPACE NUCLEAR POWER PROGRAM
PROGRESS REPORT NO. 6
(January through March 1967)

(Title: Unclassified)

Nuclear Propulsion Division Staff

July 25, 1967

AEC RESEARCH AND DEVELOPMENT REPORT

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HIGHLIGHTS AND SUMMARY

HighlightsMaterials

Tungsten Powder Compaction: High density tungsten – over 98% of crystal density – was obtained at pressures of only 1 to 2 kbar with temperature around 1100°C (p. 1).

Internal Nitriding: A tungsten alloy with 2% hafnium was hardened to an appreciable depth by combining the hafnium with nitrogen (p. 2). A commercial molybdenum alloy (TZM) showed very low creep rate in a nitrogen atmosphere at 1450°C, presumably due to nitriding of titanium and zirconium in the alloy (p. 16).

Refractory Alloy, Fuel Compatibility: Tungsten and rhenium showed no evidence of reaction with uranium nitride in tests at 2000°C in 10 torr nitrogen for 821 hr (p. 28).

Solubility of Tungsten in Silver: The solubility of tungsten in silver at 2200°C was determined to be 2 ± 1 weight ppm (p. 31).

System Analysis

Optimum Rankine Cycle System Temperature: Rankine cycle power system analysis showed that reactor coolant outlet temperature around 1600-1700°K is likely to give minimum system specific mass (p. 56).

Summary

An initial period of installation and shakedown of experimental equipment is nearly completed, and systematic data are being obtained from a number of materials investigations. Results are reported in each of the main continuing areas of materials work: Refractory alloy development, fuel properties, and corrosion and compatibility experiments.

Plans for a high-temperature tungsten alloy/lithium pumped corrosion loop have been formulated. This loop is expected to be in operation late in the present calendar year.

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Reference reactor and power system studies are currently focused on Rankine cycle power conversion at electric power levels of 300 kW and 10 MW. Engineering design and system analysis are proceeding concurrently, with emphasis on the completion of an initial model of the 10 MW system early in the coming summer. Tentative definition of the 300 kW system will follow a few months later, and revised and corrected versions of both designs will be reported early in 1968.

A few experimental efforts directed toward gaining an improved understanding of advanced power conversion techniques are taking form. Plans for fabrication of a tungsten heat pipe are an example of preparatory work now going on in this area.

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TABLE OF CONVERSIONS

TEMPERATURE CONVERSION CHART

F	0	500	1000	1500	2000	2500	3000	3500	4000
R	500	1000	1500	2000	2500	3000	3500	4000	4500
C	0	500	1000	1500	2000	2500	3000	3500	4000
K	500	1000	1500	2000	2500	3000	3500	4000	4500

Length

$$1 \text{ cm} = 0.394 \text{ in.}$$

$$1 \text{ m} = 3.28 \text{ ft}$$

Area

$$1 \text{ cm}^2 = 0.155 \text{ in.}^2$$

$$1 \text{ m}^2 = 10.8 \text{ ft}^2$$

Volume

$$1 \text{ cm}^3 = 6.10 \times 10^{-2} \text{ in.}^3$$

$$1 \text{ m}^3 = 35.3 \text{ ft}^3$$

Mass

$$1 \text{ kg} = 2.20 \text{ lb}_m$$

Density

$$1 \text{ g-cm}^3 = 62.4 \text{ lb}_m/\text{ft}^3$$

$$= 3.61 \times 10^{-2} \text{ lb}_m/\text{in.}^3$$

Speed

$$1 \text{ m/sec} = 2.24 \text{ miles/hr}$$

$$= 3.28 \text{ ft/sec}$$

Force

$$1 \text{ newton (n)} = 10^5 \text{ dynes}$$

$$= 0.225 \text{ lb}_f$$

Pressure

$$1 \text{ n/cm}^2 = 9.87 \times 10^{-2} \text{ atm}$$

$$= 1.45 \text{ lb}_f/\text{in.}^2$$

$$1 \text{ kg}_f/\text{cm}^2 = 0.968 \text{ atm}$$

$$= 14.2 \text{ lb}_f/\text{in.}^2$$

$$1 \text{ bar} = 0.987 \text{ atm}$$

$$= 10 \text{ n/cm}^2$$

$$1 \text{ torr} = 1 \text{ mm Hg (0°C)}$$

$$= 1.32 \times 10^{-3} \text{ atm}$$

Energy

$$1 \text{ joule} = 1 \text{ watt-sec}$$

$$= 0.738 \text{ ft-lb}_f$$

$$= 9.48 \times 10^{-4} \text{ Btu}$$

$$= 0.239 \text{ cal}$$

Power

$$1 \text{ kW} = 1.34 \text{ hp}$$

$$= 3.41 \times 10^3 \text{ Btu/hr}$$

$$= 7.38 \times 10^2 \text{ ft-lb}_f/\text{sec}$$

Power density

$$1 \text{ kW/cm}^3 = 28.3 \text{ MW/ft}^3$$

Acceleration due to gravity (standard for units)

$$g = 980.7 \text{ cm/sec}^2$$

$$= 32.17 \text{ ft/sec}^2$$

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ADVANCED SPACE NUCLEAR POWER PROGRAM PROGRESS REPORT NO. 6

MATERIALS

REFRACTORY METAL ALLOY DEVELOPMENT

Dispersion Hardening with Refractory Compounds

Powder Metallurgy — The study of the influences of temperature, pressure, and time on the densification of sub-micron tungsten was concluded in this period. Low temperature consolidation of tungsten can be performed between 1 and 2 kbar; these are pressures readily obtained in modern autoclaves.

Using piston-cylinder equipment, the effect of pressure on densification at 1090°C for 10 min was determined. This study is summarized in Fig. 1, where the relative density, ρ_R is given as a function of maximum pressure, P_X . Pressureless sintering work provides the zero pressure reference. Pressures above roughly 1 kbar do not improve densification. Details of the low pressure consolidation results are given in the insert of Fig. 1. A curve calculated from the Murray theoretical model for densification¹ is also given. The Murray equation is based on plastic flow as the densification mechanism. These experimental results correlate well with the plastic flow theory of densification for tungsten.

In Fig. 2, grain size is given as a function of consolidation temperature for both hot pressing (23 kbar) and pressureless sintering. For temperatures above about 1100°C, there is an increasing divergence in the grain growth characteristics of these two processes. The effect of time on densification and grain growth for pressureless sintering has not been studied to any extent. It appears, however, that both density and grain size are very sensitive to holding time for temperatures above approximately 1800°C under pressureless sintering conditions. Grain growth inhibits densification. The usual explanation is increased isolation of pores from vacancy sinks such as boundaries.

A qualitative summary of our consolidation experiments with sub-micron tungsten is given in Fig. 3. It is expected that the high density field (shaded) will be somewhat sensitive to average particle size and particle geometry.

The thermal stability of metal oxides dispersed in tungsten matrices is being studied. The objective is to attain a compact with interparticle spacing of $\approx 0.1 \mu$ and a mean oxide particle diameter of $< 0.02 \mu$ (< 10 vol % oxide). The composites tabulated in the following were prepressed, partly purified in hydrogen, and are now being consolidated:

Blend	Approx. particle size, μ	Manufacturer and technique	Comments
W-ThO ₂	0.05 (W) 0.01 (ThO ₂)	Vitro Labs. Co-vaporization in arc discharge.	Technique may be applicable to dispersing nitrides; has best promise for producing optimum dispersion.
W-HfO ₂	<0.1	CIBA. Same as above.	
W-ThO ₂	0.5	Westinghouse. Activated milling of constituent powders.	Applicable to any W-dispersoid combination.
W-ZrO ₂	≈ 0.1	U. S. Bureau of Mines (Albany, Oregon). H ₂ reduction of freeze-dried salts.	No comment.
W-ThO ₂	≈ 0.5 to 1.0	Wah Chang, Glen Cove, New York. Slurry-precipitation process.	Good only for oxides.
W-ThO ₂	≈ 0.5	LRL. Slurry-precipitation process.	No comment.
W-HfO ₂	Not determined	LRL. Oxidation/reduction of electron beam melted W-Hf alloy.	May be applicable to nitride dispersions.

Note: Improved facilities for purification and powder handling are being assembled.

Internal Nitriding of Refractory Metal

Alloys — It has now been definitely established that our previous failure to nitride tungsten-hafnium alloys was not due to any inherent difficulty but rather to the fact that the alloys supplied to us did not contain sufficient hafnium. To remedy this problem, a small button of W-2% Hf alloy (at. %) was prepared by arc melting in an argon atmosphere. The first attempt to nitride this alloy was very encouraging since we succeeded in hardening the material to an appreciable depth by heating in 1 atm of nitrogen for 43 hr at about 1800°C.

Because the power supply available with the arc melting unit was not adequate to melt the entire charge simultaneously, the resultant button was macroscopically

inhomogeneous in appearance, both before and after etching, with the bottom half exhibiting an extreme degree of dendritic segregation. Consequently, the depth of nitriding varied from region to region and so did the extent of the hardening. A uniformly nitrided layer about 160 μ (≈ 6 mils) thick was produced in the apparently homogeneous nonsegregated portion of the sample. The surface hardness of this layer was about 710 kg/mm² diamond pyramid hardness (DPH) as compared to the average base hardness of about 440 kg/mm². (Note: The relatively high base hardness may be due to the fact that the tungsten and hafnium used as melting stock were not of very high purity, particularly with regard to the interstitial content.) In other regions of the sample, the

Fig. 1. Relative density, ρ_R vs consolidation pressure, P_x , for sintered tungsten powder (GE-1 powder, 0.45μ). Consolidation temperature was $1090 \pm 10^\circ\text{C}$; time: 10 min.

depth of the nitrated layer was greater, presumably because the hafnium concen-

tration was lower. As yet, the actual hafnium concentration in the region where

Fig. 2. As-consolidated grain size vs consolidation temperature for GE-1 tungsten powder sintered 10 min.

the hardening was greatest is not known, although this is being checked by microprobe analysis.

The appearance of the nitrided layer is shown in cross-section in Fig. 4 along with the corresponding hardness profile. Although the magnitude of the hardening is not as pronounced as that obtained with molybdenum-based alloys, the results are nevertheless, highly encouraging. For example, the fact that a dispersion of HfN in tungsten was produced at 1800°C which is fine enough to give a substantial increase in room temperature hardness suggests, by analogy with internally

oxidized materials, that this dispersion will be stable almost indefinitely at temperatures below 1800°C.

Additional nitriding experiments were also carried out on a Mo-1% Hf (at.%) alloy. This material exhibited the most pronounced hardening of any of the materials so far examined. The structure and hardness profile obtained on nitriding at 1350°C for 4 hr in 1 atm N₂ is shown in Fig. 5. The light etching band in the photomicrograph defines the boundary between the nitrided zone and the unaffected core.

Co-Vapor Deposition of W-HfN* - The deposition temperature profile reported in the previous quarterly report for Run 4 was corrected (see Fig. 6). The uncorrected profile showed thermocouple readings between the reaction chamber wall and heating elements. The corrected profile has thermocouple readings taken at the inner surface of the nickel substrate tube. These latter readings were obtained by connecting a temporary setup to the existing equipment so two thermocouples (10 mil wire, Pt/Pt-10% Th) could be moved inside the substrate tube under chemical-vapor-deposition (CVD) conditions for temperature and gas flow. One thermocouple was dragged along the surface of the tube while the other thermocouple was positioned along the longitudinal axis of the tube over the first thermocouple. With this arrangement, the temperature at the center of the flowing gases and at the substrate surface

*A detailed report on the first four runs has been prepared as an LRL report, UCRL-50209.

Fig. 3. High density consolidation of tungsten powder: Temperature and pressure effects. GE-1 powder was consolidated for 1 to 20 min.

could be determined along the length of the substrate. The same flow conditions were used while establishing the corrections for each run, with one exception: The WCl_6 and/or HfCl_4 flows were simulated with equivalent argon flows. This substitution had no observed effect on the results since the high flow rate and heat capacity of H_2 masked all effects by the other gases present. Deposition rates were low enough (<10 mils/hr) that the heat of reactions would also have little effect on the local temperature. The point contact of the thermocouple with the substrate surface produced the largest uncertainty ($\approx 2\%$) in the corrected profiles.

Some results on the runs (Nos. 6 and 7) described in the previous quarterly report, as well as on Run 8, are now available.

Run 6 (W + W_2N)

The deposition temperature and coating thickness profile for Run 6 is shown in Fig. 7. These profiles are similar to those shown for Run 4 in Fig. 6. The fine grain structure ($<2 \mu$ diam), similar to the structure obtained in Run 4, was attributed to interrupting columnar grain growth by intermittent nitriding of the tungsten. Vacuum fusion results (see Table I) and x-ray diffraction results confirmed the presence of W_2N at a deposition temperature of 900°C . This W_2N content (30.5 wt %) was higher than the W_2N content (11.3 wt %) reported for Run 4 at about the same deposition temperature ($\approx 850^\circ\text{C}$). The higher N_2/W ratio for Run 6 (Table II) may account for the higher W_2N content.

Fig. 4. Nitrided sample cross section of W with 2% Hf. DPH hardness measurements (50-g load) averaged from two impressions at a given depth are plotted. The photograph shows one set of impressions. The sample was nitrided for 43 hr at 1800°C in 1 atm N₂.

The thermogravimetric analysis (TGA) curve of Fig. 8 shows evolution of N from decomposing W₂N in the coating as temperature is increased. The thin coating (4 mils) was in good condition after heating to 1100°C at <3°C/min. Metallo-

graphic examination and microhardness tests on this specimen are now in progress.

The spectrographic analysis results for this coating, the nickel substrate, and the nickel tubing used to contain the chlorides are given in Table III.

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Fig. 5. Nitrided sample cross section of Mo with 1% Hf. DPH hardness measurements (50-g load) averaged from three impressions at a given depth are plotted. The sample was nitrided for 4 hr at 1350°C in 1 atm N₂.

Run 7 (W + W₂N)

During this first attempt to co-vapor deposit W-HfN with modified equipment,

difficulties were encountered in controlling the flow of vapors from the WCl₅ and HfCl₄ pressure vessels. Premature boiling of the WCl₅ resulted in the

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Fig. 6. Deposition temperature and coating thickness profiles along length of nickel substrate tube (Run 4).

Fig. 7. Deposition temperature and coating thickness profiles along length of nickel substrate tube (Run 6).

Table I. Analytical results on tungsten deposited by CVD during Runs 6 and 7 (vacuum fusion analysis).

Description of coating	Deposition temp, °C	Interstitial content				Calculated amount of W ₂ N present, wt %
		N, wt %	O, ppm	H, ppm	C,* ppm	
Run 6: As deposited; at 25 in.	900	1.12	2030	41	155	30.5
Run 7: As deposited; at 22 in.	925	0.89	270	8	-	24.3
Run 7: At 22 in., heat treated at 1200°C for 1 hr	925	<20 ppm	98	1.6	-	0

* By combustion analysis

deposition of a tungsten layer on the nickel substrate. This layer was not nitrided since no ammonia was flowing during the reduction of this WCl₅ by the H₂ flow. This rapid deposition caused a sharp peak in the coating thickness profile at 12 in. (see Fig. 9).

After the WCl₅ flow was brought under control, the HfCl₄ flow continued to fluctuate. This latter flow consisted largely of volatile impurities instead of HfCl₄. The slight weight loss in the HfCl₄ vessel indicated that <0.2 wt % Hf could be expected in the deposited coating. The

Table II. Mole ratio of reactants for each vapor deposition run.

Run No.	Reaction	Combination	Mole ratio		Ratio of actual to ideal quantity supplied for N ₂ or H ₂
			Ideal	Actual av for run	
1	$2\text{WCl}_5 + 5\text{H}_2 \rightarrow 2\text{W} + 10\text{HCl}$	H ₂ /WCl ₅	2.5	7.25	2.9
2	$\text{HfCl}_4 + 2\text{H}_2 \rightarrow \text{Hf} + 4\text{HCl}$	H ₂ /HfCl ₄	2	77	38.5
	$2\text{Hf} + \text{N}_2 \rightarrow 2\text{HfN}$	N ₂ /Hf	0.5	2.7	5.4
3	$\text{HfCl}_4 + 2\text{H}_2 \rightarrow \text{Hf} + 4\text{HCl}$	H ₂ /HfCl ₄	2	3.5	1.75
	$2\text{Hf} + \text{N}_2 \rightarrow 2\text{HfN}$	N ₂ /Hf	0.5	0.65	1.30
4	$2\text{WCl}_5 + 5\text{H}_2 \rightarrow 2\text{W} + 10\text{HCl}$	H ₂ /WCl ₅	2.5	7.5	3.0
	$4\text{W} + \text{N}_2 \rightarrow 2\text{W}_2\text{N}$	N ₂ /W	0.25	0.4	1.6
	$\text{HfCl}_4 + 2\text{H}_2 \rightarrow \text{Hf} + 4\text{HCl}$	H ₂ /HfCl ₄	2	3000	1500
	$2\text{Hf} + \text{N}_2 \rightarrow 2\text{HfN}$	N ₂ /Hf	0.5	375	750
5	Oxidized coating due to leak	—	—	—	—
6	$2\text{WCl}_5 + 5\text{H}_2 \rightarrow 2\text{W} + 10\text{HCl}$	H ₂ /WCl ₅	2.5	13	5.2
	$4\text{W} + \text{N}_2 \rightarrow 2\text{W}_2\text{N}$	N ₂ /W	0.25	1.1	4.4
7	$2\text{WCl}_5 + 5\text{H}_2 \rightarrow 2\text{W} + 10\text{HCl}$	H ₂ /WCl ₅	2.5	10.6	4.2
	$4\text{W} + \text{N}_2 \rightarrow 2\text{W}_2\text{N}$	N ₂ /W	0.25	0.15	0.60
	$\text{HfCl}_4 + 2\text{H}_2 \rightarrow 4\text{HCl}$	H ₂ /HfCl ₄	2	13.6	6.8
	$2\text{Hf} + \text{N}_2 \rightarrow 2\text{HfN}$	N ₂ /Hf	0.5	2.2	4.4
9	Oxidized coating due to leak	—	—	—	—

Fig. 8. Thermogravimetric analysis of W-W₂N coating (Run 6). Heating rate was 3°C/min to 800°C and 1.25°C/min above 800°C.

Fig. 9. Deposition temperature and coating thickness profile along length of nickel substrate tube (Run 7).

Table III. Spectrographic analyses of vapor-deposited tungsten and W-HfN (Runs 6, 7, and 8).

Elements	Run 6 at 25 in.	Description of specimen analyzed					
		Run 7 at			Run 8 at 15 in.	Ni (3 mil) substrate	Chloride container (1/4 in. Ni tubing)
		16 in.	21 in.	23 in.			
Hf		50	15	15	10 ± 2 wt %		
Al	4	3	1-	1-	20	20	30
B		2	1-	1-			
Ba							
Be		1-	1-	1-			
Bi		10-	10-	10-			
Ca	6-	1-	1-	1-	7	1	3
Cd							
Co		3-	3-	3-	100	250	125
Cr	4	1-	1-	1-			
Cu	4	5-	1-	1-	40	40	30
Fe	125	40	2	3	125	150	200
K							
Mg	4	10	3	2	60	200	50
Mn	6	10	1	2	100	600	475
Mo							
Na		10-	10-	10-			
Nb							
Ni	400+	1000+	1000+	1000+		Major	Major
Pb		10-	10-	10-			
Sb							
Si	3-	2-	2-	2-	20	20	15
Sn		10-	10-	10-			
Sr	1-						
Ti	15	1-	1-	1-	40	10	95
V		10-	10-	10-			
Zn		10-	10-	10-			
Zr		3-	3-	3-	0.1 wt %		

Notes: (1) All values are in ppm by weight, except where noted otherwise.

(2) - signifies "less than"; + signifies "more than."

(3) A blank indicates that this element did not show up in the analysis.

spectrographic results in Table III show that only trace amounts of hafnium were deposited. The microstructure of this second layer (W + W₂N) is shown in Fig. 10.

A TGA was also made on a specimen deposited at 925°C (22 in. from inlet) during Run 7. This TGA curve indicated a slightly higher decomposition temperature than in Run 6 (see Figs. 8 and 11).

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Fig. 10. Microstructure of tungsten and tungsten + W_2N CVD coating (as deposited). Specimen was deposited at 925°C during Run 7 (Murakamis etch).

Fig. 11. Thermogravimetric analysis of W- W_2N coating (Run 7).

Since the coating from Run 7 was thicker and was clad on one side with tungsten, a higher decomposition temperature was expected for any given TGA heating rate. Preliminary vacuum fusion analyses for Run 7 in the as-deposited and heat treated (1200°C for 1 hr) conditions are listed in Table I. Rapid heating ($>1^\circ\text{C}/\text{min}$) of coating from Run 7 in the temperature range of 900 to 1200°C resulted in spalling and bubbling.

The microstructure of the coatings heat treated to 1000°C and 1200°C ($<1^\circ\text{C}/\text{min}$ heating rate) for 1 hr in 50 vol % $H_2 + N_2$ are shown in Fig. 12. The specimens were cooled from 900°C in a H_2 flow (1 atm) to avoid additional nitriding of the tungsten. After heat treatment at 1000°C the grain structure of the inner tungsten layer changed to a fine grained structure (Fig. 12a), compared to its previous columnar form (Fig. 10). The change in microstructure of the second layer

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(a) 1000°C for 1 hr (440 X)

(b) 1200°C for 1 hr (440 X)

Fig. 12. Microstructure of tungsten and tungsten + W_2N CVD coatings after heat treatment in a 50-mole % H_2-N_2 atmosphere (1 atm pressure). Specimens were deposited at 925°C during Run 7 (Murakamis etch).

($W + W_2N$) was apparent from the loss of lamina and from growth of the needle-like phase shown in Fig. 12a. Partial recrystallization and grain growth started in both layers after heat treatment to 1100°C for 1 hr. Recrystallization and grain growth were complete in both layers after

heat treatment at 1200°C (see Fig. 12b). An equiaxed grain structure or relatively small grain size ($\approx 5 \mu$ diam) was the resultant product.

The microhardness results on the coating from Run 7 also indicated that only the second layer contained W_2N (see

Table IV). While the first layer was only stress relieved (483 to 365 DPH) by heat treating to 1000 and 1100°C, a large decrease in microhardness (2315 to 365 DPH) was observed for the second layer. The decomposition of W_2N and evolution of N_2 was complete above 1200°C.

The density of the coating at 22 in. before and after heat treating was 18.5 and 18.4 g/cc respectively. These mercury porosimeter determinations also indicated that no interconnecting pores (>0.02 in. diam) were present even after the 1200°C heat treatment. The effects of higher heat

Table IV. Effects of heat treatments on the microhardness of deposits from Runs 1, 4, 6, 7 and 8.

Run No.	Coating location: distance from nozzle, in.	Deposition temp, °C	DPH hardness (200-g load)		Heat treatment	Remarks
			As deposited, av	+H. T., av		
1	8	875	553	500	1000°C, 1 hr	
	12	925	514	—	None	
	15	960	652	—	None	
4	15	800	2233	464	1000°C, 1 hr	(No change in micro-structure after 1000°C H. T.)
	22	885	1527	981	1000°C, 1 hr	
	22	885	1527	781	1100°C, 1 hr	Partial grain growth
	22	885	1527	224	1200°C, 3 hr	Grain growth during 1200°C H. T.
6	23	1000	698	—	None	First layer deposited
	23	1000	1452	—	None	Second layer deposited
	25	900	1220	—	None	First layer deposited
	25	900	1529	—	None	Second layer deposited
7	22	925	483	447	1000°C, 1 hr	First layer deposited (W)
	22	925	2315	1976	1000°C, 1 hr	Second layer deposited
	22	925	2315	365*	1100°C, 1 hr	Both layers deposited
	22	925	2315	376	1200°C, 1 hr	Both layers deposited
8	14	945	393*	—	None	First layer deposited
			974	—	None	Third layer deposited
	16	965	493*	—	None	First layer deposited
			741*	—	None	Third layer deposited
			569	—	None	First layer deposited
	18-1/2	970	1382	—	None	Third layer deposited

* 100-g load.

+H. T. = after heat treatment.

treating temperatures on the coating are now in progress.

Run 8 (W + HfN)

Attempts made before this run to minimize the difficulties encountered in controlling the flow of WCl_5 and $HfCl_4$ included (1) increasing the boiling and subliming surface area of the WCl_5 and $HfCl_4$ charges respectively, and (2) pre-heating the charges to remove the low volatilizing impurities. The WCl_5 and $HfCl_4$ charges were allowed to outgas overnight (80°C at 25 μ vacuum) before starting the co-vapor deposition run. A constant flow of WCl_5 (79 g/hr) was maintained for 3 hr. During this time interval, the run was plagued with a fluctuating $HfCl_4$ flow. The multi-layer

coating that resulted from these fluctuations is shown in Fig. 13. The correlation between the hafnium content and attack by Murakamis etchants was apparent. The spectrographic results on the entire cross-section indicated a total hafnium content of 10% (see Table III).

Figure 14 shows profiles of deposition temperature and coating thickness for Run 8. In material from previous runs (viz. 4, 6, and 7) metallographic examination revealed the W + W_2N microstructure. In contrast, W + W_2N was not observed in Run 8, presumably because of the higher deposition temperature (970°C, Fig. 14) and lower N_2/W ratio.

Further evaluation of this multi-layered coating would require an excessive amount of analytical time. More

Fig. 13. Multi-layer CVD coating of W + HfN deposited at 970°C during Run 8. Note the effect of the varying $HfCl_4$ flow rate on the deposit (Murakamis etch).

Fig. 14. Deposition temperature and coating thickness profile along length of nickel substrate tube (Run 8).

rewarding results could be obtained by attempting to deposit a uniform coating for extensive evaluation. The next attempts to co-vapor deposit a W-HfN coating were plagued with leaks resulting from NH_3 corrosion of the welded joints of Ni-304 stainless steel. Consequently, the piping

system was partly rebuilt and the WCl_5 and HfCl_4 pressure vessels and furnaces were modified to improve flow rate control.

After these adjustments, the first attempt (Run 10) to co-vapor deposit W-HfN was very promising. The WCl_5 and HfCl_4 flow rates were held constant over the entire run time (3-1/2 hr). Evaluation of this coating is underway.

Fiber Reinforcement — Preliminary studies showed that ZrO_2 fibers could be formed in tungsten by ceramic extrusion of W-8 vol % ZrO_2 powder blends (see previous progress reports). The tungsten powder used to develop the ceramic extrusion process was relatively impure ($\approx 99\%$) and had large size particles ($20\text{-}\mu$ average diameter); a more suitable tungsten powder is being sought. Several tungsten powders were cold pressed to 50,000 psi and sintered at 1700°C for 3 hr in H_2 . A summary of the results is given in Table V. As expected, the tungsten lot (C-5) with the largest surface area had

Table V. Evaluation of various tungsten powders: Physical characteristics and densities achieved in compaction and sintering.

Powder supplier and min purity	Av particle size, μ	Surface area, m^2/g	Green density (50,000 psi compaction)		Sintered density (1700°C for 3 hr)	
			g/cm^3	% theoretical	g/cm^3	% theoretical
Union Carbide 99+%	5	0.08	13.24	68.6	13.56	75.4
			13.21	68.5	14.74	76.4
Consolidated Astronautics 99.5%	10.7	0.02	12.47	64.6	12.71	65.9
			12.60	65.3	12.85	66.6
Wah Chang (C-20) 99.92%	4.95	0.09	12.65	65.5	13.63	70.6
			12.57	65.1	13.56	70.3
Wah Chang (C-10) 99.94%	3.66	0.08	12.33	63.9	13.55	70.2
			12.40	64.3	13.63	70.6
Wah Chang (C-5) 99.85%	1.02	0.71	10.57	54.77	17.21	89.7
			10.64	55.13	17.3	89.6
Wah Chang (C-3) 99.85%	0.93		In progress			

the highest sintered density (89.6%). Additional C-5 powder and finer powder (C-3) were ordered from Wah Chang. Wah Chang will also attempt to provide powder even finer than C-3 for this program.

Seven more ceramic extrusions were attempted during this quarter. The effort was directed toward minimizing slumping or blistering in binder bakeout of the as-extruded bars (≈ 0.4 in. diam). Partial replacement of the polyethylene glycol binders with Plasdone PVP binder did not improve bakeout. Addition of a binder (Dow Corning Fluid No. 200) that could be removed by prolonged evacuation (20 hr at 30μ) was also unsuccessful.

More volatile binders were tested in an attempt to improve extrusion and bakeout conditions. Binder blends of glycols and terpineol have shown great promise in meeting the requirements in that vaporization of the binder takes place at lower temperatures. The macrostructures of three extrusions with this type of blend are shown in Fig. 15.

Sixty-five vol % of binder I was used to form the ZrO_2 agglomerated balls (-60 + 100 mesh) for these extrusions (see Table VI and Fig. 15 for binder compositions). Higher binder contents would make the balls difficult to handle. The second binders (Q, P_1 and P_2) were blended into the tungsten powder before adding the ZrO_2 balls for extrusion into fibers. The composition and amount of the second binder were used to control the extrusion pressure and degree of fibering of the ZrO_2 balls.

The extrusion pressure in pounds on the 4-in. diam ram was decreased by using a less viscous binder or more binder. Binder P_1 contains a less viscous

Carbowax (No. 1000) than binder Q, and binder P_2 contains more terpineol than binder P_1 . High extrusion pressures increase the as-extruded density, which requires increased binder bakeout time to avoid slumping or blistering. Low extrusion pressures decrease fiber-length-to-diameter ratio, which should be of a very high value. This ratio was also reduced when the total binder content in extrusion 21 exceeded the binder content (65 vol %) in the balls (see Fig. 15).

There has been success in baking out binders from low density extrusions (< 7 g/cc). The as-baked densities are relatively low (5 to 6 g/cc); these values may be compared with those for cold pressed powder at 2000 psi (6.8 g/cc), 3000 psi (7.5 g/cc), 5000 psi (8.1 g/cc), and 10,000 psi (8.2 g/cc).

Fiber length-to-diameter ratio should be greatly increased, binder bakeout should result in minimum slumping and blistering, and sintered final density should be as high as possible. Many conditions that are favorable with respect to one of these requirements tend to degrade properties with respect to another, so that compromises are necessary. This emphasizes the need for a tungsten powder that has excellent sinterability to achieve high sintered densities from low density extrusions.

High Temperature Creep Test on Internally Nitrided TZM

TZM (a commercial molybdenum alloy containing 0.5 wt % Ti, 0.07 wt % Zr plus ≈ 200 ppm each of C and O) is available in sheet form. There is also a fair amount of high temperature, high vacuum creep data on this alloy. Although it is far from

Extrusion 18b.

6.5-vol % binder I + 49.5-vol %
binder Q in ZrO_2 -W.

Extrusion pressure: 12,500 psi

Density: 8.5 g/cm³.

Extrusion 19.

6.5-vol % binder I + 49.5-vol %
binder P₁ in ZrO_2 -W

Extrusion pressure: 9,400 psi

Density: 8.1 g/cm³.

Extrusion 21.

4.9-vol % binder I + 62.1-vol %
binder P₂ in ZrO_2 -W

Extrusion pressure: 7,100 psi

Density: 6.5 g/cm³

Fig. 15. Macrostructure of as-extruded tungsten bars containing 8-vol % ZrO_2 (0.4 in. diam). The compositions of the binders mentioned above are given in Table VI. The same amount of binder I (65 vol %) was used in the ZrO_2 for each of the extrusions. The type (Q, P₁, and P₂) and amount of binder in the tungsten powder were varied to control the extrusion pressure.

an ideal material on which to study internal nitriding, it was selected because it is available and because it is chemically similar to the more optimum alloys that will ultimately be studied.

Samples of this alloy were creep tested at $1450 \pm 20^\circ\text{C}$ under a dead load stress of 285 kg/cm^2 ($\approx 4000 \text{ psi}$) applied just before

the temperature was raised. The tests were made at a N_2 pressure of $\approx 1 \text{ atm}$. Under these conditions, one would predict that the carbon and perhaps the oxygen present in the alloy (presumably as ZrC , ZrO_2 , TiC , or TiO) would be replaced by nitrogen. In addition, the zirconium and titanium not combined with O or C should

Table VI. Composition of binders used for ceramic extrusion.

Binder	Density, g/cm ³	Composition		Use
		Component	Parts by vol	
I	1.140	Carbowax 600	1.1	Used in ZrO ₂ agglomeration
		Carbowax 750	1.1	
		Carbowax 4000	1.0	
Q	1.187	Carbowax 20m	3.0	Blended with W powder to control extrusion parameters
		Terpineol	1.0	
P ₁	1.187	Carbowax 20m	6.0	"
		Carbowax 1000	1.0	
		Terpineol	2.0	
P ₂	1.146	Carbowax 20m	5.7	"
		Carbowax 1000	0.8	
		Terpineol	3.5	

form a stable nitride precipitate, and this should impart improved creep resistance to the alloy.

In 370 hr of testing, the samples crept 2%. The strain rate appears to be increasing with time, although only three points have been taken. The samples will be heated a total of 600 hr, and then the experiment will be stopped. No data are available on chemistry or microstructure at this time.

The results are encouraging in that this is a remarkably low creep rate for such a high temperature. This is in no way an optimized experiment, however, even for a molybdenum-based alloy. TiN is the least stable of the group IV nitrides, and titanium would be expected to be much more mobile in the molybdenum lattice than zirconium or hafnium. Both these factors would lead to more rapid coalescence of the dispersant, with a resulting loss of creep resistance for titanium as compared with zirconium or hafnium.

Further measurements will be made at a lower temperature while awaiting fabrication of more promising alloys.

Hardening with Intermetallic Compounds

The room-temperature strength and ductility of a 70% W, 30% Re alloy has been studied. The material tested had been hot rolled at 1450°C and then stress relieved 1 hr at 1400°C. The microstructure consisted of two phases, with sigma particles dispersed in bands throughout a solid solution matrix.

Specimens were deformed in four-point bending at a constant crosshead speed of 0.02 in./min. The average yield strength in the rolling direction was 210,000 psi. The yield strength was taken at the point of deviation from linearity on the load-deformation curve. The average ultimate strength was 300,000 psi. The total strain at fracture was about 0.75%, of which approximately one-third was plastic deformation.

The average yield strength and ultimate strength perpendicular to the rolling direction were 180,000 and 220,000 psi, respectively. The strain at fracture was around 0.40% with one-tenth of this being plastic strain.

The bend ductility in both the longitudinal and transverse directions was improved when specimens were tested at 100 and 140°C. However, the plastic strain at fracture was less than 1% in all cases. Thus, for this alloy in the stress-relieved condition, the brittle-ductile transition temperature lies above 140°C.

The data for the previous tests are listed in Table VII. The variation between the longitudinal and transverse properties is due to differences in the texture of the plate in those directions. Preferred orientation studies showed a significant difference in texture for the two directions tested. This points out the need for determining whether the uniaxial creep behavior in the longitudinal and transverse directions is also different.

To determine baseline data for comparison with future results on tungsten-rhenium alloys, a creep curve was

obtained for pure tungsten (Fig. 16). Primary creep ended after 4 hr. The minimum creep rate at 1400°C and 10,000 psi was 6.1×10^{-3} /hr. This creep rate is roughly 10 times higher than results reported by Gilbert, Flinn, and Yaggee.²

Fig. 16. Deformation vs time curve for pure tungsten. Test conditions were temperature: 1400°C, and stress: 10,000 psi. The minimum creep rate was 6.1×10^{-3} /hr.

Table VII. Bend test data for a 70% W, 30% Re alloy.*

Specimen	Yield strength, kpsi	Ultimate strength, kpsi	Elastic strain, %	Plastic strain, %	Test direction		Temperature, °C
					Longitudinal	Transverse	
1	230	306	0.51	0.36	x		ambient
2	213	303	0.51	0.22	x		ambient
3	216	312	0.52	0.23	x		ambient
4	183	262	0.44	0.20	x		ambient
5	174	220	0.37	0.05		x	ambient
6	183	223	0.36	0.04		x	ambient
7	163	272	0.45	0.45	x		100
8	225	330	0.53	0.90	x		100
9	211	302	0.51	0.66	x		140
10	202	273	0.46	0.27		x	100
11	221	280	0.46	0.18		x	100
12	210	257	0.43	0.14		x	140

*All specimens were taken from the same plate.

Initially the specimen was in the wrought condition, but it recrystallized during testing. No grain boundary voids, which are characteristic of creep-tested tungsten specimens at fracture, were visible in the post-test microstructure for magnifications up to 1000X. One obvious difference between material tested by Gilbert et al., and the present material is grain size. The post-test grain size of the present material is 2 to 3 times larger than that reported in Ref. (2). It was reported that coarse grained tungsten creeps faster than fine grained tungsten.^{2,3} The discrepancy in creep rates can be rationalized in terms of this reported grain size effect.

Chemical Vapor Deposition of Tungsten-Rhenium Alloys

Coherent deposits of tungsten-rhenium alloys can be produced by hydrogen reduction of the mixed fluorides at a hot surface. Potentially this is a process for coating or welding of refractory metal alloys or for preparation of tubing. The present plating experiments involve the exposure of a heated, rotating, cylindrical mandrel to a transverse flow of the gas mixture along a 1-in. length.

Plating Equipment Development -

Development work was continued on the new abrading tool which uses an uncooled, hydrogen blanketed, tungsten-wire brush in place of the water-cooled, tungsten carbide, single point rubbing tool. Deposits with very fine, equiaxed grains were produced; there was no evidence of porosity. The hydrogen blanket did not completely eliminate plating on the brush, but it is expected that changes in the gas

flow pattern will reduce the rate to an acceptable value.

Effect of Plating Variables on Composition and Microstructure -

Screening work on the effects of plating variables on deposition rate, composition, and structure of deposits was extended into the temperature range 500 to 800°C. Results are shown in Figs. 17, 18, 19, and 20.

The rate data given in Fig. 17 are for a mixture of WF_6 - ReF_6 containing 6.8% ReF_6 , and include the 1000°C results discussed in Progress Report No.5. The new results at lower temperatures show the same trends except that the rates are lower and the effect of mole ratio (H_2/MF_6) on deposition rate is smaller. A cross plot of this data at the maximum rate ($H_2/MF_6 = 3$) is given in Fig. 18: It is apparent that there is a strong velocity effect at higher temperatures and that the maximum rates approach a saturation value at higher velocities. Estimated rates at saturation (from Fig. 18) were used for the Arrhenius plot in Fig. 19. The activation energy (11,000 cal/mole) is somewhat high for a gas-diffusion controlled process and lower than would be expected for reaction rate controlled processes. It is in a reasonable range for adsorption or desorption, however, and suggests that at lower temperatures (<600 to 700°C) the deposition rates for tungsten may be surface controlled at easily obtainable gas velocities.

The rhenium rates, as discussed in the following, suggest that the activation energy for rhenium deposition is much lower and probably in the range where a gas phase diffusion process could be the controlling mechanism.

Fig. 17. Effect of temperature and mole ratio of H_2/MF_6 on plating rate for several flow rates. Gas pressure was 10 torr, and there was 6.8% of ReF_6 in the MF_6 gas.

The effects of temperature on the deposition rates of tungsten and rhenium, under a particular set of plating conditions are shown in Fig. 20 (taken from Table VIII). It is apparent that the effect of deposition temperature on composition (high Re content at low temperatures) is due primarily to the insensitivity of rhenium deposition rate to temperature (low activation energy).

Local deposition rate and composition curves for an unrotated specimen are given in Fig. 21. The total rates are measured metallographically. Local

rhenium concentrations were determined by microprobe analysis.

The large decrease in rhenium concentration toward the leeward side was presumably a result of rapid depletion of ReF_6 concentration in the gas adjacent to the specimen. This is consistent with a gas-phase diffusion-controlled process for rhenium mentioned previously, in contrast with a surface-controlled reaction for tungsten. Approximate calculations show that the rhenium plating efficiency was about 50% as compared to 23% for the tungsten. Since the gas flow was laminar

Fig. 18 Effect of gas flow velocity on maximum deposition rate. Gas pressure was 10 torr, the H_2/MF_6 ratio was three, and there was 6.8% of ReF_6 in the MF_6 gas.

and the cross section of the mandrel was 50% of the draft tube area, there is a strong implication that all of the rhenium in the ReF_6 contacting the mandrel was incorporated into the deposit.

Effect of Heat Treatment on Micro-structure and Mechanical Properties —

The room temperature mechanical properties of specimens deposited at various temperatures between 500 and 1000°C

Fig. 19. Effect of temperature on deposition rate of tungsten-rhenium. Gas pressure was 10 torr, and there was 6.8% of ReF_6 in the MF_6 gas.

Fig. 20. Effect of plating temperature on deposition rate of tungsten and rhenium. Gas pressure was 10 torr, and there was 14.3% of ReF_6 in the MF_6 gas. Flow rates were 1000 cm^3/min of H_2 and 70 cm^3/min of MF_6 (H/MF_6 ratio = 14).

Fig 21. Variation of deposition rate and composition around an unrotated specimen. Pressure was 10 torr, temperature was 600°C, and there was 6.8% of ReF_6 in the MF_6 gas. Flow rates were 500 cm^3/min of H_2 and 70 cm^3/min of MF_6 .

and heat treated at temperatures up to 2000°C are given in Table VIII. Plating conditions other than temperature were maintained constant throughout this series.

Mechanical properties deteriorated as the deposition temperature was increased. This degradation occurred when the deposition rate exceeded about 0.35 mils/

Table VIII. Room temperature properties of W-Re chemical vapor deposits for various plating temperatures. Specimens were plated at 10-torr pressure; flow rates were 1000 cm³-min⁻¹ of H₂ and 70 cm³-min⁻¹ MF₆.

Run No.	Plating temp, °C	% Re, (gas)	% Re, (deposit)	Deposition rate, mils/min	Ultimate tensile strength, kpsi, and (% elongation)						
					As plated	1000°C	Heat treated 1 hr at temperature indicated				
							1200°C	1400°C	1600°C	1800°C	2000°C
662	500	6.8	30.5	0.11	Cracks visible before grinding for specimens						
661	550	6.8	—	0.15	—	—	—	—	—	—	—
545	600	14.3	26.0	0.25	55.0 (0)	58.5 (0)	124.0 (0)	198.0 (0.1) 201.5 (>0)	186.0 (0.4)	143.0 (0.5)	—
543	650	14.3	21.0	0.31	60.6 (0)	81.2 (0)	89.0 (0)	40.0 (0) 125.0 (0)	131.0 (>0)	141.7 (0.5)	139.0 (0)
546	700	14.3	19.0	0.35	46.4 (0)	37.8 (0)	—	102.0 (0)	112.6 (>0)	141.5 (>0)	120.0 (0)
547	750	1.3	18.5	—	39.0 (0)	25.5 (0)	—	87.5 (0)	71.0 (0)	70.0 (0)	—
548	800	14.3	15.5	0.42	87.5 (0)	39.0 (0)	—	63.5 (0)	81.0 (0)	—	—
550	900	14.3	15.5	0.48	1.0 (0)	12.0 (0)	—	8.5 (0)	—	25 (0)	—
552	1000	14.3	14.5	0.61	26 (0)	16 (0)	—	10 (0)	—	44 (0)	—

min. Specimens deposited at rates in excess of this value have generally been characterized by "open" grain boundaries, porosity, and a low density structure. High temperature deposits with sounder microstructures (produced by suppressing the deposition rate) are being evaluated.

The lower temperature deposits containing 19% or more rhenium were all two-phase alloys. Optimum properties in this group were obtained in the 26% Re alloy (Run 545), which exhibited a relatively intimate and well dispersed mixture of the two phases.

The specimen deposited at 500°C (Run 662) contained 30.5% Re even though the concentration of ReF₆ in the gas phase had been reduced by 50%. The micro-cracking probably originated in the large quantity of hard, continuous second phase present in this deposit. Hardness values exceeding 2500 DPH have been measured in the second phase.

Maximum tensile strengths at room temperature were obtained after heat treating in the range 1400 to 2000°C. Results indicate that strengths above

200,000 psi with acceptable ductility can be achieved by CVD.

URANIUM NITRIDE AND RELATED STUDIES

UN Synthesis

A crude quartz and glass apparatus was assembled to confirm the reaction reported by Funk and Böhland⁴:

Evidently the reaction was written in this way for ease in balancing the equation. Actually the compound U₃N₄ is unknown. The authors claim complete reaction in 1 hr at 800°C. The reaction proceeded smoothly, starting at temperatures much below 800°C. The green UF₄ powder was converted to a fine chocolate brown powder. X-ray powder diffraction showed strong UN₂ lines. UO₂ lines were also evident in this first attempt, indicating a need for much tighter atmospheric control in future experiments. This reaction is of interest since UF₄ is readily available.

If it can be obtained or manufactured in ultra-pure condition, it may be possible to provide a direct, single-step synthesis route for UN powder.

Another reported reaction⁵ is the reduction of UF_6 with NH_3 . This suggests the possibility of simultaneously synthesizing and forming UN by thermochemical vapor deposition following an overall reaction such as the following:

This reaction would be run at a high enough temperature and low enough pressure to form UN as the stable nitride and maintain NH_4F in the vapor state (say 1000°C and 0.001 atm NH_3).

If UN deposition from the vapor is feasible, it suggests the possibility of co-depositing tungsten-uranium nitride cermets, building layered spheres in a fluid bed, etc. These possibilities will be explored as time permits.

UN Fabrication

A sample of UN powder obtained from CANEL and isostatically pressed at 100,000 psi reached a green density value of 69.6% td* and sintered to 92.3% td at 2250°C under nitrogen. The complete sintering cycle is indicated in Fig. 22. Subsequent chemical analysis indicated substoichiometry (approx. $\text{UN}_{0.97}$), but no evidence of liquid phase sintering or a uranium phase was seen in polished sections. The most striking feature of the microstructure was the presence of

sharply defined high-density islands in a lower density matrix, as observed microscopically. Microscopic examination of the UN powder indicates a substantial number of large particles (about 30μ) in the fine powder. These may be the source of the high density islands in the sintered UN.

Two batches of UN powder from Y-12 (Oak Ridge) are being evaluated. The UN was prepared at Y-12 by nitriding metallic uranium powder, obtained by successive hydriding and dehydriding of U. The batches contained 3700 ppm and 1400 ppm of O, respectively. Their N/U ratio is apparently slightly greater than unity, judging from both Y-12 and LRL chemical analyses. Both materials were isopressed at 100,000 psi. Batch 1 pressed readily to 71.8% td, forming strong pellets. Batch 2 tended to delaminate after pressing. Both batches are nominally similar materials made under like conditions. The greatest apparent difference identified to date is O content. The higher O material (batch 1) pressed better than the other batch. (Batch 1 sintered to 90.5% td in the same firing that produced 92.3% td in batch 2.) The sintering cycle was the same as that shown in Fig. 22 for the CANEL powder.

Nitrogen Diffusion in Uranium Nitride

Annealing temperatures up to 1970°C have been obtained through the introduction of a greater capacity, high frequency, induction generator (220 V, 136 A and 30 kW), a larger induction coil, and a new set of capacitors. These higher temperatures yield deep penetrations (about 100μ) of N^{15} in a relatively short length of time (24 to 36 hr).

* td = theoretical density.

Fig. 22. Sintering cycle for CANEL UN powder.

Several samples of Battelle arc-cast UN (stoichiometry not yet determined) were activated using the reaction $N^{15}(\alpha, n)F^{18}$ with 9.8-MeV α particles hitting the samples at a 45° angle to reduce α -particle penetration. Within an hour of activation, the samples were autoradiographed with Kodak type A film. Exposures of 1/2, 1, 3, 6, 10 and 20 min (on one slide) yielded characteristic optical densities which could be translated into activities.

Figure 23 shows a plot of A/A_0 vs depth below surface, where A is the F^{18}

activity at a point $y \mu$ below the original surface of the sample, and A_0 is the activity at the original surface of the sample ($y = 0$). The vertical coordinate scale is one which gives linear plots for solutions of the diffusion equation applied to this process:

$$1 - \frac{A}{A_0} = \operatorname{erf}\left(\frac{y}{2\sqrt{Dt}}\right)$$

This particular run was at 1730°C , 152 torr N_2 , and was annealed for 74 hr. A straight line drawn through the points crosses the line $A/A_0 = 0.020$ at $y = 168$.

Fig. 23. Nitrogen concentration as a function of depth below surface of UN (error function scale).

From these values one obtains $D = 9.8 \times 10^{-11}$ cm²/sec for the diffusion of N in UN. Other values for D are presented in Table IX and were obtained in a similar fashion.

Several new samples of arc-cast UN (for the activation method of evaluation) were annealed at 1980, 1910 and 1850°C. These are scheduled to be α irradiated in the near future. A single crystal of UN was annealed and will be evaluated by the sectioning method, followed by a mass spectrographic analysis of the N¹⁵/N¹⁴ ratio in each section.

Table IX. Values of diffusion coefficient, D, obtained for diffusion of N in UN at various temperatures and pressures.

Temperature, °C	Nitrogen pressure, torr	D, cm ² /sec
1910	116	1.96×10^{-10}
1910	14	1.07×10^{-10}
1792	129	1.3×10^{-10}
1730	152	9.8×10^{-11}

X-Ray Diffraction Studies of the U-N System

The present x-ray furnace was modified to allow evacuation to 10^{-5} torr followed by filling to desired N₂ pressures. This process can be done at any temperature. Marked formation of UO₂ surface layers on the samples indicated that the atmosphere was not clean enough for meaningful measurements. Preliminary measurements will be made with the present system only to delineate problems in experimental techniques and to determine the extent of the effects.

A new x-ray furnace, approaching design completion, will have a vacuum capability of 10^{-10} torr at 2500°C. The shell is bakeable, which should insure clean atmosphere potential.

Compatibility: UN and Refractory Materials

An experiment involving UN/W, UN/W-25% Re, UN/Re, and UN/Ta compatibility couples was terminated after 821 hr at 2000°C and 10 torr nitrogen pressure.

The samples used were cylinders about 0.3 in. in diameter by 0.1 in. thick and were cut from longer specimens. The UN polycrystalline specimens were obtained from the Battelle Memorial Institute and were fabricated by hot isostatic pressing. These specimens had a density of 95% of theoretical, a modal grain size of 30 μ , and were found to contain 260 ppm O, 90 ppm C, and 5.51% N. Spectrographically determined contaminants were (in ppm by weight): Fe: 30, Si: 40, Ni: 10, Ca: 10, Mg: 2, Mo: 1 and Cu: 3. The specimens of polycrystalline tungsten, single crystal rhenium, and polycrystalline specimens of 75% W, 25% Re alloy contained less than 10 ppm total metallic impurities.

A typical compatibility sample consisted of a vertical stack of two metallic discs of the same composition with a uranium nitride disc sandwiched between. All contacting surfaces were polished to a 10 μ in. finish with diamond paste on silk. The specimens were finally ultrasonically cleaned and rinsed in methyl alcohol. The compatibility samples were contained within a tungsten crucible and held immobile by a top-loading tungsten

plunger. Four different couples were run simultaneously.

The usual procedure for achieving these conditions was to load the couples into the furnace and then bake out the entire assembly at 400°C and 5×10^{-8} torr. The samples were then heated to 1150°C at 5×10^{-9} torr, and the chamber was flushed and pressurized with 10 torr of N₂. Finally, the temperature was raised to 2000°C.

After thermal testing, the samples were macroscopically examined for surface irregularities, remeasured, and reweighed. Samples were sectioned longitudinally, polished, etched, and microscopically examined.

For the first three couples, examination showed that no interfacial reactions had occurred and no apparent interdiffusion of the components had taken place. The tantalum had been converted to TaN as anticipated. All the UN samples had been plastically deformed by the 1 psi load, as evidenced by circular depressions on contacting surfaces about 0.010 to 0.015 in. deep. The UN samples had lost 11 to 16% of their initial weight, apparently by vapor phase transport to cooler portions of the furnace during the test period. A four-fold increase in grain size of the UN was observed from 30 μ to 120- μ average diameter. Metal samples had not lost weight and were dimensionally stable. Tests are currently being extended to time intervals of 5,000 to 10,000 hr for tungsten and tungsten-rhenium alloys.

Thermoelectric Data on Uranium Sulfide

A review of thermoelectric materials was made. Uranium sulfide (US) appears

to be one of the most promising compounds. In addition to good thermoelectric properties, it is stable at high temperatures and is compatible with tungsten to 2500°K.

The efficiency of a thermoelectric generator (N) was given^{6,7} as the following function of temperature and a material figure of merit (Z):

$$N = \frac{(1 + ZT_m)^{1/2} - 1}{(1 + ZT_m)^{1/2} + \frac{T_\ell}{T_h}} \frac{T_h - T_\ell}{T_h}$$

T_h = high temperature (°K)

T_ℓ = low temperature (°K)

T_m = mean temperature (°K)

$$Z = \alpha^2 / \rho K$$

α = Seebeck coefficient (V/°K)

ρ = electrical resistivity (ohm-cm)

K = thermal conductivity (W/cm-°K)

For US at temperatures up to 1500°K:

$$\alpha = 50 \text{ to } 70 \mu\text{V}/^\circ\text{K}^{8,9,10}$$

$$\rho = 10^{-4} \text{ to } 4 \times 10^{-3} \text{ ohm-cm}^{8,9,10,11}$$

$$K = 0.1 \text{ to } 0.15 \text{ W/cm-}^\circ\text{K}^8$$

These values depend more upon the way the US was prepared than upon the temperature.^{8,9,10,11} The efficiency of US as a thermoelectric generator operating with $T_h = 2000^\circ\text{K}$ and $T_\ell = 1500^\circ\text{K}$ is estimated at about 5%, assuming $\alpha = 70$, $\rho = 10^{-4}$, and $K = 0.1$. Certainly a better efficiency than this is very unlikely unless the electrical resistivity decreases sharply at temperatures above 1500°K.

These results indicate that US has sufficient potential to justify a fuller evaluation. A proper evaluation depends

upon a determination of α , ρ , and K as a function of stoichiometry in the temperature range of interest. Experimental measurements at high temperatures on the variation of ρ and α with U/S ratio are planned, and synthesis of US is presently underway.

Powder Characterization

Preliminary powder characterization of UN with makeshift facilities was attempted to develop familiarity with handling problems and possible agglomeration features of UN while awaiting the completion of a glove box line. Samples from three lots of UN used in the fabrication of UN components (see Progress Report No. 5) were submitted for evaluation. The two most important parameters, surface area and particle size, were measured first.

Surface Area — The Perkin-Elmer sorptometer was calibrated and used to determine the surface area (B. E. T.) of W powder and UN. Modifications had been made to allow evacuation to 10^{-6} torr and bakeout of the sample while it is connected to the sorptometer. High vacuum bakeout of the samples has yielded improved results. A special fixture was designed and built to provide for the following:

- 1) Loading of the UN powder into sample vials inside an argon glove box.
- 2) Protection of the powder from oxidation during transfer, connection to unit, and bakeout.
- 3) Protection of the operator and equipment from radioactive contamination through use of in-line filters.

The effect of various filters (1.2 to 5- μ pore size) was determined by repeating the surface area determination of one tungsten powder (C-20) with each pore size. The results varied from 0.092 to 0.090 m^2/g on this previously analyzed sample (0.11 m^2/g). These results agree within the expected accuracy of the equipment at these low surface area values.

The UN lots were baked out for 18 hr at 200°C in vacuum (10^{-6} torr) before determining the surface areas. The surface areas and calculated mean diameters (assuming spherical material) were as follows:

Lot	Surface area, m^2/g	Equivalent diameter, μ
CANEL (Can G)	0.53	0.79
Y-12 batch 1	0.20	1.72
Y-12 batch 2	0.33	1.27

Microscopic Analysis — An attempt was made to verify the tabulated results qualitatively with a microscope. A sample of each lot was dispersed by an ultrasonic probe in a beaker filled with Dow Corning (silicone) Fluid No. 200. Using transmitted light on a metallograph, the powders were examined microscopically at 200X. The maximum particle size of the CANEL lot was slightly greater than that of the other lots, but many more fine particles were also apparent in the CANEL lot. This accounts for the higher surface area. The two Y-12 lots appeared about the same. Equipment will be made available in the powder-characterization glove-box line to view the dry UN powder.

Particle Size — A Mine Safety Appli-
ance unit for particle size determination
was adapted for handling pyrophoric and
radioactive materials. The small liquid
sedimentation tubes in this unit prevent
the particles from becoming air-borne
and require a relatively small sample (a
few hundred milligrams). Two calibration
runs were made with depleted UO_2 powder
from United Nuclear Corp. The results
from these runs were quite close:

Run No.	Range
1	94% between 2 to 10 μ diam, 50% < 4.5 μ
2	92% between 2 to 10 μ diam, 50% < 4.4 μ

Particle size determinations were made
on the UN batches 1 and 2 from Y-12.
Variations in dispersant liquid and samp-
ling procedure were tried in an effort to
improve the consistency of results among
different test runs made on each batch.
Representative results are shown in
Figs. 24 and 25.

CORROSION OF REFRACTORY METALS AND UN IN LIQUID METALS

The space power reactor concepts at
LRL depend on removal of heat from the
reactor core by flowing liquid metals.
Corrosion of fuel cladding by the reactor
coolant could set an upper limit on the
reactor operating temperature. The LRL
liquid metal corrosion program will
include:

- 1) Solubility measurements of refrac-
tory metals and UN in liquid metals.
- 2) Studies of the mechanisms of liquid
metal corrosion.

3) Measurements of corrosion rates
in capsules and loops of prime candidate
coolants and containment metals.

Solubilities in Liquid Metals

Experimental — Work continued on the
solubility of tungsten in silver. It was
noted in Progress Report No. 5 that
analytical results reported earlier were
in error since tungsten-containing drills
had been used for sampling the quenched
silver solutions. Analytical results
from these first samples showed that the
solubility of tungsten in silver at 2100-
2200°C was not more than 100 ppm. The
earlier work was repeated with the
temperature range of the measurements
extended to 2378°C. Samples are being
taken by drilling with tungsten-free drills.
To date, only the analysis for one sample
heating has been completed. This shows
that the solubility of tungsten in silver at
2200°C is 2 ± 1 ppm.

Compatibility studies of UN with silver
are continuing. It was reported in
Progress Report No. 5 that 117 ppm of
uranium in silver were found after heating
UN with silver in a tungsten crucible for
27 hr at $1775 \pm 5^\circ\text{C}$. Analysis of the UN
which was used for this test shows that it
contained 200 ppm O, 100 ppm C, and
 $5.36 \pm 0.05\%$ N. If it is assumed that the
rest of the sample was uranium, the test
sample has the substoichiometric compo-
sition $\text{UN}_{0.96 \pm 0.01}$. Since the uranium
activity decreases as UN becomes richer
in N, the solubility of stoichiometric UN
should be less than the measured value.
Experiments are continuing to further
nitride and purify UN before performing
additional compatibility tests.

Fig. 24. Particle size distribution of UN powder (Y-12, batch 1)

Liquid Metal Loop and Capsule Programs

Liquid-metal loop and capsule programs are being initiated at LRL on the compatibility of liquid metal and fuel cladding under conditions representative of those in proposed reactors. Important objectives of the loop and capsule programs are: 1) Development of a capability to fabricate and join pieces of W-based alloys proposed as reactor cladding materials, and 2) development of techniques for measuring corrosion rates

of the refractory alloys in flowing liquid metals.

Liquid Metal Loop Program — The purpose of the loop program is to examine corrosion from liquid metal under times, flow rates, and temperatures similar to reactor conditions with alloys fabricated, joined, and stressed as anticipated in the space power system. In addition, a major purpose of the first loop will be to proof test LRL's capability for testing materials in contact with flowing liquid metal.

Fig. 25. Particle size distribution of UN powder (Y-12, batch 2).

The first tungsten alloy tested will be 45% W, 25% Re, and 30% Mo* because of its relative ease of fabrication. Eventually at least one tungsten-rhenium binary alloy and at least one advanced tungsten alloy will be loop tested. The advanced alloy might be a precipitation-hardened, vapor-plated, or high-pressure extruded material.

Some target parameters for the first W-25Re-30Mo loop are given in Table X, and a detailed description of the loop and

its components will be found in the Engineering Design section, p.

The temperatures sought in the first test are considerably higher than those used in other AEC and NASA corrosion programs. Whether these temperatures are practicable will be determined by tests of prototype liquid-metal pumps and loop heating elements, tests of W-25Re-30Mo creep strength, and proof tests of W-25Re-30Mo welds; all these tests will be carried out prior to loop assembly.

The loop will be contained in a vacuum of $\approx 10^{-8}$ torr during the corrosion test

*This alloy will be referred to from here on as W-25Re-30Mo.

Table X. Target parameters for the first series of liquid metal loop tests.

Parameter	Target value
Liquid metal	Li
Refractory metal	W-25Re-30Mo
Max Li temperature	1900°K
Min Li temperature	1800°K
Tube i. d., heated section	0.135 in.
Length of heated tube	2 ft
Tube i. d., cooled section	0.42 in.
Fluid velocity, heated section	20 ft/sec
Vacuum in containment vessel	10^{-8} torr
Type of fluid flow	Turbulent forced convection
Flow rate per channel	0.06 lb/sec
Power transfer by Li	≈ 7 kW
Loop pressure drop	≈ 10 psi
Loop internal pressure	≈ 100 psia

and will be radiantly heated by a tungsten mesh element and cooled by radiation to the vacuum bell jar. An electromagnetic conduction pump will be used if prototype tests of the pump are successful. Temperatures will be measured by tungsten-rhenium thermocouples. An electromagnetic flow meter is being designed. Tungsten alloy pieces for the loop are being obtained from GE-NMPO in Cincinnati; they will be joined at LRL by electron beam welding.

The extent of corrosion of base metal and weld regions will be studied by examining the loop tube walls after the conclusion of tests. Corrosion extent and location will be determined by weight change, ultrasonic thickness measurement, and radiographic, fluorescent

penetrant, electron microscopic, and metallographic techniques. Corrosion mechanisms will be studied using x-ray fluorescence, x-ray diffraction, electron beam microprobe, and surface-activation analysis techniques. Bulk metal and lithium composition will be measured by emission spectrographic and mass spectrographic methods.

Capsule Program — A new type of corrosion capsule was designed for the LRL corrosion program. A space power system flow path is simulated by electromagnetically pumping liquid metals from a heated end to a cooled end of a cylindrical capsule. A flat plate is placed lengthwise within the capsule to form a flow loop inside the cylinder.

The capsule tests will provide a relatively simple method of measuring corrosion rates. Although these rates are not expected to give truly quantitative predictions of corrosion rates in loops and reactor cores, they are expected to give better than qualitative indications. The capsule tests will be used to investigate the proposed ranges of reactor parameters which might affect corrosion rate and to sort unimportant parameters from important parameters.

Corrosion parameters to be studied with capsules may include cladding alloy composition, time, temperature, flow rate, temperature gradient, temperature cycling, effects of foreign materials such as cladding impurities and reactor fuel material, stress, fabrication and joining methods, and corrosion inhibition techniques.

The list of tentatively planned capsule tests in Table XI shows the sort of material combinations which are contemplated.

Table XI. Tentative capsule tests.

Test number	Test conditions
C-1	Ternary alloy + Li + welds
C-2	Ternary alloy + welds + Li + UN
C-3	Binary alloy + Li
C-4	Binary alloy + Li + UN
C-5	Advanced alloy + Li
C-6	Advanced alloy + Li + UN
C-7	Alloy* + Li + O, C and/or H
C-8	Alloy* + Li + higher temperature
C-9	Alloy* + Li + higher flow rates
C-10	Alloy* + Li + temperature cycling
C-11	Alloy* + Li + stressed capsule
C-12	Alloy* + Li + corrosion inhibition
C-13	Alloy* + Li + Ta

(Alloy* = prime candidate alloy)

ANALYTICAL

Determination of Light Elements in Uranium Compounds

The electron microprobe has been used to investigate the distribution of carbon, oxygen, and nitrogen, and to identify phases in uranium compounds.

Oxygen can be determined in the presence of uranium despite a nearby U peak ($U M_{\alpha 1,2}$ 3rd order) by reducing the excitation voltage to 5 kV. The U peak is practically eliminated, and O in UO_2 (11.8% O) gives a peak-to-background ratio of 25. Oxygen contents of 2 to 3% can probably be determined.

The carbon ($C K_{\alpha}$) band appears as a shoulder on the $U N_{VI}O_{IV}$ line, but a semi-quantitative estimation of carbon is possible. The situation is much improved

by going to the second order of the carbon peak. A quantitative approach must await the availability of uranium carbide standards.

The nitrogen peak has high underlying background from uranium, which can be subtracted. Using pulse-height discrimination, one can remove most of the uranium contribution. Multichannel pulse height analysis can serve to show the relative amounts of nitrogen and uranium in an area. Nitrogen in UN ($\approx 6\%$ by weight) is readily seen, and 1 to 2% can probably be determined.

Determination of Amount of Hafnium in Tungsten-Hafnium Alloy

This method was developed to support the research with dispersion-hardened alloys. The tungsten-hafnium alloy is dissolved in a NaOH- $NaNO_3$ fusion at 500°C. After the melt is dissolved in water, a gelatinous hafnium hydroxide is precipitated with NH_4OH . Filtration of this precipitate, together with some occluded tungsten, is followed by maceration in 125 ml of NH_4Cl and digestion at 80 to 90°C for 1/2 hr. Then 50 ml of 15% mandelic acid solution is added and the digestion is continued for 2 hr. The hafnium tetramandellate is collected on a No. 42 filter paper and ignited to HfO_2 at 950°C. The ignited HfO_2 can be weighed or dissolved by a potassium pyrosulfate fusion, the melt dissolved in dilute HCl, and the solution analyzed by the EDTA xylene orange method.

Results from analysis of prepared samples are shown in Tables XII and XIII.

Table XII. Analytical results on solutions prepared from tungsten sheet stock and solutions of HfO_2 or Hf metal.

mg Hf taken	mg Hf found (EDTA method)	% recovery
24.61	24.43	99.27
33.27	33.37	100.30
33.73	33.55	99.47
16.86	16.66	98.85
20.10	19.93	99.14
30.15	29.93	99.23
40.20	40.03	99.56

Table XIII. Analysis of standard samples prepared at LRL and pressed into pellets.

Theoretical % Hf	Hf% found (EDTA method)
0.50	0.48
1.00	0.98
2.00	1.94
4.00	3.96
8.00	8.10

This general procedure is also applicable to the determination of hafnium in molybdenum-hafnium and rhenium-hafnium alloys.

Determination of Trace Uranium in Silver

A sensitive analytical procedure was needed to assist in studying uranium diffusion in silver melts. The presence of silver causes interference in both the colorimetric and fluorimetric analysis of uranium, requiring a separation prior to determination.

Silver drillings were dissolved in dilute nitric acid, a solution of pure iron carrier

added, and uranium coprecipitated with iron by the addition of ammonium hydroxide. The supernatant was discarded and the precipitate dissolved and re-precipitated. The supernatant was again discarded and the precipitate dissolved in a small amount of perchloric acid. The iron in this solution was then extracted with cupferron-chloroform perchloric acids and aliquots removed for uranium analysis.

For drillings containing ≈ 100 ppm uranium, a colorimetric procedure with arsenazo was used.¹² For lower uranium concentrations, the standard fluorimetric determination with a fluoride flux was used.¹³ The precision is $\pm 5\%$ relative at higher uranium values and $\pm 10\%$ relative at lower uranium values.

Trace Fluoride Analysis

Two procedures were developed for the direct determination of fluoride in molybdenum, rhenium, and tungsten. Fluoride can also be determined in any of the binary or ternary combinations of these metals or of their water-soluble salts. In both methods, the sample is fused with sodium hydroxide and sodium nitrate in a platinum crucible, and the melt is dissolved in water. In one procedure, 0.5 M sodium chloride elutes the fluoride, ahead of the metal, through a Dowex 1×8 anion exchange column. The fluoride is determined spectrophotometrically in the eluate by the cerium-Alizarin Complexone method. The simpler procedure is to adjust the pH of the melt solution to 5.8 to 6.1 and measure its pF with an Orion Research, Inc. fluoride ion activity electrode; no separation of fluoride from the metal is necessary. Both of these procedures will determine 1 to 100 μg of

fluoride in a gram sample with a standard deviation of about $\pm 1 \mu\text{g}$.

Determination of Molybdenum in Tungsten

All chemical methods available for the determination of small amounts of molybdenum in tungsten require one or more separation steps. However, the determination can be carried out by atomic absorption without separation of the molybdenum from the tungsten. Tungsten suppresses the absorption of light by

molybdenum but this inter-element effect between molybdenum and tungsten can be eliminated by the method of standard additions; it is also necessary to apply a correction for scattered light.

This method was used for samples that contained 0.01 to 0.05% Mo. With a Perkin-Elmer Model 303 atomic absorption spectrophotometer with the standard air-acetylene burner, the flame was adjusted to the fuel rich side and the analytical line was at $3130 \text{ \AA}$. A relative standard deviation of $\pm 2\%$ was obtained.

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EXTRAPOLATED THERMODYNAMIC PROPERTIES OF SODIUM AND POTASSIUM

INTRODUCTION

In general, the mass per unit output power of a Rankine cycle space nuclear power system will pass through a minimum at some value of working fluid temperature. The temperature at which this occurs appears to be at or above the limit of most experimental thermodynamic data. It is thus necessary to have a reasonably accurate method of extrapolating the known thermodynamic data to temperatures and pressures well above the present limits.

To date, study has concentrated on the alkali metals, with emphasis on sodium and potassium. Our major sources of experimental data are General Electric¹⁴ and U. S. Naval Research Laboratory (NRL).^{15,16,17} The maximum temperature at which data are reported in any of these references is <1700°K.

Three essentially different methods of extending thermodynamic data have been investigated. These are denoted as "Equation of State," "Corresponding States," and "Quasi-Chemical Equilibrium." While reliable extrapolation of superheated vapor properties to higher temperature values appears feasible, a satisfactory method of extrapolating saturated vapor properties has not been found.

Equation of State

If the p, v, T data fit accurately some equation of state [$p = p(v, T)$], the thermodynamic variables enthalpy and entropy are determined as follows: Assume that the specific heat at constant pressure at

some pressure, p_o , for all temperatures is known. Then it can be shown from familiar thermodynamic relationships that

$$C_p(p, T) = C_p(p_o, T) - T \int_{p_o}^p \frac{\partial^2 v}{\partial T^2} dp,$$

where the integration is along the isotherm T . The enthalpy is given by

$$h(T, p) = h(T_o, p_o) + \int_{T_o}^T C_p(p_o, T') dT' + \int_{p_o}^p \left[v(T, p') - T \frac{\partial v(T, p')}{\partial T} \right] dp',$$

and the entropy is given by

$$S(T, p) = S(T_o, p_o) + \int_{T_o}^T \frac{C_p(p_o, T')}{T'} dT' - \int_{p_o}^p \frac{\partial v(T, p')}{\partial T} dp'.$$

Obviously the data of p, v , and T must be fitted with a high degree of accuracy for the above equations to give accurate results.

A virial equation of the form

$$\frac{pv}{RT} = 1 + \sum_{n=1}^M A_n v^{-n}$$

has been used in Refs. 15, 16, and 17 to reproduce the experimental data. There the constants A_n (the virial coefficients) were obtained by a least-squares fit to the experimental data with $M = 4$.

Within the range of the experimental results, this equation will faithfully reproduce the data. However, it is merely

a power series with an arbitrary number of terms (five). There is thus no guarantee that it can predict, with acceptable accuracy, data outside of the region in which it has been "calibrated." It was therefore decided that this was perhaps not the best avenue of approach to the problem.

Corresponding States

The theorem of corresponding states implies that the thermodynamic properties of different substances are the same when measured at the same reduced state. (The reduced value of a variable is the ratio of its actual value to its value at the critical point.) For real substances this principle works best when the substances to be compared have the same critical compressibility factor, $Z_c = p_c v_c / RT_c$ (the subscript c denoting the critical value), and the same class of intermolecular bonding, or, for the elements, the substances are in the same group on the periodic chart. Thus, in order to predict the thermodynamic properties of a number of materials having the same Z_c and bond class, it is necessary to know the properties of only one.

Unfortunately, Z_c for potassium is ≈ 0.21 and for sodium, Z_c is ≈ 0.17 . These are sufficiently different to lend little confidence in using either of these elements to obtain the properties of the other.

ANALYSIS VIA QUASI-CHEMICAL EQUILIBRIUM

Enthalpy-entropy relationships for sodium and potassium were computed upon the assumption of chemical equilibrium between the monatomic, diatomic, and tetratomic molecules of these elements. k_2 and k_4 ,

The equilibrium was assumed to be maintained through the two reactions (A standing for sodium or potassium),

$$2A - A_2 = 0 \quad (1)$$

and

$$4A - A_4 = 0, \quad (2)$$

with each of the components obeying the perfect-gas equation of state.

The existence of the diatomic molecule was verified spectroscopically for all of the alkali metals.¹⁸ However, there is only indirect evidence (see Refs. 15 and 16) that of the higher order polymers present in the mixture, the even (namely the tetramer) is statistically favored over the odd polymer (trimer).

Of course, each of the polymer species will have some departure from the perfect-gas equation of state. However, each species behaves more ideally as temperature is increased along an isobar. The lowest temperature at which the gaseous state exists at a given pressure defines the saturated gas state. Thus, if it can be demonstrated that a high precision of the thermodynamic data is generated by this approximation along the saturated gas curve, it may then be possible to attach high confidence to the precision of the data at higher temperatures along isobars originating at the saturation conditions.

Define x_j to be the mole fraction of the j th species of molecule in the mixture. Then

$$\sum_{j=1, 2, 4} x_j = 1. \quad (3)$$

From the law of mass action, the x_j values are further related to each other and to the pressure-independent equilibrium constants,

$$k_2 = \frac{x_1^2}{x_2} p \quad (4)$$

and

$$k_4 = \frac{x_1^4}{x_4} p^3. \quad (5)$$

Van't Hoff's law relates the equilibrium constants to the molar enthalpies (h_j) of the species of the mixture by

$$\frac{d \ln k_2}{dT} = \frac{2h_1 - h_2}{RT^2} \quad (6)$$

and

$$\frac{d \ln k_4}{dT} = \frac{4h_1 - h_4}{RT^2}. \quad (7)$$

The molar enthalpy of a perfect monatomic gas is

$$h_1 = 5/2 RT; \quad (8)$$

for a diatomic gas,

$$h_2 = 7/2 RT + E_{\text{vib},2} - Q_2^0; \quad (9)$$

and for the tetrameric gas,

$$h_4 = 8/2 RT + E_{\text{vib},4} - Q_4^0. \quad (10)$$

As the molecules are expected to have a rather weak bond, their vibration energies have been approximated by

$$E_{\text{vib},2} = B_2 RT$$

and

$$E_{\text{vib},4} = B_4 RT, \quad (11)$$

with B_2 and B_4 independent of temperature.

In order to obtain a solution of Eqs. (3), (4), and (5) for the x_j , it is necessary to first obtain values for B_2 , B_4 , Q_4^0 , Q_2^0 , and for the constants of integration of Eqs. (6) and (7), $\ln k_2^0$ and $\ln k_4^0$, respectively.

Directly integrating Eqs. (6) and (7) yields the form $\ln k_j = a_j + b_j/T + c_j \ln T$, where $j = 2, 4$. Reference 15 shows that $\ln k_j = \alpha_j + \beta_j/T$ fits the experimental data quite adequately, so that it is unreasonable to expect the experimental data to yield accurate values of the c_j . Therefore, the numerical values of α_j and β_j supplied by NRL in Ref. 16 were used directly to calculate the equilibrium constants. Further, the value of Q_2^0 has been determined experimentally by NRL for both potassium and sodium. This leaves us with just B_2 , B_4 , and Q_4^0 as undetermined constants, which are obtained from a least-squares fit of our model to the NRL data on enthalpy vs temperature.

Now, from calculated values of the x_j , the molecular weight of the mixture can be determined as

$$\mu = \sum_{j=1,2,4} x_j \mu_j, \quad (12)$$

where μ_j is the molecular weight of the j th species.

The gas density is obtained from the perfect-gas equation of state

$$\rho = \frac{\mu p}{RT}; \quad (13)$$

and the enthalpy per gram of the mixture is

$$H = \frac{\sum_{j=1,2,4} x_j h_j}{\mu}. \quad (14)$$

The specific entropy of the mixture is calculated from

$$\left. \frac{\partial S}{\partial H} \right|_p = \frac{1}{T}$$

or

$$S(p, T) = S(p, T_0) + \int_{T_0}^T \frac{dH}{T}, \quad (15)$$

integrating along the isobar p .

The values of $S(p, T_0)$ are obtained from published data for the saturated gas and liquid states, but as extended by extrapolation as discussed in the following paragraphs. Then for application of Eq. (15), T_0 is chosen to be the temperature corresponding to vapor pressure, p .

In order to extrapolate the data to pressures above the experimental region, the following empirical procedure was used: In 1953, Watson¹⁹ reported that the temperature dependence of the enthalpy of vaporization, ΔH , of a great many different materials is quite accurately given by

$$\Delta H(T_r) = \kappa(1 - T_r)^{0.38}, \quad (16)$$

where T_r is the reduced temperature (T/T_c) and κ is a constant. In particular, Eq. (16) holds quite well for both potassium and sodium. It is thus assumed that the entropy of vaporization is accurately given by

$$\Delta S(T_r) = \kappa' \frac{(1 - T_r)^{0.38}}{T_r} \quad (17)$$

Figure 26 shows that the average value of the saturated liquid and gas entropies $\bar{S}(T) = \frac{1}{2} [S_l(T) + S_g(T)]$ is a much weaker function of temperature than either of its components for potassium. This is also true for sodium. As a means of extrapolation, therefore, it has simply been assumed that $\bar{S}$ remains constant up to the critical point, as indicated by the dotted

Fig. 26. "Continued $\bar{S}$ " extrapolation of the "vapor dome" of potassium.

line in Fig. 26. Values of S for the gas or liquid are then obtained as

$$S_{g,l}(T) = \bar{S}(T) \pm \frac{1}{2} \Delta S(T). \quad (18)$$

It is, of course, possible to extrapolate the enthalpy along the vapor dome in an entirely analogous manner. By so doing, it has been found that $\bar{H}(T_r) \approx \alpha + \beta T_r$. In Fig. 27 is plotted the saturated gas enthalpy, $H_g(T)$, of sodium as supplied both by NRL and our own "continued- $\bar{H}$ " extrapolation.

RESULTS

In Fig. 27 the saturated gas enthalpy of sodium as given by NRL and the continued $\bar{H}$ extrapolation is compared to the calculations of the "quasi-chemical" method. It is seen that at about 1800°K (vapor pressure ≈ 50 atm), there is a 1% discrepancy in the saturated gas enthalpy as estimated by the two methods, and that the discrepancy is increasing rapidly with increasing temperature. Below that temperature, the quasi-chemical equilibrium approximation yields reasonably precise results. It has been found that, for potassium, a discrepancy of 1% in the saturated gas enthalpy occurs at a vapor pressure of about 30 atm.

Note that the data generated here for sodium at pressures greater than 50 atm are suspect, likewise for potassium above 30 atm pressure. As noted before, the data as predicted by an extrapolation to high temperatures along an isobar should be precise when the fit to experimental data at low temperatures is precise on the same isobar. Delineated in Figs. 28 and

Fig. 27. Sodium saturated gas enthalpy vs temperature from various sources.

29 are the pressure limits above which the data are unreliable.

The divergence of the quasi-chemical equilibrium approximation from the "experimental" enthalpy data results from at least two sources: First, there is no reason to expect that polymerization of the gas will stop at the tetramer as pressure is increased (pressure tends to increase exponentially with temperature along the vapor dome). Second, as pressure is increased, each molecular species in the gas tends to depart from the perfect gas law behavior of Eq. (13).

Fig. 28. Mollier diagram (enthalpy vs entropy) for sodium. Computed by method of "Quasi-chemical Equilibrium."

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Fig. 29. Mollier diagram (enthalpy vs entropy) for potassium. Computed by method of "Quasi-chemical Equilibrium."

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REACTOR, SYSTEM, AND COMPONENT ENGINEERING

REACTOR DESIGN

Reactor design efforts continued along general technology lines exemplified by reactors for the Rankine cycle reference power system designs SPR-4 (300 kW_e) and SPR-6 (10 MW_e). A number of new concepts have been proposed but few calculations have been carried beyond the point of showing general feasibility.

The larger reactors (exemplified by SPR-6) have a central cavity through which coolant is returned, surrounded by a region in which fluid control elements are placed. The latter are discussed elsewhere in this report. In the smaller, reactivity-limited reactors (exemplified by SPR-4), it is not clear that the central region is available for this purpose. This is not simply a matter of criticality but of control kinetics as well.

A reactor design typical of the SPR-6 size is shown in Fig. 30. This drawing is intended only to clarify certain features for analytical purposes and is not meant to bear inspection in detail. The reactor is supported within the pressure vessel on the downstream side by a hemispherical structure. The structure consists of welded tungsten rods of approximately equal length which are predominantly loaded in compression.

A thin membrane extends up from the skirt of this support, fitting closely around the active-core fuel-element bundle. A radially inward hydrostatic

pressure transmitted through this membrane stiffens the bundle into a rigid structure. A preliminary examination indicates that a rather low pressure is sufficient to prevent fuel element bowing.

The upstream end of the reactor is positioned within the pressure vessel by a spline structure that accommodates both radial and axial core dimensional changes. This spline is shown in Fig. 30 as a set of radial fingers attached to the pressure vessel through close-fitting slots in a slightly heavier extension of the core membrane just forward of the upstream core face. In this arrangement, rubbing is involved and might lead to self-welding. Another type of spline capable of bending in the radial and axial directions, but not in the circumferential direction, is being studied.

The operational loads are low, and no strength problems are foreseen except for launch loads which can presumably be supported by a removable auxiliary structure (perhaps, e. g., solidified lithium). Stiffness requirements are being studied from a control standpoint.

For the larger reactors, the most promising fuel elements are the hybrid type. For smaller reactors, the elements will be either pin-type B or internally cooled tubes (see Progress Report No. 5).

The multiple tube sheets shown in Fig. 30 permit circulation of interstitial and fuel bonding fluids; this may be required to remove fission gasses, replenish free nitrogen, etc. This

Fig. 30. General configuration of a 60 MW_{th} space power reactor designed for 2% burnup in 10,000-hr lifetime. The outside diameter of the pressure vessel is 65 cm.

Fig. 30 continued.

tube-sheet arrangement should only be considered representative of the concepts.

Pressure vessel cooling is being studied and is discussed elsewhere in this report. This will involve trade-offs in weight between the vessel and other components. These trade-offs are tied to the control problem due to the interference of vessel, coolant, and possible insulation with side-reflector control.

Means of achieving fine reactor control have been studied, and it appears that this must be accomplished by mechanically coupled external reflectors. It is expected that coarse control will be accomplished internally by isotopic mixtures, fluid-vapor interchange, etc., either in the central region shown or throughout the core proper. Dynamic coarse-control studies are just beginning. An analog reactor-control simulator was brought into operational status. This simulator models a spatially uniform temperature reactor with six delayed neutron groups.

Reactor Pressure Vessel Cooling

Radiation cooling of the reactor pressure vessel may be precluded due to the magnitude of the gamma and neutron heating and the likely presence of a reflector external to the pressure vessel, which would act as a radiation shield. However, a large amount of cooling is available with the subcooled potassium at radiator exit conditions.

Two concepts have been considered for cooling the pressure vessel. These concepts are discussed in terms of typical conditions for a large power system. In design A (Fig. 31) a portion of the lithium leaving the boiler separates from

the main stream and is cooled by the subcooled potassium in a preheater. The cooled lithium is used to cool the reactor pressure vessel and is then added to the main lithium stream prior to its passing through the reactor.

In the case shown in Fig. 31, the pressure vessel is cooled to a maximum temperature of 1410°K. At this temperature a tantalum alloy could be used. Thin tungsten cladding would be used internally to prevent contact with the lithium. A large weight savings in the pressure vessel would result. If the pressure vessel were uncooled, its temperature would be approximately 1800°K and a tungsten alloy weighing approximately 4000 kg would be used. The tantalum alloy pressure vessel and the required preheater together weigh ten times less.

Design A involves some thermal inefficiency in transfer of heat from the relatively hot lithium to the cooler potassium. For the case considered in Fig. 31, 2.6 MW is added to the lithium in the pressure vessel (due to the assumed internal heating), but 11.7 MW must be removed from the lithium in the preheater. The power handled by the preheater can be reduced to 2.6 MW by addition of another pump and a separate coolant loop. In this case the pressure-vessel coolant flow and the reactor coolant flow would not be mixed.

A more thermally efficient design would be to pass the subcooled potassium directly through the pressure vessel and then through the boiler, as shown in Fig. 32. Unless the potassium and lithium pressures in the reactor were equalized, a pressure vessel separating the two fluids would be required. Optimum operating

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Fig. 31. Design A for cooling the pressure vessel of the reactor. Typical conditions for large reactors are assumed.

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points and weights have not been determined for this design.

Reactor Control Concepts

Side-Reflector Control Concepts for High Power Reactors — Several methods of side-reflector control and devices for providing driving power were investigated for use with the central pipe configuration reactor (high power).

No attempt was made to examine the effect of any concept on reactor kinetics, control systems, or other components in the power system (i. e., boiler, shield, etc.); instead the attempt was only to investigate schemes which might, after further analysis, provide a feasible method of control. The results thus far from this investigation are summarized below:

Reactivity requirements that must be controlled by any mechanism selected are:

- 1) Ground safety.
- 2) Temperature or reduced reactivity effect.
- 3) Operational shutdown and reserve.
- 4) Operational losses.

If a single mechanism is chosen to meet these requirements, a wide range of adjustable control would be necessary, demanding the use of thick side reflectors. Thicker reflectors are heavier, difficult to cool, and require heavier shields. It has been proposed, therefore, that the largest overall reactivity requirement, ground safety, be controlled by initially filling the fuel core with a strong neutron absorber, Li^6 , and subsequently mixing this isotope with the reactor coolant, Li^7 , or the remainder of the primary loop just prior to startup in orbit. On the ground

Fig. 32. Design B for cooling the pressure vessel of the reactor. Typical conditions for large reactors are assumed.

and during launch, the lithium would be solid and would not mix. The use of a movable side reflector could augment this method of ground control by remaining in the least reflective position during all ground operations.

Provision for vernier control to provide for operational reactivity losses, startup, and reserve reactivity can be

incorporated into a side-reflector movement.

The adhesion problem present with metal-to-metal contact in a high vacuum environment is acknowledged. Detailed consideration of the problem was avoided however in this preliminary investigation. Pressurization of the environment in which the control components move (and lubrication) is assumed to be feasible at this point.

Two representative methods of providing reactivity control through reflector motion are shown in Figs. 33 and 34.

Figure 33 illustrates the use of axially moving reflector segments in two con-

centric layers. Both would be fully retracted from the core for shutdown and could be (independently) closed to various degrees for control during operation. The degree of reliability provided by this independent action of separate segments could be further enhanced by splitting the segments into a number of azimuthally separate sections.

Figure 34 shows a more familiar configuration with reflector segments rotating toward or away from the core to regulate neutron leakage.

Liquid Reactor Control System - The interest in high operating temperatures

Fig. 33 Split concentric-reflector system with axial motion.

in space reactors points to the possible use of liquids for control. Li^6 is an excellent neutron absorber for the control of high-temperature fast reactors because of its absorption peak at 1/3 MeV. Further advantage may be taken of the Li^7 isotope. Different mixtures of Li^6 and Li^7 , occupying about 20% of the core volume, sway k_{eff} by 30%. Predetermined or time-dependent mixtures can thus be applied to a variety of control situations that would be impossible with solids.

The geometric temperature effect on reactivity can be decreased by a proper selection of the lithium isotopic composition in the interstitial* and bonding fluids. The bonding fluid is the heat-transfer medium between the fuel and cladding. It experiences a displacement relative to the fueled core that results from differences in the thermal-expansion coefficients for itself, the fuel, and the cladding.

Operational losses in reactivity due to fuel burnup, etc., can likewise be decreased by a proper selection of the Li^7 enrichment in the bonding fluid. Here it is the swelling of the fuel during operation that displaces lithium from the core, causing partial self-control.

Operational shutdown or scram of the reactor in space is readily accomplished by injection of Li^6 into tubular voids within the fueled core. Removal of this lithium for restarting in space can be achieved by means of compressed gas or evaporation.

Vernier control of the reactor may be needed only for positive and negative

Fig. 34. Rotary segment reflector.

reactivity amounts of less than \$1.00 because of partial or total compensation of miscellaneous reactivity losses, as described. The mechanism is identical to that suggested above for operational shutdown, except that both Li^6 and Li^7 are used in separate channels for negative and positive control.

One disadvantage of this control system is the reactivity hazard resulting from total expulsion of all liquid media in the fueled core. To circumvent this difficulty, the overall concentration of Li^6 should be required to be above a specific value in each reactor; this would not always be possible.

Applicability of this concept depends in large measure upon the neutron energy spectrum of the reactor. System kinetics require detailed attention.

The advantages of no moving parts and minimum reactor size (minimum shield size) indicate that further attention should be given to this concept.

* This discussion applies to large central-pipe reactors having hydride-type fuel elements.

Two-Phase Fluid Control Concept -

A method of fluid reactor control which appears to minimize the need for moving parts and seals is presented schematically in Fig. 35. It would operate as follows: The control fluid in the liquid phase passes

Fig. 35. Loop for two-phase fluid-control concept.

into a duct in the control element. The control element in this scheme corresponds to an unfueled core element or an external reflector element. The fluid flows through a porous matrix and evaporates at some point in the matrix. The heat of vaporization is obtained by γ heating of

the liquid itself, by conduction from the γ -heated matrix material, and by transfer into the control element if the temperature gradient is favorable. The vapor leaves the porous material and passes out of the control element through a duct. The vapor is then condensed and the resulting liquid is pumped back into the control element to complete the cycle.

The rate of evaporation is determined by the rate of heat generation in the control element and the rate of heat transfer into the control element. If liquid is pumped into the control element faster than it is evaporated, the proportion of liquid will increase and, conversely, if liquid is pumped in more slowly than the rate of evaporation the proportion of liquid in the control element will decrease. Control of the thickness of liquid can be obtained in two ways:

- 1) By varying the flow rate of liquid into the control element. This can be accomplished by varying the power input to the pump or by a bypass line around the pump with a variable valve.
- 2) By varying the amount of heat transferred into the control element from its surrounding environment and thereby controlling the rate of evaporation. This can be accomplished by varying the temperature of the control element, which in turn is controlled by the pressure in the control element since a two-phase fluid is present. The pressure in the control element can be controlled in two ways: a) The temperature, and hence pressure, of the condenser remaining fixed, the degree of pressure drop through an adjustable control valve (see Fig. 35) will determine the pressure in the control element, or b) The pressure drop in a

fixed valve being determinate, the regulated temperature, and hence pressure, of the condenser will determine the pressure in the control element.

Now consider the stability of the device. If the liquid in the control element is used as a reflector, an increase in reactor power will increase the rate of heat generation in and heat transfer to the control element, thereby increasing the rate of evaporation and decreasing the thickness of the reflector. Conversely, a drop in reactor power will decrease the rate of evaporation, increasing the thickness of the reflector and increasing the criticality of the reactor. Thus the system has a negative power coefficient of reactivity.

On the other hand, suppose the liquid in the control element is a heavy absorber.

Similar reasoning leads to the conclusion that a poison-type control element would not be inherently stable.

Accidents such as pump malfunction, a leak of liquid from the piping, or a loss of cooling in the condenser would lead to reduced liquid in the control element and would thus be safe for a reflector element and unsafe for a poison element. Other accidents can be hypothesized which would be unsafe for a reflector element, such as a run-away pump or a leak in the vapor piping.

An evaporating liquid control system is attractive in concept, particularly if used as an internal moderator-reflector element for vernier control. Further evaluation of its practicability awaits detailed design calculations.

SYSTEM ANALYSIS

Fig. 36. Specific mass vs temperature for Rankine cycle power system. Results are shown for 300-kW_e and 10-MW_e systems using cesium and potassium as working fluids. System parameter values are listed in Table XIV.

System studies of high and low power Rankine cycle power plants were continued. The availability of liquid-metal transport and thermodynamic properties in a usable form permitted a preliminary comparison of working fluids. The results of these studies are presented in Fig. 36.

A more detailed listing of some of the characteristics of the systems at specific temperatures appears in Tables XIV and XV. It can be seen from this table that increasing radiator mass causes high system mass at lower temperatures while increasing containment vessel mass (boiler, e. g.) causes the increase in system specific mass at higher temperatures.

These results must be considered preliminary since extrapolated working fluid

Table XIV. Parameter values defining the power systems of Fig. 36.

Output power	300 kW _e	10 MW _e
Payload radius	125 cm	2.5 m
Distance, reactor to payload	12.8 m	100 m
Reactor burnup	0.0075	0.02
Enrichment, U ²³⁵	0.8	0.4
Meteoroid non-penetration probability	0.90	0.99
Shield thickness (neutron)	65 cm LiH	118 cm LiH
Turbine rpm	12,000	12,000
No. turbines	1	4
Pumps	2 electric centrifugal	2 electric centrifugal
Loops	2	2
Auxiliary cooling and radiator	1	1
Reactor outlet-to-turbine inlet temp difference	130°K	130°K
Turbine temperature ratio	0.75	0.75
Radiator pressure drop	20%	20%
Radiator armor	Be	Be
Materials	TZM, pure tungsten	TZM, pure tungsten
Turbine blades	Sylvania A strength	Sylvania A strength
Operation time	10,000 hr	10,000 hr

properties were used. Also, some components in the system are not properly modeled over large power and temperature ranges. Changes in the model and related assumptions can cause significant variation in the values shown. A preliminary conclusion, however, is that minimum system specific mass is less if potassium, not cesium, is the working fluid.

Turbines are critical components in all systems. Cesium turbines have fewer stages than potassium turbines. In the 300 kW_e systems shown, no turbines are overstressed. In the 10 MW_e systems, all cesium turbines are overstressed, and potassium turbines in systems with reactor outlet temperatures greater than 1560°K are overstressed. Such conditions

can be alleviated by: 1) Reducing speed from 12,000 rpm to 7700 rpm, which results in a system specific mass of 7.6 kg/kW at 1800°K, 2) increasing the number of turbines from 4 to 10, which results in a system specific mass of 7.9 kg/kW at 1800°K, or 3) incorporating stronger materials.

The turbine model upon which the system studies are based is optimized for potassium and is applicable to the study of cesium turbines only as a first approximation. Turbine efficiency, number of stages, velocity ratios, inlet temperature reduction, and losses will be studied in more detail.

System studies and detailed component analyses require reasonably accurate,

Table XV. Characteristics of 300 kW_e and 10 MW_e systems using potassium as the working fluid. Specific masses which are omitted are ≤ 0.1 kg/kW_e.

Power, MW	0.3	10	0.3	10	0.3	10
Reactor outlet temp, °K	1420	1420	1640	1640	1835	1835
Specific mass, kg/kW _e						
Reactor	0.8	0.3	1.0	0.3	1.3	0.4
Shield	1.2	0.6	1.1	0.4	1.0	0.3
Li reactor coolant	0.2	—	0.2	—	0.2	—
Boiler	—	—	0.2	0.2	5.8	3.1
Turbine	0.8	0.2	1.0	0.4	1.8	0.9
Alternator and radiator	4.6	0.8	4.6	0.8	4.6	0.9
Li pump	—	—	—	—	—	—
K pump	—	—	—	—	0.2	—
Structure	1.1	1.0	0.7	0.5	0.5	0.3
K working fluid	0.2	0.8	—	0.2	0.2	—
Power distribution	—	—	—	—	—	—
Controls	0.3	—	0.4	—	0.4	—
Primary piping	—	—	0.2	—	1.1	0.2
Secondary piping						
Radiator	<u>1.8</u>	<u>9.2</u>	<u>0.8</u>	<u>3.8</u>	<u>0.5</u>	<u>2.1</u>
System (Total)	11.4	13.3	10.4	7.0	17.8	8.7
K flow rate, kg/sec	0.9	29.9	1.1	32.4	1.3	34.3
Li flow rate, kg/sec	4.3	136	4.9	143	5.5	148
Reactor power, MW	1.94	61.7	2.21	64.2	2.5	66.2
Cycle efficiency, %	15.5	16.2	13.6	15.6	12.0	15.1
Radiator area (M ²)	91	2700	54	1600	37	920
Number turbine stages	9	4	12	6	13	7
Turbine efficiency	0.76	0.78	0.70	0.79	0.66	0.80
Turbine inlet pressure, bars	6.8	6.8	20.5	20	42.3	42.3
Turbine exit pressure, bars	0.5	0.5	2.4	2.5	6.5	6.5
Turbine inlet temp, °K	1290	1290	1510	1510	1705	1705
Li pressure, bars	0.8	5.8	1.8	6.9	4.5	9.5
Turbine blade stress	OK	OK	OK	Over stressed	OK	Over stressed

consistent, and accessible property data for all working fluids and coolants under consideration. Two computer subroutines were prepared to provide a central data

source for power system studies, both on and off the computer. One subroutine (called EVAP) generates thermodynamic property data for liquid metals in the

saturated and supersaturated regions. Subroutine EVAP is a revision (using improved data) and extension of subroutine KVAP, which was described in Progress Report No. 1. The purpose of the second subroutine (called TRANP) is to generate transport and other miscellaneous property data for all the alkali metals.

TRANP provides data on viscosity, thermal conductivity, specific heat at constant pressure, density, surface tension, electrical resistivity, and sonic velocity for saturated liquid and vapor conditions. The materials currently included are lithium, sodium, potassium, rubidium, cesium, mercury and NaK-78. Temperature is input and a specified property value is computed.

Temperature-property correlations were obtained by least-squares fits to tabular property data, the primary source of which was the compilation by Weatherford *et al.*²⁰

Since very little experimental work has been done on the determination of liquid-metal properties above 1500°K the system studies depend in large measure on extrapolated property data at temperatures above that value.

RADIATOR ANALYSIS

Direct-Condensing Tube-Fin Radiator

The radiator type considered thus far in the system studies is a direct-condensing tube-fin radiator with a flat rectangular configuration. The radiator consists of a central tapered inlet duct, a return duct on either side of the inlet duct, and a large number of finned tubes connecting the inlet and return ducting. The tubing is protected from meteoroid

bombardment by a shell barrier. The working fluid exhausts from the turbines into the inlet duct, where it is distributed among the tubes. The fluid condenses and is somewhat subcooled in the tube-fin array. The subcooled liquid is collected in the return ducts.

TOAST is a computer subroutine used to aid in the design of a minimum-mass tube-fin radiator. Calculations performed by TOAST yield optimum values for tube diameter, tube length, fin width, and fin thickness. In the version of TOAST used for the 300-kW_e SPR-3 reference design, the meteoroid barrier could be ignored in the thermal analysis. Essentially, the fin radiated all the heat, and its peak temperature was the fluid temperature. The meteoroid barrier thickness, t , scales with the vulnerable area, A , and the survival probability, P , in the following way:

$$t \propto \left(\frac{A}{-\ln P} \right)^{1/4} \quad (19)$$

The barrier thickness must be taken into account for high power, high survival probability systems, and the simplifying assumptions cannot be made for the SPR-6 system. TOAST was rewritten to include the heat rejected by the barrier, the temperature drop in the barrier-covered portion of the fin, and an exact calculation of the tube and fin view factors for this more dominant barrier case.

The revised code resulted in a minimum mass for the SPR-6 radiator of 56,000 kg with no tube-to-barrier contact. (Heat transfer from the fluid-carrying tube to the shell barrier is by radiation only). It is possible to design a considerably lighter radiator by specifying perfect tube-to-barrier contact. For this

case, the code yielded a minimum mass of about 21,000 kg. However, it was discovered that the perfect contact case resulted in a barrier temperature at which a significant amount of the barrier would vaporize during the mission. The code was further revised to allow for this material vaporization. The final code yielded a minimum mass of 28,000 kg for the perfect contact case. (The mass of the no-contact case was not affected by the vaporization revision because of the low barrier temperature.)

The high radiator mass calculated for SPR-6 is primarily due, either directly or indirectly, to the thickness of the meteoroid barrier. The barrier mass makes up approximately 60% of the total tube-fin barrier mass for the perfect-contact case and 70% of the total for the no-contact case.

Radiator Configuration, Flat vs Conical

Figure 37 shows the physical arrangement of a cylindrical reactor, a shield, a

radiator, and a spherical payload. In order to protect the payload from radiation, the shield must place both the payload and the radiator in the shadow from the reactor. The shadowing of the radiator is necessary to prevent radiation scattering. Two possible configurations for the radiator which result in geometrically different shields are a flat trapezoid and a truncated cone.

The radiator masses and the shield masses for the two configurations were compared for radiators of equal thermal performance. Typical calculations indicate that the flat configuration results in a lower system mass.

Briefly, the analysis is as follows: The surface area of each radiator is calculated. The effective radiating area of the flat radiator is assumed equal to its total two-sided surface area. The effective radiating area of the conical radiator is calculated as $A_c (1 + F)$, where A_c is the surface area of the outside of the truncated cone and F is the view factor

Fig. 37. Geometric model for radiator mass comparison.

from the inside of the cone. Comparisons are made between radiators with equal effective radiating areas. This equality can be achieved in any number of ways since the radiator length, h , or the radiator half width, c , may differ for the two configurations. The two cases which were considered in this analysis are:

$$\text{Case 1: } h_{\text{flat}} = h_{\text{cone}}$$

$$\text{Case 2: } c_{\text{flat}} = c_{\text{cone}}$$

The radiator masses are approximated by setting mass proportional to actual surface area (i. e., a radiator structure of fixed thickness and average density). The axially varying cross sections of the required shields are determined and the shield volumes calculated. The shield for the conical radiator has circular cross sections; the shield itself is a truncated cone. The cross sections of the flat radiator shield consist of a circle (to shadow the payload) with semi-circular-ended rectangular wings (to shadow the radiator). The shield masses are assumed proportional to their volumes.

Calculations were performed with typical proportions for a high power system, as indicated in the following (refer to Fig. 12):

$$\begin{aligned} \ell/r &= 2.4 \\ s_1/r &= 1.0 \\ t/r &= 4.0 \\ s_2/r &= 10.0 \\ r_p/r &= 5.0 \\ p/r &= 200.0 \end{aligned}$$

The results of these calculations are shown in Fig. 38. The radiator mass ratio (flat over conical) always favors the flat configuration and can approach a value of 0.5 when the radiator becomes long and slender (high h/r value, small radiating

Fig. 38. (a) Ratio of shield mass for flat radiator to that for a conical radiator of the same area, and (b) similar ratio of radiator masses. The mass ratios are plotted as a function of radiating area (relative to reactor size) for various fixed values of radiator length, h , or width, c (relative to reactor size).

area), since the inner cone surface becomes useless as a radiator. The shield mass comparison tends to favor the flat radiator except in the case of a long and slender shape, but even here the advantage of the cone is slight.

Comparisons made on the basis of equal (and large) values of h/r are felt to be more meaningful than those for

equal c/r, since presumably the design would take advantage of as much length as possible for either shape in order to minimize the radiator width and hence the shield mass.

Heat Pipe Radiator Concept

One of the principal problems in the design of space power systems is the dissipation of waste heat by radiation into space. This problem is especially severe at high power levels such as are considered in SPR-6. Even with favorably high radiation temperatures, very large surface areas are required.

Radiator arrays which use a single circulation system, i. e., ones in which there is no segmentation and all fluid carrying tubes have a common source, must be designed with extremely high structural integrity since high (e. g., 99%) probability of survival is mandatory. In addition to the predicted meteoroid hazard, ordinary structural failure modes (corrosion, fatigue, etc.) must be considered.

Radiator designs considered at LRL and elsewhere have almost always revolved around two approaches. The first of these is the classical tube and fin model in which vapor out of the turbines or

energy converter is caused to flow through a multiplicity of tubes where heat is rejected by: 1) Direct radiation from the tubes to space, and 2) conduction through the fins and then radiation to space. A typical fin-tube geometry is shown in the following sketch at approximately half scale (dimensions are given in cm).

Pertinent characteristics of this radiator obtained from a TOAST calculation are listed as follows:

Heat rejected	50 MW
Inlet fluid temperature	1250°K
Number of tubes	497
Tube length	6.5 m
Radiator width	13 m
Radiator length	32 m
Area (projected)	410 m ²

Masses

Inlet duct	1,440 kg	5% of total
Outlet duct	1,240	5
Barrier	15,500	56
Fins	9,430	34
Tube	70	
Fluid (K)	8	
Total radiator	27,700 kg	100%

The mass for meteoroid protection is not explicit in the data on masses. In addition to the 56% barrier mass, there is 14% fin mass to conduct heat from the

tube to the outside diameter of the barrier, giving a total of 70% attributable to meteoroid protection.

To gain some mass reduction, a second approach to radiator design has been used.²¹ This is one in which the solid fin is replaced by what is termed a vapor fin. A representative geometry for a vapor-fin radiator is shown in the following sketch.

Haller et al. show that for systems in the power range 500 to 1000 kW_e designed for 500-day life, substantial radiator mass savings (as much as 50%) may be realized with the vapor-chamber fin-tube radiator. The mass saving is stated to be less for higher power systems.

An alternative to finned radiators is the heat pipe radiator. In this concept, the inlet and outlet ducts originally used for vapor delivery and fluid return become the primary leg of a condenser/heat exchanger. Meteoroid protection of this ducting is inexpensive because its exposed surface area is low. One end each of a large number of heat pipes is inserted into this ducting. These heat pipes operate in parallel, function independently from one another, and form the separate secondary leg of the heat exchanger. Because many independent heat pipes are involved, they can be designed at minimum mass for a specified probability that a certain fraction will remain unpunctured during

the mission.²² This arrangement can be described in simplified terms as a large U-shaped tube out of which protrude the heat pipes in a plane array, as shown in Fig. 39.

A preliminary estimate of the mass of a heat-pipe radiator was obtained with the following assumptions:

Heat rejected: 50 MW

Rejection temperature: 1250°K

Max radiant heat flux: $Q_r = 10 \text{ W/cm}^2$

Max condensing heat flux, primary fluid-to-heat pipe: $Q_c = 50 \text{ W/cm}^2$

Max axial heat transport in heat pipe: $Q_a = 1000 \text{ W/cm}^2$

Heat-pipe diameter: $D = 8 \text{ cm}$

From the last two assumptions, one finds that the total energy transport in each heat pipe is 50 kW, so that 1000 heat pipes are required.

The length, ℓ , of the heat pipe end within the ducting was determined by equating the radial condensing heat transfer to the maximum axial heat transfer in the heat pipe:

$$Q_c (\pi D \ell) = Q_a \left(\frac{\pi D^2}{4} \right), \quad (20)$$

yielding for the assumed case $\ell = 40 \text{ cm}$.

It was assumed that the heat pipe of external length L radiates from both sides of a flat plate of width D and length L . The required length, L , was determined by equating the radiant heat transfer to the maximum axial heat transfer in the heat pipe:

$$Q_r (2DL) = Q_a \left(\frac{\pi D^2}{4} \right), \text{ yielding } L = 314 \text{ cm} \quad (21)$$

Fig. 39. Heat pipe radiator concept.

The advantage of the heat pipe is seen in comparing the latter two lengths. A heat transfer amplification of eight can be achieved and this at nearly isothermal conditions.

At 1250°K the vapor pressure of potassium working fluid would be about 5 atm. If the heat pipe is made of niobium alloy (allowable stress of 5000 psi), a pipe wall thickness of 0.060 cm is required. The density of niobium is 8.4 g/cm³. With these assumptions, the mass of the heat pipe is:

Structure	1136 g
Capillary	3040
Fluid	<u>1232</u>
Total	5408 g

To the mass of the heat pipes must be added the mass of the heat exchanger shell. It is conservatively estimated that the mass of the shell is equal to the mass of the heat pipes.

The shell mass includes meteoroid protection of the shell and a short length of the heat pipes (to protect the shell against oblique shots through the heat pipe penetrations). The heat-pipe wall thickness is increased inside the shell to prevent buckling of a heat pipe by the primary fluid in the event that a heat pipe vents.

Estimated radiator mass values of the solid-fin and vapor-fin types for the same thermal performance are compared

with those for the heat pipe radiator in the following table:

	Heat pipe radiator	Vapor fin radiator	Solid fin radiator
Specific mass, kg/kW	1.06	1.95	2.78
Relative mass	1	1.84	2.62

In addition to the potential savings of mass in the heat pipe radiator, there is a reliability advantage because each pipe is independent. The heat pipe scheme can provide a very redundant system, so that a means of detecting leaks and isolating damaged segments is not required.

TUNGSTEN HEAT PIPE FABRICATION TECHNIQUE

It has been demonstrated analytically and experimentally^{23,24} that the design of the wick structure in a heat pipe plays a very significant role in the overall heat transport capability of the pipe. In the wick it is desirable to provide small-diameter pores to give high pressure drop at the meniscus and large-diameter liquid flow passages to minimize drag forces. This is probably best done with a two-component structure since the two requirements are diametrically opposed. The two-component structure might consist of open channels covered with layers of fine mesh screen.

Investigations at LRL have been directed toward the more difficult of the wick fabrication problems: that of putting deep channels on the inside of small-diameter (1 cm) pipes of significant length (≈ 35 cm). The end objective of

the study is to be able to produce a tungsten alloy heat pipe which can be operated at $\approx 2000^\circ\text{K}$ as an emitter of a thermionic diode; such a pipe will contain a large number of channels separated by thin fins. The optimized groove structure can of course be used to equal advantage at lesser temperatures for other applications.

A cylindrical molybdenum mandrel was fitted with slotted wheels at each end. The slots in the periphery of the wheels have parallel sides separated by a distance equal to two fin thicknesses and one channel width. The lands left on the wheel are one channel-width wide. Each wheel slot is fitted with two tungsten ribbons and one molybdenum ribbon running the length of the mandrel from wheel to wheel. Shorter molybdenum ribbons are placed opposite the wheel lands in a similar manner. The assembly consists of alternate tungsten and molybdenum ribbons tightly packed (slightly looser at the outer diameter) around the Mo cylinder. The assembly is shown in this condition in Fig. 40. In the next step, tungsten will be vapor deposited on this assembly to obtain the desired tube wall thickness. Subsequently, the molybdenum components will be dissolved. End pieces will be attached, also by vapor deposition.

A preliminary evaluation of the proposed method was made using copper to

Fig. 40. Tungsten-molybdenum ribbon assembly to be used in fabrication of tungsten heat pipe.

represent tungsten and aluminum for molybdenum. Electrolytic deposition was used in place of vapor deposition. The test was highly successful. Figure 41 shows selected views of this copper heat pipe. There are 90 fins, each 0.0125 cm thick by 0.1 cm high. The groove width is 0.0225 cm.

CORROSION LOOP PRELIMINARY ENGINEERING DESIGN

An outline of the liquid metal loop program and a discussion of its objectives were given in the "Materials" section, p. 32. The preliminary engineering de-

sign of the tungsten alloy^{*}/lithium corrosion loop is summarized below. The shape of the loop, shown in Fig. 42, was selected to be consistent with available material forms, and fabrication and test facilities. All heavy components of the loop are supported in a vertical column above the pump electrode. The loop is free to expand from that point of support. Guide slots are provided elsewhere to constrain expansion to the loop plane only. The return leg, the only overhanging component,

^{*}In the initial tests, W-25Re-30Mo will be used.

(a) Before etching of aluminum mandrel and aluminum filler strips

(b) After etching of aluminum

(c) Finish machined

Fig. 41. Copper-aluminum electroplated heat pipe made to evaluate proposed method of vapor-depositing tungsten on molybdenum.

is a single length of preformed tubing comprising less than 2% of the total loop mass.

Heat is supplied to the loop by a concentric radiant heater and is rejected to the vacuum system walls mainly by

Fig. 42 Pumped corrosion loop.

radiation but in part by conduction at the pump bus bars. Heat rejection is controlled by secondary "bias" heaters, which vary the sink temperature apparent to the rejection leg of the loop. Pumping of the fluid in the reference design is done electrically by a straight-through conduction pump. Ability to fill, drain, and

pressurize the loop safely is provided by tanks which are supported from a column extending from the upper elbow. Argon pressurization lines and lithium transfer lines connect the loop to outside systems through these tanks.

In operation, the loop will be evacuated, filled from an external source, and pressurized through both tanks so that the fluid loop is a simple hydrostatic system operated under externally controlled pressure. The loop is brought up to temperature isothermally, and the required temperature difference is then established by control of the bias heater.

Heat Source

The heat source selected for the preliminary design is a radiant heating element in the form of a split cylinder entirely surrounding a loop vertical section. This loop heat addition(test) section is composed of a thick-walled tube, 0.5-in. o. d., 0.135-in. i. d., and 24 in. long. The heater element when assembled is 2 in. in diameter and 25.5 in. long. Because of the high length-to-diameter ratio of the heater element, precautions are taken to minimize uneven expansion and warping. The element is constructed symmetrically with the two halves mechanically interlocked and tension bands wrapped around the heater at assembly. The element, shown in Fig. 43, is supported at the upper arms with the lower end guided but free to expand. The electrical connection of the lower end is provided by stacked tungsten-foil straps. A wire mesh design is being carried as an alternative, pending performance tests on the reference design.

The shield pack surrounding the heater element is a free-standing 10-layer

Fig. 43. Heater electrode for pumped corrosion loop.

structure of half cylinders interleaved together, plus upper and lower shield packs to limit axial heat losses. Heater element arm pass-throughs and visual access holes for pyrometer measurement are provided.

With the 10-layer shield pack, the element was calculated to deliver 10 kW thermal power to the loop at 1900°K with an input of only 17.5 kW electrical power to the element at 2520°K. Data

from tungsten element manufacturers shows expected lifetimes in excess of 1000 hr at temperatures up to 2800°K.

Pump

The pump selected for the preliminary loop design is a straight-through conduction pump and is shown in Fig. 44. An indentation was made in the vacuum vessel wall so that the pole faces of an external magnet could be brought into

Fig. 44. Corrosion-loop pump body. The material is W-25Re-30Mo alloy.

close proximity to the pump section. Tungsten alloy electrodes are diffusion bonded to a length of 0.5-in. o. d. tubing to form the pump body. Vertical extensions of the electrodes engage the electrical pass-throughs, which support the entire loop. Holes drilled in the electrodes redirect the current and minimize thermal conduction losses from the loop.

Shielding the pump against radiant heat losses is complicated by the requirement that the pump, its shielding, and the vacuum vessel wall must all fit within the

1-in. air gap of the magnet. Gold-plated shields and vessel walls will be used to minimize heat transfer in this region. Calculations have shown a minimum heat loss thru the pump on the order of 3 to 4 kW, which is one-third of the thermal input power of the loop.

While the efficiency of this simple conduction pump is expected to be very low, only about 4-watts pumping power would be required to obtain the desired performance at 100% efficiency. The conduction pump was chosen since it can be fabricated per existing tungsten alloy techniques. A more extensive pump investigation program is described elsewhere and will provide the basis of an alternative selection should the performance of the conduction pump prove inadequate.

Heat Rejection

Heat is rejected from all surfaces except the heated section. Temperature control is achieved by various means of limiting this rejection. The problem of the pump electrode was already discussed. Of the total heat added in the heated section, about one-third is rejected at the pump, one-third in the bias control section, and one-third in other sections of the loop, such as upper and lower crossovers, elbows, loop guides, etc. Rough control of heat rejection is attained by adding or removing tungsten foil shields from such structure as necessary to bring the loop thermal balance within the controlling range of the bias heaters.

The bias heater elements are an open-mesh structure of about 40% porosity. By varying the power to the elements, more or less heat is allowed to be radiated from

the loop rejection leg to the vessel walls through the bias element. Element temperatures of 2230°K and power of 35 kW were calculated as sufficient to totally block heat flow from the control section of the loop. Because of the critical nature of the thermal control function of these heaters, two separate elements with parallel electrical connections are specified to allow normal shutdown should one fail. Replacement of failed elements has been kept a simple operation.

Junction Boxes (Elbows)

The necessity of providing one or more pipe tees to allow filling and draining of the loop required design of a fitting to permit weld joining of components without undue strain at the joints. Considerable simplification of loop fabrication is achieved by the use of the massive but versatile three-axis J-boxes shown in Fig. 45. Ample mechanical rigidity is obtained to relieve stresses on the welds, which are of the electron-beam standing edge type. The access ports are closed by seal welded plugs and backed up by mechanical fittings. The J-boxes are machined from solid billets of extruded and forged tungsten ternary alloy. Two of these joints were required by the fill-drain system selected.

Tanks and Piping

The fill-drain and expansion tanks, Fig. 46, are diffusion-bonded from the nominal loop alloy. Integral weld necks allow later attachment of connecting tube fittings by electron beam welding.

The height of the tanks was determined by expected density- and flow-induced

Fig. 45. Corrosion-loop junction box.

head differences plus incidental dynamic level variations of ± 2.5 in. without entrainment of cover gas. The volume of each tank was sized to hold the entire lithium charge plus 10% to minimize losses in the event of an accidental blowdown. The volume of the Li charge is approximately three times the net circulating system

Fig. 46. Corrosion-loop expansion tank.
volume (12.2 in.³). This results in a normal static fill level of from one-fourth to one-third the height of the tanks.

The diameter of connecting lines is sized so as to provide dynamic damping and to minimize both thermal and fluid interchange between the circulating and fill systems.

Figure 47 is a diagram of the loop with auxiliary components and interconnecting piping.

Loop Containment and Test Facility

The entire elevated-temperature loop assembly will be supported from an instrumentation spool within a 24-in. diameter ion-pumped vacuum chamber. The loop chamber hardware being prepared is compatible with both the 6000 liter/sec horizontal and 2400 liter/sec vertical vac-ion pumps shown in the center and upper field of Fig. 48. The vacuum test area shown will be used for a variety of high-temperature tests, including the corrosion loop.

Low Temperature NaK Test Loop

A room-temperature NaK loop was put into operation during this quarter and was used to test one model of the rotating dc-field induction pump. Figure 49 shows the complete system, with the 0.95 cm o.d. tube helix in the pump (lower left).

Figure 50 is a diagram of the various NaK loop components. Eutectic grade NaK is used (freezing point 262°K) with an argon cover gas. Maximum system pressure is 3.5 bar; above this pressure the relief valve allows the NaK to flow into the dump can. The cylindrical sodium-potassium reservoir (with glass end-windows) is normally half-full during loop operation. During pumping, the flow path is from the bottom of the reservoir through the pump

Fig. 47. Corrosion-loop lithium supply system.

and back into the reservoir through the top line. This gives a visual indication of flow and also serves to trap oxide formations in the reservoir.

NaK charging of the loop is done only after the system has been cleaned, evacuated, and flushed with argon gas a number of times. Some oxides form over long periods of time, but these are pumped into the reservoir and have not caused blocking of the flow path. Operation to date has been essentially free of problems as far as contamination is concerned.

The system instrumentation consists of a 0.43-cm orifice and three pressure transducers. Flow is detected by monitoring the pressure drop across the orifice and across the pump. Pump output pressure is monitored directly. Initially, strain-gauge pressure transducers compatible with NaK were installed. Operation of the loop soon indicated the desirability of being able to change these transducers without opening the loop to air. Flexible diaphragms (bellows assemblies) were tested and found to be suitable for isolating

Fig. 48. High vacuum test facility. It is planned to install the high temperature corrosion loop atop system GE-3.

Fig. 49. NaK test loop with dc helical induction pump.

the transducer element from the liquid metal through some intermediate fluid. This also eliminates the necessity of using transducers compatible with NaK and allows more precise pressure measurement. These diaphragm units have been installed.

The following prototype pump ducts were fabricated from stainless steel for testing in the rotating dc field pump:

- 1) 0.95-cm o. d. tubing. A 9-1/2-turn double helix (Fig. 51). Wall thickness 0.1 cm.

- 2) 1.25-cm o. d. tubing. A 7-1/2-turn double helix. Wall thickness 0.1 cm.

- 3) 1.6-cm $\times$ 0.32-cm rectangular channel. A six-turn double helix (Fig. 52). Fabricated from 0.038-cm sheet stock.

The analytical output curves for these ducts were shown in Progress Report No. 5. Best results were expected with the rectangular duct.

The 0.95-cm o. d. tube helix yielded lower than expected performance, showing a maximum pressure rise of about 2 psi and a maximum flow rate of about 1 gal/min. Preliminary tests showed that performance of the two other configurations was also below expectation, but time was not available for careful measurements

Fig. 50. Room temperature NaK loop. The various numbered and lettered components are valves.

before this experimental setup had to be dismantled in order to prepare for testing of conduction pumps of the type selected for the high-temperature corrosion loop (already discussed).

Two types of dc conduction pumps were selected for testing in the NaK loop. These are shown in Fig. 53. The simplest consists of a simple straight tube with conducting sidebars and is the basic design proposed for the 1800°K corrosion loop. This unit will be tested in conjunction with the dc magnet shown in Fig. 54, and will

provide a design guide for the high temperature configuration, and serve to indicate the range of current and flux density required for the corrosion loop. Space and material restrictions in the corrosion loop greatly limit the range of design for this type of pump.

The second dc pump is a hairpin type which could fit into a particular flanged housing on the corrosion loop pressure vessel. This configuration has some installation advantages, although no plans exist at present for incorporating it into

Fig 51 Fluid duct coil for dc helical induction pump The outside diameter of the tubing is 0.95 cm

Fig 52 Built-up fluid duct coil Duct has a square cross section 1.6 x 0.32 cm

Fig. 53. Two types of dc conduction pumps to be tested.

the corrosion loop. The dc current is supplied through a center bus bar and returned through two outer side bars. Its

performance is not expected to be any better than that of the straight-section pump.

Fig. 54. Conduction pump dc magnet.

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