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To: Mr. J. M. Simmons, Chief
Fuels & Materials Development Branch
Division of Reactor Development
United States Atomic Energy Commission
Washington 25, D. C.

From: L. M. Raring, P&WA - CANEL

Subject: Fuel and Materials Highlights:
SNAP-50 and Advanced Programs

cc: Mr. A. J. Alexander, USAEC, CANEL Project
Office (2)

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CNLM-6155

February 18, 1965

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by H. C. T.C. date SEP 17 1973

Mr. J. M. Simmons, Chief
Fuels & Materials Development Branch
Division of Reactor Development
United States Atomic Energy Commission
Washington 25, D. C.

Dear Jules:

The attached abstracts of the highlights of our fuels and materials work may be useful to you. Part I covers the SNAP-50 work and Part II the advanced work. I am including extra copies in case you may wish to pass one along to Merrill Whitman or others in the Division.

It is particularly interesting to note the close coupling between the research work your Branch has sponsored and the SNAP-50 engineering program. Fuels and structural alloys are especially noteworthy. The UN and UC research, which we started only about four or five years ago practically from scratch, is now firmly established in the SNAP-50 program. Our latest irradiation tests on UN have been particularly encouraging. Also, the work we started several years ago to improve the strength-temperature design margins of the Cb-1 Zr alloy is now fully integrated in the SNAP-50 program. The FWC-11 alloy is showing excellent strength and fabricability. Our advanced alkali metal work - corrosion studies and chemical and physical properties - has also been fully exploited in the SNAP-50 program, from analytical studies to test specifications. These facts reflect a prompt response of advanced fuels and materials research planning and performance to anticipated engineering needs.

I hope these summaries will be useful to you and I look forward to our March 1st meeting to plan and discuss the FY 1966 program.

Very truly yours,

PRATT & WHITNEY AIRCRAFT

SPECIAL REVIEW FINAL DETERMINATION	Reviewers	Class.	Date
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L. M. Raring
Chief, Metallurgical & Chemical
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ANNUAL REPORT
SIGNIFICANT TECHNICAL ACCOMPLISHMENTS
FUELS AND MATERIALS DEVELOPMENT
CALENDAR YEAR 1964
PRATT & WHITNEY AIRCRAFT - CANEL

PART I
SNAP-50 PROGRAM

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9 III

I Fuels Development

A. Irradiation Evaluation

1. Twenty-five irradiation tests were analyzed with the following major findings:

- (a) Both UC and UN performed well under test conditions simulating 21st reactor service. A UN test showed no adverse effects after nearly 6000 hours at an average cladding temperature of 1975F; burn-up was 1.0% (of total U atoms). A similar UC test, terminated after 2500 hours because of equipment failure, showed close to 0.5% burn-up with no adverse effects. These results further substantiated the feasibility of UC and UN for the 21st-50 reactor application. The UN performance was particularly significant in this regard.
- (b) UN also performed well in another irradiation test in which the surface temperature was between 2100F and 2200F. A burn-up of 1.2% was achieved in 1600 hours. Pin swelling was less than 1.0% and gas release less than 12%. A 3000 hour test to 1.0% burn-up at approximately 2200F surface temperature showed a 2.0% pin swelling and 32% gas release.

Data became available February, 1967.

2. These irradiation tests were made with Cb-1 Zr alloy clad lined with tungsten. Fuel and clad dimensions, void volume, and irradiation conditions were representative of design conditions to the extent permitted by test reactor limitations.
3. Good correlation was established between gas release, volume change, and burn-up for both UC and UN. These correlations were relatively independent of temperature, at least within the range tested (1800-2200F surface and 2200-3000F center-line).
4. Both fuels showed progressive swelling with burn-up but the rate was higher for UC: a limiting volume change of 8.0% (which produced excessive pin swelling) was reached with UC at about 1.2% burn-up. In the case of UN, the swelling rate remained quite low as burn-up progressed beyond 1.0% but a sudden surge of gas release occurred between 1.5 and 1.6% burn-up. The calculated gas pressure associated with this release (about 20% of total gas produced) approached the strength limit of PWC-11 alloy cladding. Burn-ups beyond 1.6% for UN would thus require stronger cladding (such as W-Re) or lower gas release rates.

5. The burn-up capability of UC [REDACTED] was not improved by
- (a) reduced density to facilitate fission gas release with minimum swelling
 - (b) the addition of small amounts of ZrC to UC
 - (c) the use of a central void or extra void length to reduce fission gas pressure

These must be considered as preliminary tests since they covered only restricted temperature and burn-up conditions.

6. In general the irradiation test analyses showed good correlation between structure and chemistry of the fuel on the one hand and irradiation performance on the other. It was indicated that the superior irradiation performance of UN was probably associated with a fine dispersed phase identified as UO_2 .

B. Compatibility Evaluation

1. The following major observations are based upon a total of 89 tests:
- (a) Tungsten provides an excellent chemical barrier between UC or UN and Cb-1 Zr cladding. In the case of UN, no significant reactions occurred in out-of-pile tests in 7000 hours at a temperature of 2250°F. In-pile tests showed no significant effects for times up to 6000 hours
- [REDACTED]

- 4 -

at 2000°F. (These represent maximum test conditions investigated.) Even where lithium was admitted to the fuel-barrier-clad interfaces, only limited reaction was noted in 7,000 hours at 2250°F.

- (b) In the case of UC, tungsten was effective in preventing clad reactions at temperatures and times up to 2050°F and 5000 hours, respectively (maximum conditions tested). Under these same conditions, reaction was severe when lithium was admitted to the system. In-pile, the lithium free system did not show appreciable effects after 3000 hours at 2200°F.
- (c) Tantalum was less successful as a fuel-clad barrier. In the case of UN, it did not significantly improve stability over that of the basic fuel-clad system. For UC systems, the tantalum gradually absorbed carbon from the fuel at 2200°F to form an essentially massive carbide barrier. This slowed down the reaction rate but hyperstoichiometric fuel compositions were required to prevent formation of free uranium. Tantalum was therefore dropped from further consideration as a UC-clad barrier for 2200°F service.

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(d) At lower temperatures (2050°F max.) UN was compatible with Cb-1 Zr for times up to 6000 hours: in-pile tests for times to 1700 hours showed only negligible reaction. Reaction between UC and Cb-1 Zr cladding became objectionable at temperatures between 2000°F and 2200°F, in long time tests (> 3000 hours).

C. Production

1. Approximately 25 kg of UN and UC powder was prepared. The production cycle time for UC was cut in half through process development. Yields were increased through refinement process control. Closer control of the physical condition of the uranium metal resulted in improving sintering qualities of the converted fuel powders.
2. Approximately 1200 pellets of UC and UN were produced. A semi-automatic cold pressing technique was developed resulting in increased production rates.
3. A total of 300 fueled pins were assembled with Cb-1 Zr or FWC-11 cladding for irradiation and compatibility test. Improvements were made in fabrication practices and an electron beam welding technique was developed.

4. Improved tungsten barrier quality was achieved through the adoption of vapor deposited coatings to replace loose tungsten foils. Quality of vapor deposited tungsten was improved through process development. An electro polishing technique was developed for final finishing of vapor deposited coatings to specified dimensional limits. Initial results to develop welded W-Re sleeve barriers were encouraging.

II Structural Materials

A. Fuel Cladding

1. Priority was given to the PWC-11 alloy with a nominal composition of Cb-1 Zr-0.090 C. This alloy was developed under the Advanced Materials Program to replace Cb-1 Zr alloy.
2. The PWC-11 alloy rupture strength was as much as three times the strength of Cb-1 Zr at temperatures between 2000°F and 2400°F. This exceeded the development goal and met SNAP-50 design targets, which the Cb-1 Zr alloy did not.
3. Approximately 130 creep rupture tests of fuel cladding materials were conducted. The test specimens were taken from commercial tubing production lots and were dimensionally representative of fuel element design requirements. Tests were performed in lithium at temperatures between 2000°F and 2400°F, stresses between 1000 and 10,000 psi, and times between 50 and

and 5000 hours. The specimens were loaded internally through high pressure helium to simulate fission gas pressure generated during irradiation.

4. The fuel cladding materials tested included the following:

<u>Designation</u>	<u>Developed by</u>	<u>Nominal Composition</u>
PWC-11	PWA - CANEL	Cb-1 Zr-.09 C*
D-43	DuPont	Cb-10 W-1 Zr-0.1 C
T-111	Westinghouse	Ta-8 W-2 Hf-0.01 C
CS-1831	PWA- CANEL	Cb-1 Zr

*carbon range - 750 - 1050 ppm

The tube specimens were generally .250 in. diameter with a .020 in. wall. In some cases they were lined internally with a thin walled tantalum or tungsten sleeve. Bonding between the sleeve and the outer tube was uncertain.

5. Processing variables and conditions were evaluated, particularly:
- (a) solution and age heat treatments
 - (b) high temperature, long time exposure to lithium, vacuum, and inert gas environments
 - (c) cold swaging after solution treatment
6. Extrapolation to 10,000 hours shows the following approximate strength comparisons:
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<u>Alloy</u>	<u>Condition</u>	Extrapolated ⁽¹⁾ <u>Rupture Strength</u> 10,000 hrs, 2200F psi	Minimum ⁽²⁾ <u>Rupture</u> <u>Ductility</u> %
PWC-11	Annealed, 2200	1000	30
PWC-11	(Swaged (Sol. H.T. - 2900F (Aged - 2200F	1500	3
PWC-11	(Sol. H.T. - 2900F (Swage (Age - 2200	2100	3
PWC-11	(Sol. H.T. - 2875 (Age - 2200	2200	3
PWC-11	(Sol. H.T. - 2700 ⁽³⁾ (Age - 2200	1700	16
D-43	Annealed - 2200	1600	26
D-43	(Sol. H.T. - 2900 (Swage (Age - 2200	2300	6
T-111	Annealed 2200	6000	30
Cb-1 Zr	Annealed 2200	750 ⁽⁴⁾	--

- (1) Extrapolated from test times between 50 and 5000 hours, using Larson-Miller coefficients determined through long time (10,000 hrs) Cb-1 Zr tests.
- (2) Ductility measured as percent diametric growth before failure. Data is based upon relatively short time tests.
- (3) Current standard heat treatment.
- (4) Included for comparison.

7. Some of the more important observations were:

- (a) Solution heat treat temperatures must be kept below the

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grain coarsening range to avoid excessive grain growth, and to improve rupture ductility. Lowering of the solution treatment temperature is accompanied by some strength loss.

(b) Cold swaging or overaging reduced rupture strength.

(c) Close fitting tungsten or tantalum sleeve inserts improve rupture strength by 5 to 10%.

8. Preliminary evaluation of W-25 Re alloy suggests strengths at 2200F of around 5 to 7 times that of PWC-11 and twice that of T-111 alloy. Based upon this and the additional advantages of excellent fuel and coolant compatibility, seamless W-Re tubing was obtained for thorough testing: initial results were promising. A development program was also started on fabrication of welded W-Re tubing.

B. Pressure Vessel and Piping Materials

1. Principal attention was given to the evaluation of alloys to replace the Cb-1 Zr composition used on the LCRE program. The basic objective was to improve the strength-weight margins in the design of the high temperature SNAP-50 structural components.
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2. A two-fold creep strength improvement was shown by FWC-11 alloy over the original Cb-1 Zr (LCRE) structural alloy. Based upon 3000 hour tests, the estimated stress to produce 1% creep in 10,000 hours at 2000°F were:

Cb-1 Zr - 2700 psi

FWC-11 - 5000 to 6000 psi

The spread in the FWC-11 strength represents the effect of different working temperatures: The higher strength value is associated with a 2900F extrusion and the lower value with a 2300°F extrusion.

3. Rupture tests of FWC-11 alloy extrapolated to 10,000 hours showed strengths of between 6500 and 12000 psi at 2000F. This is more than double the rupture strength of Cb-1 Zr alloy under the same conditions.
4. Strength evaluation tests of other advanced commercial and CANEL developed columbium and tantalum alloys indicated the following strength potentials:

<u>Alloy</u>	<u>Composition</u>	2000F	
		<u>1% Creep</u> <u>10,000</u> <u>Hrs.</u> <u>psi</u>	<u>Static</u> <u>Yield</u> <u>Strength</u> <u>psi</u>
FWC-188*	Cb-18 W-8 Hf	9,000	45,000
T-222	Ta-9.5 W-2.5 Hf	10,000	60,000
FS-85	Cb-27 Ta-10 W-1 Zr	7,000	---
D-43	Cb-10 W-1 Zr-0.1 C	5,000	35,000

*Developed under CANEL Advanced Material Program.

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5. The PWC-11 alloy was selected for further engineering test evaluation. It was felt that the Cb-1 Zr alloy technology developed under the LCRE program would be more directly applicable to the PWC-11 alloy than to alloys with wider compositional variations. This was confirmed by subsequent success with large scale melting, extrusion, die forging, tube drawing, and welding.
6. A total of approximately 200 structural alloy tests, mainly creep-rupture, were performed. Besides uniaxial creep-rupture, they included tensile and bi-axial tube burst and were conducted in lithium, vacuum, argon, or helium.
7. The PWC-11 alloy demonstrated excellent welding qualities as evaluated by restrained patch weld tests. A moderate annealing treatment effectively suppressed post weld aging of the alloy.

C. Surface Coatings

1. Major effort was directed toward the evaluation of oxidation protective coatings to meet SNAP-50 pre-launch requirements of 1000 hours in 1000F air. Best results were obtained with PK-35. This is a slurry coating based principally on tin, aluminum, titanium and chromium and developed under the Advanced Materials Program. Process modifications required to meet shop practice and equipment needs were identified.

2. Tests in 2000F argon were initiated to evaluate coatings for protection of PWC-11 components in contaminated inert gas environments. Other tests showed only minor interaction between the PWC-35 coating and PWC-11 alloy substrate: approximately 0.002 inches of structural alloy was lost in 2500 hours at 2000F.

D. Irradiation Evaluation

1. Design was completed and fabrication initiated on an irradiation experiment to assess the effect of fast neutron irradiation in the properties of PWC-11 alloy.

III Alkali Metal Coolant Research and Corrosion Studies

A. Loop Tests

1. The chief purpose of these tests was to evaluate structural materials under representative SNAP-50 corrosion conditions, particularly as regards temperatures and times.
2. Compatibility of structural materials with alkali metals was evaluated through twelve loop tests:
 - (a) Eight lithium tests in which fuel cladding and structural alloy specimens were exposed to flowing lithium at 2200F for times between 200 and 2200 hours. In all cases, the loop material was Cb-1 Zr alloy. The alloys under tests (PWC-11, PWC-33, W-25 Re, T-111, FS-85) were inserted in the hot (2200°F) section of the circuit.

- (b) Three Cb-1 Zr alloy loops in which potassium was boiled at around 1900°F for 3000 hours. The specimens under test were inserted in the boiling, condensing, and condensate regions of the loops.
- (c) One type 316 stainless steel loop through which NaK was pumped isothermally (1250°F) for 3000 hours. Specimens of Cb-1 Zr alloy, inserted in the loop circuit, were withdrawn at intervals for investigation.
3. The principal purpose of the lithium loops was to determine the stability of PWC-11 alloy coupled with Cb-1 Zr alloy (low carbon) under dynamic flow and thermal conditions. In three cases, PWC-11 alloy specimens showed no significant strength loss and only minor carbon depletion after 200 hours (1 test) and 1000 hours (2 tests) in 2200°F flowing lithium. In another loop, significant carbon loss was observed after 2200 hours in 2200°F lithium. In this case, oxygen contamination occurred during test through impurities in the inert gas environment. Additional testing is in progress to resolve uncertainties and to evaluate stability in a monometallic system.
4. The boiling potassium loop tests demonstrated that Cb-1 Zr, PWC-11, and TZM (molybdenum alloy) are all fully compatible with Cb-1 Zr and potassium under the test conditions noted. All these alloys are prominent candidates for boiler, piping, pump housing, and turbine component applications. One of the
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potassium loops was modified to provide a materials/temperature analogue of a direct condensing system and included type 316 stainless steel in the low temperature (1200°F) regions. Preliminary evaluation showed no obviously severe effects. Flow rates, however, were far short of design conditions.

5. The NaK loop provided a first approximation of an indirect, single phase, radiator system. No severe Cb alloy-stainless steel reactions were observed under the isothermal test conditions. Some possibility of nitrogen transfer difficulty was indicated.

B. Physical Property Measurements

1. The vapor pressure of potassium was determined at temperatures between 1455°F and 2230°F for application to Rankine cycle analyses.
 2. The vapor pressure of lithium was measured between 1900°F and 2800°F for system design and hazards analysis.
 3. Viscosity and electrical resistivity data were established for molten lithium. The resistivity data to 2630°F confirmed thermal conductivity values extrapolated from measurements at lower temperatures.
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IV Materials Laboratory General Services

A. Analytical

1. New or improved techniques were developed for the analyses of tungsten base alloys, remote (hot-cell) analyses of irradiated fuel samples, and porosity determinations on fuel pellets.

B. Braze Assemblies

1. Evaluation of a number of braze alloys for application to columbium components in lithium or NaK service led to the selection of Ti-8.5 Al. Brazed samples successfully withstood 10,000 hours exposure to NaK and lithium under simulated test components conditions.

C. Electrical Insulation Improvement

1. Inferior electrical heater and thermocouple performance in connection with irradiation test work led to a detailed investigation of ceramic used. It was found that impurities such as SiO_2 , present in most commercially available ceramics were responsible for contamination of cladding. Specifications were provided and chemical controls established with markedly improved service performance. Processing methods were established to improve the electrical resistivity of insulation in thermocouples and heaters.

D. Ultra High Vacuum Effects

1. Studies of the effects of simulated space pressure combined with service temperatures on structural alloys were made with the following results:
 - (a) The PWC-11 alloy showed complete chemical stability at 2000°F under a nominal pressure of 1×10^{-10} torr for 1000 hours. The presence of excessive oxygen in the metal did not affect stability of the carbon.
 - (b) It was tentatively established through short time reaction rate tests in the range of 10^{-5} to 10^{-7} torr that oxygen partial pressure in vacuum chambers should be maintained below 6×10^{-9} torr to provide adequate protection to a thin walled Cb-1 Zr/lithium system at 2000°F for 10,000 hours.

V Special Materials and Process Development

A. Bearing Materials

1. Bearing materials were evaluated for service in lithium at 1000°F and NaK at 600°F. These tests are prerequisite to the selection of materials for the full scale liquid metal pump test program.
 2. Two types of tests were conducted: compatibility and wear. Approximately twenty different materials were tested for compatibility with lithium at 1100°F for times up to 7000 hours.
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In general, cermet of refractory metal compounds such as WC, TaC, MoC, or TiC with molybdenum or columbium binders stood up well. Others with small percentages of cobalt (< 5%) as the binder were satisfactory. Greater percentages of nickel or cobalt led to lithium attack.

3. The wear tests were made in both lithium (1000°F) and NaK (600°F) using a shoe-disc specimen couple. About 50 tests were made: best performance in both fluids was obtained with a WC cermet (Kennametal 7178) run against itself. Plasma sprayed WC coatings and carburized coatings on Cb-1 Zr alloy showed promise in combination with Kennametal 7178 shoes. A bearing material coating on the pump shaft is preferred because it allows a smaller pump and avoids attachment design problems.

B. Liquid Metal Pump Drive Motor Materials

1. Work in this area was confined to development and evaluation of metal-to-ceramic joints required in fabrication of the bore seal assembly. The seal protects the stator core materials against alkali metal attack: ceramic is required to meet electrical properties requirements.
2. Following initial screening tests of a number of experimental braze alloys, Ti-8.5 Si was selected for fabrication development. Three thick wall BeO/Cb-1 Zr brazed cylindrical assemblies were fabricated and tested: the first leaked at the

joint and the second through the BeO body. The third, representing improved techniques, endured twenty-five 1200°F/1800°F thermal cycles in lithium plus a 1000 hour exposure to lithium at 1100°F. Tests are presently in progress to determine the lithium containment capability of thin walled BeO.

C. Moderator and Shield Materials

1. A comprehensive review of the BeO and LiH literature was conducted to catalog thermal, chemical, and mechanical properties for SNAP-50 design reference. Specific design cases were identified where either no pertinent data was available or where extrapolations were considered to be particularly uncertain. Test requirements to meet minimum data needs were defined.
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ANNUAL REPORT
SIGNIFICANT TECHNICAL ACCOMPLISHMENTS
FUELS AND MATERIALS DEVELOPMENT
CALENDAR YEAR 1964
PRATT & WHITNEY AIRCRAFT - CANCEL

PART II
ADVANCED MATERIALS PROGRAM

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AUTHORIZED CLASSIFIER

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I Fuels Research and Development

A. Irradiation Studies

1. A mechanism was devised to explain high temperature swelling and fission gas behavior in UC and UN. This mechanism was based upon optical and electron microscopy and physical measurements relating fuel swelling and fission gas release with the formation and growth of gas voids in the grain boundaries.

The basic steps in this mechanism are as follows:

- (a) Small fission gas bubbles migrate, presumable under the influence of a temperature gradient, until they reach grain boundaries where they become bound. This is accompanied by fuel swelling with relatively little gas release.
 - (b) Elongated intergranular voids are formed as a result of bubble coalescence. When the elongated voids become connected, gas release is greatly accelerated.
 - (c) The elongated voids tend to spheroidize because of thermodynamic instability. The degree of sphericity depends upon the diffusion rates of the fuel atoms. Spheroidization delays void interconnection and the related gas release.
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2. UN performed better than UC with regard to gas release and swelling under similar conditions of burnup and temperature. For a given degree of swelling, however, UN released a larger fraction of fission gas than UC. This was consistent with the slower self-diffusion rate and therefore the reduced tendency for gas void spheroidization in UN than UC. Up to a limiting burn-up level, however, UN showed less swelling and lower gas releases in spite of the greater tendency for gas voids to become interconnected. When swelling approached 20% (density decrease) 70% of the gas was released. This indicates that practically all of the fission gas was present at the grain boundaries at the time voiding became continuous.

3. Electron microscopy of irradiated UN fuel specimens showed a high transgranular fission gas bubble density. UC has exhibited a structure in which bubbles were located predominantly at grain boundaries.

B. Physical Studies and Properties Tests

1. Gas Nucleation and Migration

A finely dispersed precipitate in UN was identified as UO_2 by electron microscopy and diffraction studies. The particle density was in the order of 10^{13} to 10^{15} particles/cm³.

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Analysis of the fuel showed 1000-2000 ppm oxygen. This fine dispersion was stable for long periods (3000 hours) at 1250C. Coalescence occurred under irradiation at this temperature, however, and the particle density was reduced to about 10^{12} particles/cm³. It was postulated that this dispersed phase in UN slows down the migration of fission gas to the grain boundaries, thus minimizing fuel swelling and gas release at a given burn-up level. UC, with a higher swelling rate with burn-up, did not show a dispersed phase.

2. The heat of sublimation of elemental uranium was 125 kcal/mole as determined by thermodynamic Langmuir UC analysis of vapor pressure data. The generally accepted value is 117 kcal/mole. The vapor pressures of N₂ and uranium over UN_(s) were defined through Knudsen experiments in the temperature range 1910K to 2265K by the equations

$$\begin{aligned}\log_{10} P_U &= 6.32 - 2.53 \times 10^4 T^{-1} \\ \log_{10} P_{N_2} &= 8.49 - 2.92 \times 10^4 T^{-1}\end{aligned}$$

The standard heat of formation at 298K was -74.5 kcal/mole by Third Law analysis of the vapor pressure data.

3. The thermal conductivity of stoichiometric UC varied from .223 watts/cm°C at 1015°C to .184 watts/cm°C at 1550°C. Above 1400°C the thermal conduction was predominantly by an electronic mechanism. Contamination with 2600 ppm oxygen and 1400 ppm nitrogen lowered the thermal conductivity 20% at 1100°C. A negative deviation, corresponding to only 10% for 80% dense UC, was found in the simple conductivity-porosity relationship.
4. The thermal conductivity of UN was significantly higher than UC, ranging from .272 watts/cm°C at 1000°C to .286 watts/cm°C at 1375°C. The electronic contribution to thermal conduction does not appear to be large.
5. The effect of temperature on the compressive creep rates of UC and UN between 1100°C and 1300°C at 6000 psi were as follows:
<u>Composition</u>	<u>Creep Rate In/In/Hr</u>
UC (4.85% C)	$210 \times \frac{-22,000}{T}$
UC (4.80% C)	$23,000 \times \frac{-26,000}{T}$
UN	$242 \times 10^7 \times \frac{-45,000}{T}$
6. A one mil thick tungsten barrier prevented chemical interactions between stoichiometric UC and Cb-1 Zr alloy for 10,000 hours at 1200C.

C. Preparation

1. An arc plasma technique was developed for the production of UN spherodized particles. Nitrogen losses which occurred were re-stored by heating in a nitrogen atmosphere under controlled temperature-pressure conditions.

II Structural Alloy Development

A. Cb-Zr-C Alloy Development

1. The addition of approximately 0.1 weight percent carbon to the Cb-1 Zr alloy produced a 100 to 150% improvement in tensile and rupture strengths between 1095 and 1200C.
 2. The Cb-1 Zr-0.1 C alloy (PWC-11) could be readily fabricated at high temperatures or at room temperature with no significant change in practices developed for the Cb-1 Zr alloy.
 3. The elevated temperature strength properties of PWC-11 were strongly dependent upon thermal-mechanical factors. Temperature-reduction parameters associated with maximum strength of forged material were established. Good correlation was shown between fine structural detail (electron microscopy) and strength.
 4. Cold working of forged material reduced the elevated temperature (1200C) strength by about half. Solution heat treatment was effective in restoring most of this loss in cold worked sheet and tubing.
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5. Recovery of cold worked sheet started at approximately 1800°F with full recrystallization between 2600 and 2700°F in one hour. Grain coarsening occurred above 2800 to 2900°F.
6. Age hardening of welded PWC-11 was suppressed by post weld annealing at 1200°C with full restoration of bend ductility. The alloy was fully ductile in the as-welded condition.
7. Additional strength improvements were obtained by increasing the zirconium and carbon concentrations to 3 atom percent. Tungsten additions did not improve the strength-density ratio.

B. Non-Aging Weld Alloys

1. The relationship: $(a/o) \text{ Yttrium} = 1.30 (a/o) \text{ Oxygen} + 0.15$; was derived to express the loss of oxygen as a function of yttrium loss during the non-consumable arc melting of a series of Cb-Zr and Cb-Zr-C alloys. Yttrium additions decreased coring and grain size of arc cast materials. A Cb-1 Zr-1 Y alloy was ductile in both the as-welded and aged conditions suggesting the possibility of elimination of post weld annealing treatment.

C. Physical Metallurgical Studies of the Cb-Zr-C System

1. The columbium rich corner of the Cb-Zr-C system showed three phases at room temperature: beta (bcc, columbium-zirconium solid solution; delta (hcp), Cb_2C with as much as 3% zirconium

in solution; and gamma (fcc), a continuous series of solid solutions between ZrC and CbC. These phases were structurally analogous to those in the respective binary systems. No new ternary phase were observed.

2. The 1538C (2800F) isotherm of this corner of the phase diagram was characterized by: 1) a beta plus delta two phase field, 2) a beta plus gamma two phase field, and 3) a beta plus delta plus gamma three phase region, which lies between the two phase fields. The columbium rich corner of the three phase was located at about 1.25 weight percent zirconium and less than 400 ppm carbon.
3. Two models were proposed for the strengthening of alloys in this region: (1) warm worked unrecrystallized material derived its strength from dislocation tangles in a subcell network, approximately one micron square, pinned by fine carbides; and (2) solution heat treated material was strengthened through the precipitation of a fine carbide particles along the grain boundaries.

D. Low Density - Alkali Metal Resistant Alloys

1. Two classes of alpha precipitation strengthened titanium alloys, Ti-Al-W-B and Ti-Al-C-Zr, showed strength levels equal to or better than that of 316 stainless steel in preliminary testing at 1200F. The Ti-Al-C-Zr alloy demonstrated a pronounced heat treatment response presumable through carbide solutioning and aging.

III Space Powerplant Coolants and Working Fluids

A. Solubility Studies

1. The apparent solubility of molybdenum in potassium with 500 ppm oxygen exhibited an Arrhenius-type temperature dependence in the range of 260C to 600C. This relationship is expressed by the following equation:

$$\log_{10} S \begin{matrix} \text{(atom fraction)} \\ \text{of Mo} \end{matrix} = -0.126 - \frac{3270}{T(^{\circ}\text{K})}$$

At temperatures between 600C and 1200C, the apparent solubility of molybdenum was a function of oxygen concentration in the potassium and was independent of temperature. A molybdenum to oxygen atom ratio of one to four found in the potassium samples was in excellent agreement with the separated reaction product identified as K_2MoO_4 . The solubility of columbium in lithium showed a slight temperature dependence over the range of 760C to 1540C but was independent of oxygen and nitrogen additions. The following equation was derived from averaged data:

$$\log_{10} S \begin{matrix} \text{(atom fraction)} \\ \text{of Cb} \end{matrix} = -4.777 - \frac{1094}{T(^{\circ}\text{K})}$$

B. Corrosion Mechanism Studies

1. The corrosion model developed to explain the behavior of Cb-1 Zr alloy in 1100C lithium proved applicable also to tantalum base alloys and carbon strengthened columbium base alloys.

2. Oxygen contamination of approximately 1000 ppm in Ta-9W, Ta-8 W-2 Hf (T-111) and Cb-1 Zr-0.1 C (PWC-11) alloys resulted in lithium corrosion of specimens quenched from 2000°C to simulate as-welded condition. Post weld annealing at 1200°C effectively stabilized T-111 and PWC-11 alloys but not the Ta-9 W alloy at this oxygen concentration. The stabilizing reaction was identified with hafnium-oxygen and zirconium-oxygen interactions.
3. Carbon addition to the Cb-1 Zr alloy system did not noticeably impair the stabilization effectiveness of zirconium.
4. Biaxial rupture tests showed no stress-induced corrosion effects in T-111 or PWC-11 alloys at stresses up to 10,500 psi and 4,000 psi respectively.
5. Alkali metal carbonates were stable in lithium at temperatures up to 400°C but were unstable at 600°C. Alkali cyanide was unstable in lithium at 600°C.
6. Iron was decarburized by lithium at 600°C and above. In the case of non-chromium alloys, carbon transferred from lithium to the alloy at 800°F. At 900°F, carbon transfer was reversed and decarburization occurred.

C. Materials Compatibility in Boiling Potassium

1. The Cb-1 Zr alloy showed negligible weight changes and no noticeable deposits in two 3000 hour natural convection boiling potassium loop tests at 1070°C maximum. The mechanical strength of test specimen inserts of PWC-533 alloy (Cb-5 Mo-3 Zr-3 Ti-0.1 C) in one loop and PWC-11 alloy (Cb-1 Zr-0.1 C) in the other was not affected.
2. A PWC-533 alloy monometallic natural convection boiling potassium loop was not essentially affected by test operation at 1095°C for 3000 hours.

D. Oxidation Protective Coatings

1. Silicide coatings on columbium were improved by use of magnesium, instead of tin, as a transitory liquid metal carrier.
 2. A three-layer coating comprised of silicide first layer, a tin-aluminum-titanium-zinc-chromium middle layer and a tin-aluminum-chromium-titanium outer layer provided lifetimes in 1100°C air consistently greater than 500 hours. The improved performance was identified with a barrier-like behavior of the silicide layer which retarded consumption of the Cb Al₃ phase by base metal.
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IV Space Radiator Fabrication Development

A. Compatibility

1. Beryllium reactions with the following metals at 650°C and 760°C in 800 hours varied from moderate to severe: Cu, Ni, Pd, Pt, Co, Cr, Fe, and Zr. Under the same conditions, reactions were only slight with Ag, Cb, Mo, Ti, V, and W.
2. Other radiator material combinations, excluding beryllium, were compatible at temperatures to 760°C and times to 800 hours.

B. Joining

1. Silver brazing was generally unsatisfactory for joining beryllium to stainless steel and columbium alloys.
 2. Brittle phase formation between beryllium and stainless steel was suppressed by diffusion bonding with silver.
 3. Several silver base alloys showed promise for joining of beryllium to other space radiator materials by diffusion bonding.
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