19. Materials Development for Isotopic Power Sources

R. G. Donnelly

Support of isotopic power programs includes work on general technology programs for ^{244}Cm and ^{90}Sr , and two application-oriented programs, SNAP-21 and SNAP-23. In addition, materials consulting was provided on the Isotope Kilowatt Program design evaluation study.

On the Curium Program we are selecting, developing, and testing encapsulating materials for ^{244}Cm -fueled heat sources for use in space. The immediate concern is for thermionic generator applications in the range of 1600 to 2000°C. This temperature range limits the choice of container materials to the refractory metals.

The purpose of the Strontium Program is to select optimum encapsulating materials and to develop capsule sealing techniques for ^{90}Sr -fueled isotopic heat sources designed to power thermoelectric generators. These generators require fuel capsule operation at temperatures to about 1000°C for extended periods of time. Iron-, nickel-, and cobalt-base alloys are the primary candidate encapsulation materials.

The SNAP-21 generators are designed for undersea applications and the SNAP-23 generators are for terrestrial applications. Qualified and reproducible welding and inspection procedures are necessary to better assure the integrity of the fuel containers for both normal and possible accident conditions.

CURIUM PROGRAM

Fabrication of Tungsten Capsules

R. E. McDonald

Two concepts are being investigated in the capsule testing portion of the Curium Program. These are vented and nonvented capsules fueled with 1 kw (thermal) of a ^{244}Cm fuel. With the technology developed over the past few years for the extrusion of tungsten,¹ two unalloyed arc-cast tungsten billets were

extruded in the Materials Processing Laboratory to produce pipe for the 3-in.-diam vented capsules. Two larger billets were extruded at the Fansteel Metals Center under our supervision to produce pipe for 4-in.-diam unvented capsules. Details of these extrusions are presented in Chapter 16 of this report. These four extrusions represent the largest arc-cast tungsten pipe extruded to date. Capsule bodies were machined from the extruded pipe, and end caps are being forged.

Development of CVD Tungsten Cladding Techniques

W. C. Robinson, Jr.

The chemical vapor deposition (CVD) technique was evaluated for the buildup of a heavy-wall tungsten vessel on a thin-wall tungsten container for curium fuel because this technique has the advantage of providing a capsule with no welds. This work required the development of a method for simulating the fueled thin-wall capsule and a modification of the usual deposition parameters to allow for the unusually high thermal gradients expected in the assembly during deposition.

Tungsten crucibles 1/2 in. in diameter $\times$ 2 in. long with an 0.030-in. wall thickness were used to simulate a 200-w (thermal) curium-fueled container on which a deposit was to be made. The steep temperature gradient obtained with a 200-w internal heater in the bottom third of the capsule was balanced with an induction heater to produce a uniform temperature over the entire length of the sleeve. Parameters were ultimately determined for the production of a nodule-free deposit with a maximum variation of 0.003 in. from the mean deposition thickness.

Mechanical Properties of Capsule Materials

R. W. Swindeman R. L. Stephenson

A significant fraction of the helium produced by the alpha decay of ^{244}Cm will probably be released by the fuel at thermionic temperatures. To assure integrity of a

¹R. E. McDonald and G. A. Reimann, *Floating-Mandrel Extrusion of Tungsten and Tungsten Alloy Tubing*, ORNL-4210 (February 1968).

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Fig. 19.1. Larson-Miller Parameter for T-111 Generated from Constant-Load Isothermal Creep Data. T is the temperature in $^{\circ}\text{K}$, and t is the time in hours.

capsule containing this isotope, the designer must either include a vent to exhaust the helium or provide sufficient void space to maintain stresses in the capsule wall at a tolerable level. In the nonvented concept one can take advantage of the predictable pressure-temperature history and optimize the design in terms of the power, weight, and life requirements.^{2,3}

The objective of the mechanical testing program is to obtain creep and rupture data for candidate capsule materials such as tungsten and tantalum alloys. Collecting data suitable for design purposes is emphasized. In addition, some tests are performed to assess the validity of the assumptions used in the design model.

With the decay of the curium fuel an unvented capsule will experience an increasing pressure but decreasing temperature, the latter affording an improvement in the creep resistance of the capsule material. Advantage may be taken of this behavior if a suitable model is available to predict creep under varying stress and temperature from constant-load, isothermal creep data. Three basic assumptions are required. (1) The fraction of damage incurred at any stress and tempera-

²J. P. Nichols and D. R. Winkler, *A Program for Calculating Optimum Dimensions of Alpha Radioisotope Capsules Exposed to Varying Stress and Temperature*, ORNL-TM-1735 (April 1967).

³R. L. Stephenson, *An Approximate Method for Determining Allowable Stress Rates for Capsules Containing Helium-Producing Isotopes*, ORNL-TM-1436 Rev. (November 1965).

Fig. 19.2. Rupture Life of T-111 as a Function of Stress Rate for Constant Stress Increase Rate and Exponential Decrease of Temperature from 1315°C .

ture is given by the ratio of time spent under those conditions to the time to failure under those conditions; when the sum of all the damage fractions is unity, failure occurs. (2) The time to failure at any stress and temperature may be interpolated from a parametric curve, based on experimental data, that relates time, temperature, and stress. (3) The parametric curve may be extrapolated to times, temperatures, or stresses outside the range of actual experimental data.

Because the equipment required to test the validity of these assumptions for tungsten and Ta-10% W is not yet available, we tested the tantalum alloy T-111 at lower temperatures. Figure 19.1 shows a time-temperature-stress correlation for rupture of T-111 based on the Larson-Miller parameter and constant-load isothermal data. Using this correlation we calculated the rupture life of T-111 under conditions of varying stress and temperature. Four tests were then performed in which the stress rate was maintained at a constant value during each test, while the temperature was decreased from 1315°C at an exponential rate corresponding to that for an alpha-emitting isotope with a half-life of 1 year. Experimental and calculated behavior for a number of stress rates are compared in Fig. 19.2. The agreement is very good.

Vaporization of Refractory Alloys

R. L. Wagner

The vaporization of TZM at pressures less than 10^{-7} torr and at $1650 \pm 35^\circ\text{C}$ was found to occur by the selective loss of the more volatile components. For example, after 67 hr the concentrations of titanium and zirconium in the deposit formed in a cooler portion of the system were seven times those in the original alloy. Extending the exposure time progressively decreased the concentration of these components in the deposit as a result of their depletion from the alloy. Since the vaporized components are important with respect to creep resistance of this alloy, these results indicate that the maximum permissible service temperature for TZM in vacuum is below 1650°C .

Brazing Alloy Development

N. C. Cole D. A. Canonico

The efficiency of an isotopically powered thermionic generator depends on good heat transfer from the heat source to the thermionic emitter. Optimum heat transfer would be obtained with a continuous metallurgical bond, and brazing appears to be an attractive joining method for this application.

Current technology indicates that the prime candidate material for both the capsule and emitter will be tungsten. Hence, the first requirements for braze filler metals are that they wet and flow on tungsten. In addition, brazing temperatures are limited on the high side to the melting point of pure Cm_2O_3 (2200 to 2300°C) and on the low side (approx 1900°C) by the requirement for some strength at operating temperatures of 1650 to 1850°C . Stability in vacuum at these temperatures is also required.

Table 19.1. Brazing Temperatures of Experimental Alloys for Brazing Tungsten

Alloy	Composition (wt %)	Brazing Temperature ($^\circ\text{C}$)
New Alloys		
100	Pt-30W	2300
110	Pt-50Rh	2050
Alloys Previously Developed		
4D	Ta-25Ti-25Zr	2100
TVN	V-30Ta-30Nb	2000
TVT ^a	V-35Ti-30Ta	1750

^aBrazing temperature outside the desired range.

We developed four new highly promising alloys and reevaluated a number of other alloys that were previously developed for refractory alloy brazing under the High-Temperature Materials Program. The compositions and brazing temperatures of some of these alloys are presented in Table 19.1. Several of the previously developed alloys appear to satisfy the wetting, flow, and temperature requirements; however, the high vapor pressure of some of the alloying elements, such as titanium and zirconium, may compromise the usefulness of these alloys. Accordingly, we undertook the development of new brazing alloys that do not include elements with high vapor pressures.

The first four alloys listed in Table 19.1 were used to make simulated capsule-to-emitter brazes. Visually, all of the brazes exhibited good filleting and flow characteristics. These specimens have undergone nondestructive tests including radiographic, penetrant, and ultrasonic inspections. All were considered acceptable based on the first two tests. However, two (4D and 110) exhibited nonbond indications during ultrasonic testing. These indications in all instances were localized and represented no more than 10% of the total cross-sectional area of the specimen.

Physical Properties of T-111

D. L. McElroy M. Barisoni
T. G. Kollie

The temperature dependences of certain physical properties are needed to 2200°K at pressures less than

Table 19.2. Smoothed Values of Electrical Resistivity and Specific Heat of T-111 from 300 to 1600°K

Temperature ($^\circ\text{K}$)	Electrical Resistivity ($\mu\text{ohm-cm}$)	Specific Heat ($\text{cal g}^{-1} \text{ } ^\circ\text{C}^{-1}$)
300	17.65	
400	21.75	0.0341
500	25.86	0.0347
600	29.84	0.0354
700	33.80	0.0360
800	37.55	0.0366
900	41.35	0.0372
1000	45.00	0.0377
1100	48.60	0.0381
1200	52.20	0.0384
1300	55.75	
1400	59.25	
1500	62.75	
1600	66.20	

10^{-6} torr to properly assess the heat transfer characteristics of the candidate curium-fuel containment materials. The properties of interest are thermal conductivity, electrical resistivity, total hemispherical emittance, and specific heat. The development of methods to measure the thermal conductivity of these materials to these high temperatures is described in Part I, Chapter 9 of this report.

We completed a series of measurements of the electrical resistivity, emittance, and specific heat of T-111. Smoothed values of the resistivity and specific heat as functions of temperature between 300 and 1600°K are given in Table 19.2. The values of the resistivity are greater than those determined for unalloyed tantalum, but the increase with temperature is smaller than expected for a 10% alloy (T-111 contains 8% W and 2% Hf). Furthermore, these values are nominally 1.7 $\mu\text{ohm-cm}$ lower than we previously obtained on another T-111 sample.⁴ The causes for these effects are receiving further study. The specific heat of T-111 exhibits greater temperature dependence

than reported for unalloyed tantalum, suggesting that the addition of 8% W increases the electronic density of states. This effect may, in turn, be related to the electrical resistivity anomaly cited above.

The total hemispherical emittance of T-111 is shown in Fig. 19.3 as a function of temperature for various surface and thermal treatments. This property is unstable in the range of 800 to 1150°K, an effect that is similar to that observed for pure tantalum.⁵ The emittance E_t of sample C during cooling from 1700°K in a vacuum of 5×10^{-7} torr can be represented by

$$E_t = 0.013 + 1.31 \times 10^{-4} T, \quad 1200 \text{ to } 1700^\circ\text{K} \quad (1)$$

⁴J. P. Moore, R. S. Graves, and T. G. Kollie, *Metals and Ceramics Div. Ann. Progr. Rept. June 30, 1967*, ORNL-4170, pp. 77-78.

⁵G. L. Abbott, *Total Normal and Total Hemispherical Emittance of Polished Metals - Part III*, WADD-TR-61-94 (1963).

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- T-111, POLISHED, SAMPLE A
- T-111, 11- μ in., ANNEALED
- ◇ T-111, SAMPLE C ON REHEATING
- ▲ Ta, ON HEATING (REF 1)
- T-111, 11- μ in., SAMPLE B
- ◆ T-111, SAMPLE C ON COOLING FROM 1700°K
- ▲ Ta, ON COOLING FROM 1700°K (REF 1)

⁴G. L. ABBOTT, *TOTAL NORMAL AND TOTAL HEMISPHERICAL EMITTANCE OF POLISHED METALS - PART III*, WADD-TR-61-94, U.S. NAVAL RADIOLOGICAL DEFENSE LABORATORY (1963).

Fig. 19.3. The Temperature Dependence of the Total Hemispherical Emittance of T-111 and Tantalum for Various Thermal Treatments and Surface Finishes.

On further cooling to below 1200°K, the emittance increases to values represented by

$$E_t = 0.058 + 1.31 \times 10^{-4} T, \quad 700 \text{ to } 1200^\circ\text{K}. \quad (2)$$

If the sample is not heated above 1600°K, the latter equation can be used to determine E_t in the range 700 to 1500°C.

STRONTIUM PROGRAM

Compatibility

J. R. DiStefano

Isotopic fuels such as SrTiO_3 , Sr_2TiO_4 , and SrO are currently being developed for use in thermoelectric

power conversion systems. To provide a reliable container for these heat sources, we are examining the compatibility of nickel, iron, and cobalt alloys — Hastelloy C, type 316 stainless steel, and Haynes alloy No. 25, respectively — with these compounds at temperatures to 1100°C. Nonradioactive strontium compounds have been used in the initial phase of this program to simplify handling and evaluation.

The test system is shown schematically in Fig. 19.4. The results of tests for 1000 hr at 1100°C indicate that Sr_2TiO_4 is the most inert strontium compound. No significant weight, chemical, or microstructural changes were noted in either the alloys or fuel specimens in tests involving Sr_2TiO_4 . Weight losses and subsurface voids were found in the alloys exposed to SrTiO_3 . A surface

ORNL-DWG 68-10672

Fig. 19.4. Schematic Drawing of Compatibility Test Capsule.

reaction zone containing large amounts of Cr, Mn, Ti, and O was present in the SrTiO_3 . Each alloy specimen exposed to SrO exhibited a weight gain, an increase in oxygen concentration, and a reaction zone 0.003 to 0.004 in. deep.

Room-temperature tensile tests of the sleeve specimens indicated that the interactions did not significantly alter the yield strength, ultimate tensile strength, or ductility of the alloys. Although a considerable weakening of the alloys occurred compared with before-test data on as-received material, the same effects were noted in control specimens that were heat treated in argon for 1000 hr at 1100°C. This effect, therefore, was attributed to grain growth and other microstructural changes not related to interactions with the strontium compounds. Longer time tests are under way, and those involving ^{90}Sr have been scheduled.

Welding

D. A. Canonico

Improvements in weld penetration capability are of interest for strontium-fueled heat sources. Although adequate penetration has been achieved by the electron-beam welding technique,⁶ there is incentive to improve weld penetration with the simpler gas tungsten-arc (GTA) welding equipment.

During the past year we investigated various parameters and joint designs for increasing weld penetration capability by the GTA process. Test welds were made on flat-plate specimens with a simple butt-joint configuration. No weld filler metal was added. First we used type 304 stainless steel. Although not a candidate capsule material, this material was selected because of its low relative cost and ready availability. Hastelloy C was also used when it became available. The butt-joint was used and a wide range of welding parameters, including preheat, were investigated. In addition, we studied the method of chilling the specimen during welding. These studies included gripping the specimen very close to the weld as well as about 1 in. away. The effect of variations in joint design and of titanium additions was studied briefly.

The results of these experiments are summarized in Table 19.3 for welds made with the optimum welding parameters. Penetrations of approximately 0.150 in. were achieved when the specimen was properly chilled. Preheating the weld to 300°C to simulate the effect of a

Table 19.3. Effect of Preheat and Joint Design on GTA Weld Penetration for Type 304 Stainless Steel and Hastelloy C

Joint Design	Preheat (°C)	Weld Penetration ^a (in.)
Type 304 Stainless Steel		
Butt	None	0.132 ^b
	300	0.180
Hastelloy C		
Butt	None	0.156
	300	0.180
Open	None	0.155
	300	0.172
Titanium insert	None	0.163
	300	0.172

^aWelding conditions: 300 amp, 10 v, 12 in./min travel speed, 1/8-in.-diam W-2% ThO₂ electrode, helium torch gas, chill grip level with top of joint.

^bChill grip approximately 1 in. below top of joint.

strontium fuel increased the depth of penetration to approximately 0.180 in., which is about 75% of the end cap thickness used. Table 19.3 shows that the two alternate joint designs (open and titanium insert) offer no advantage over the simple butt design.

SNAP-21 PROGRAM

Electron-Beam Welding Development

R. W. Gunkel

The SNAP-21 heat source capsule is a thick-walled Hastelloy C tube, 3.200 in. in diameter × 3.310 in. long, with 0.200-in.-thick walls and end caps. Gas tungsten-arc welding was first investigated for welding the caps in this capsule, but it failed to consistently produce joints having the required 0.100 in. penetration of defect-free weld metal without melting the edge of the capsule.⁶ This edge must be retained as a reference for ultrasonic inspection of the weld area. Electron-beam welding was subsequently investigated, and it produced high-quality joints having the desired combination of penetration and inspectability.

The weld geometry shown in Fig. 19.5(a) met the penetration and inspectability requirements on all nonpreheated capsules and on most capsules preheated to 300°C (the expected temperature of an isotopically fueled capsule of this design). However, edge melting was encountered in some of the preheated capsules, and methods were investigated to ensure a narrower weld.

⁶R. G. Donnelly, *Metals and Ceramics Div. Ann. Progr. Rept. June 30, 1967*, ORNL-4170, pp. 230-31.

The addition of a beam-corrector coil to the electron gun created a narrower and deeper weld of the type shown in Fig. 19.5(b). With such a narrow weld, however, a small amount of misalignment or out-of-roundness could lead to incomplete fusion. With ap-

propriate changes in beam focus together with the beam-corrector coil, we could produce joints of the type shown in Fig. 19.5(c). With this weld the joint is completely fused and the capsule edge can be reliably prevented from melting.

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Fig. 19.5. Cross Sections of SNAP-21 Electron-Beam Welds. (a) Initial weld geometry in which corner melting was occasionally encountered. (b) Narrow weld, alignment critical. (c) Optimum joint geometry. Etched. 16X. Reduced 19%.

Nondestructive Testing

K. V. Cook

We have adapted nondestructive testing techniques for two separate tasks. The first is testing the capsule material and the initial bottom closure weld before fueling. The second is remote inspection of the closure weld of fueled capsules.

We designed and fabricated a mechanical scanning system for capsule parts. This system duplicates the scan required for the hot-cell ultrasonic inspection of the closure welds. With this and the electronic portion of the SNAP-21 scanner we evaluated bottom closure weldments of unfueled capsules in our laboratory by the same technique to be used on fueled capsule closure welds in the hot cell. Fluorescent penetrants were also used for inspection of the bottom welds.

We drafted preliminary acceptance criteria for the ultrasonic inspection of closure welds based on the interpretation of an x-y recording of the cylindrical joint area as projected on a plane surface. A sample recording of our ultrasonic reference standard made to simulate a SNAP-21 capsule is shown in Fig. 19.6. Each diagonal pen trace represents one circumferential path around the capsule, and the spacing between traces represents an 0.006-in. increment along the capsule axis. The traces are skewed so that the vertical deflection of the pen caused by discontinuity indications can be detected. Holes with diameters from 0.015 to 0.070 in. were machined on a circumference about 1/8 in. from the top of the mockup capsule and

Fig. 19.6. Recording of Ultrasonic Response from SNAP-21 Capsule Calibration Standard with Various Hole Sizes.

at such a radial depth as to simulate flaws at the weld joint. An 0.015-in.-diam electro-discharge machined (EDM) hole served as the primary reference. This standard is used to calibrate and to recheck calibration of our ultrasonic instrumentation during inspection of all SNAP-21 capsule closure weldments.

Two fueled capsules were evaluated ultrasonically by remote techniques in a hot cell. Four closure welds (two bottom and two top) were inspected and found to be acceptable according to the criteria adopted.

SNAP-23 WELDING DEVELOPMENT

R. W. Gunkel

The SNAP-23 heat source capsule is a thick-walled Hastelloy C tube, 5 in. in diameter $\times$ 7.860 in. long, with 0.400-in.-thick walls and 0.600-in.-thick end caps. The original specification required a minimum weld penetration of 0.110 in. with an edge-weld design that included an 0.062-in.-diam machined groove 0.120 in. below the surface at the base of the weld. The purpose of this groove is to prevent propagation of cracks from the root of the weld and to promote plastic deformation in a region other than that including the weld metal if the capsule is subjected to high hydrostatic pressure during operation.

Fig. 19.7. Cross Section of a SNAP-23 Joint Electron-Beam Welded Without Preheat. Etched, 7X. Reduced 29%.

Techniques were developed for making satisfactory welds when the base metal was not preheated (Fig. 19.7). However, several attempts to produce similar welds in specimens preheated to 300 to 400°C (the temperature range for a fueled capsule) were unsuccessful. With preheat, the groove was filled with weld

metal and the effect of the groove was therefore nullified. In an attempt to solve this problem we are conducting experiments on joints in which the groove is larger and is located at a lower position with respect to the root of the weld.