391
2-10-77

LA-6618-MS

Informal Report

MASTER

Dr 685
UC-23 and UC-25

Issued: January 1977

Fabrication of Noble Metal Alloy Filter Vents for Radioisotope Thermal Generators

by

R. E. Honnell

los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87545

An Affirmative Action/Equal Opportunity Employer

**This work supported by the US Energy Research and Development
Administration, Division of Nuclear Research and Applications.**

**Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
Price: Printed Copy \$3.50 Microfiche \$3.00**

This report was prepared as an account of work sponsored
by the United States Government. Neither the United States
nor the United States Energy Research and Development Ad-
ministration, nor any of their employees, nor any of their con-
tractors, subcontractors, or their employees, makes any
warranty, express or implied, or assumes any legal liability or
responsibility for the accuracy, completeness, or usefulness of
any information, apparatus, product, or process disclosed, or
represents that its use would not infringe privately owned
rights.

FABRICATION OF NOBLE METAL ALLOY FILTER VENTS FOR RADIOISOTOPE THERMAL GENERATORS

by

R. E. Housell

ABSTRACT

Procedures are described for fabricating a filter vent of Pt-30 wt% Rh alloy for use in a 25-W radioisotope heat source. The filter vent is designed to operate at 1273 K with a helium leak rate between 0.01 and 0.001 cm³ (STP)/s.

I. INTRODUCTION

A continuing program at the Los Alamos Scientific Laboratory (LASL) is the fabrication and testing of radioisotopic heat sources for use in thermoelectric generators (RTG) that derive their power from energy released by decay of radioactive isotopes, primarily ²³⁸Pu. One use for an RTG is as a power supply aboard space craft, for example, the Viking craft was equipped with an RTG.

Because the primary decay modes of ²³⁸Pu are by alpha particles (helium) and by spontaneous fission, the fuel container requires a filter vent to release the helium while retaining particulates, or it may pressurize and rupture. The procedures used in fabricating the filter vents for the 25-W heat sources under evaluation at LASL follow.

II. MATERIAL AND DESIGN CONSIDERATIONS

A 25-W heat source is fueled with approximately 60 g of ²³⁸PuO₂, which release 28.8 cm³ (STP) of helium per year. A filter vent that leaks between 0.01 and 0.001 cm³ He (STP)/s will handle this gas load

and limit fuel cell pressure to ≤ 7 kPa (1 psi) during all possible flight conditions.

The filter vent must be compatible with both the ²³⁸PuO₂ and its fission products over a mission life of 100 Ms (3.2 yr) while operating at 1273 K. The helium leak rate of the filter vent must not change during its lifetime because of pluggage by particulates or because of pore closure by sintering. The filter vent must also have high impact strength and oxidation resistance. These requirements narrowed the choice of materials to noble metal alloys; Pt-30 wt% Rh - 8 wt% W and Pt-30 wt% Rh were selected for the fuel cell and filter vent, respectively.

The fabrication procedure was to hot-press layers of 120-mesh US Standard screens in which the screen openings were filled with spheres to form a frit. A 5.08-mm-diam section of the frit was electron-beam-welded into the fuel cell lid. A fabrication scheme using a frit formed from sphere-filled screens was selected over a frit prepared by powder metallurgy techniques because the former would provide better strength and grain size stability. The procedures for fabricating filter vent assemblies are outlined below. A detailed description of the procedure follows.

1. Prepare filings from Pt-30 wt% Rh ingots.
2. Ultrasonically wash filings in 50% nitric acid.
3. Rinse twice in distilled water.
4. Rinse once in USP absolute ethanol.
5. Melt filings in stabilized arc plasma to form spheres.
6. Size spheres to $-120/+140$ mesh.
7. Make a chemical analysis.
8. Punch 25.4-mm-diam coupons from 120-mesh Pt-30 wt% Rh screen.
9. Inspect coupons for uniformity.
10. Attach transparent tape to one side of coupon and press, 14-21 MPa (2-3 ksi).
11. Fill all screen holes with Pt-30 wt% Rh spheres.
12. Stack five or more coupons filled with spheres in a graphite die with Grafoil spacers at punch/stack interface.
13. Hot-press in argon.
14. Anneal filter vent frit in air 2 h at 1123 K.
15. Ultrasonically clean in detergent (Alconox, 1 tablespoon/gal).
16. Thoroughly rinse in flowing distilled water.
17. Rinse in absolute ethanol.
18. Anneal in dry hydrogen 2 h at 1173 K.
19. Loosely wrap the filter vent frit in tantalum getter foil and vacuum anneal 2 h at 773 K.
20. Determine helium leak rate of the annealed frit.
21. Electrically discharge machine inserts from the frit and machine to press-fit into holders.
22. Ultrasonically clean the filter vent inserts in hexane.
23. Ultrasonically clean the inserts in ethanol.
24. Rinse the inserts in alcohol.
25. Anneal the inserts in air 2 h at 1123 K.
26. Anneal the inserts and holders in hydrogen 2 h at 1173 K.
27. Vacuum anneal the inserts and holders 2 h at 773 K using tantalum getter foil.
28. Inspect inserts and holders.
29. Press-fit insert into holder.
30. Electron-beam-weld insert to holder (Hamilton Machine).
31. Determine helium leak rate of assembly.
32. Ultrasonically clean assembly in A.R. grade chloroform.
33. Ultrasonically rinse in ethanol.
34. Electron-beam-weld decontamination cover to filter vent assembly.
35. Inspect weld.
36. Package.

III. PREPARATION OF Pt-30 wt% Rh SCREEN FILLER

Three methods were evaluated for producing spherical screen filler. These included producing residue from electrical-discharge machining using a Pt-30 wt% Rh alloy electrode, forming splatter residue from levitated melts impinging on a cone-shaped spindle, and forming residue by dropping either chopped wire or filings through a plasma. Of these methods, the plasma-sphere filler was the best quality material in the 105- to 125- μ m-diam range.

There was no discernible difference between fillers formed from a plasma feed of chopped wire or filings; however, the product yield from chopped wire was 95% or more vs 8% or less for filings. The filter vent for the 25-W RTG used plasma-sphere filings because there was no readily available source of chopped Pt-30 wt% Rh alloy wire. Figure 1 is a photomicrograph of the filler cross section, and Fig. 2 is a SEM photograph of the filler surface. They show quenched melt morphology-shrinkage voids and a crazed surface finish. The chemistry results are given in Table I and show iron and copper impurities of 1000 and 200 ppm, respectively. Because the impurity content of the starting rhodium and platinum metals was not established before alloying, it is not known whether the contaminants were initially present or were introduced in the processing steps. Copper contamination could have resulted when the platinum and rhodium were alloyed in a cooled copper hearth button furnace, and iron contamination when the ingots were filed. Iron pickup in the ingot filings was anticipated so the filings were ultrasonically washed (2 to 3 h) in 50 vol% nitric acid, rinsed twice in distilled water, and given a final ethanol rinse before forming spheres. These precautions should have removed all the iron.

Fig. 1.
Plasma spheroidized Pt-30 wt% Rh ingot filings.

Fig. 2.
SEM photograph of spheroidized Pt-30 wt% Rh ingot filings.

TABLE I
CHEMICAL ANALYSES OF Pt-30 wt% Rh SCREEN FILLER

<u>Element</u>	<u>Content</u>	<u>Element</u>	<u>Content</u>
Pt	69.5%		
Rh	30.3%		
Li	<10 *	Ga	<30
Be	<3	Ge	<30
B	<30	Sr	<3
Na	<100	Zr	<30
Mg	3	Nb	<100
Al	<30	Mo	<10
Si	5-30	Ru	<30
K	<300	Pd	150
Ca	2-15	Ag	3-10
Ti	<3	Cd	<30
V	<10	Sn	<30
Cr	<10	Sb	<100
Mn	<10	Ba	<3
Fe	1000	W	<1000
Co	<10	Os	<300
Ni	6	Ir	<100
Cu	200	Au	200
Zn	<100	Pb	<100

*Values expressed as parts per million unless otherwise indicated.

IV. SCREEN PREPARATION

Using a precision die set, 25.4-mm-diam disks were cut from 120-mesh (US Standard), Pt-30 Rh screen. The disks were ultrasonically cleaned in detergent, rinsed in distilled water, and inspected for weave uniformity and for debris in the screen openings. One face of each disk was covered with transparent tape, and the disk was pressed between steel platens at a pressure of 14 to 21 MPa (2-3 ksi) to flatten the screen and extrude the tape's adhesive into the screen openings. Rubbing the filler through the untaped side of the disk filled the openings with $-120/+105\text{-}\mu\text{m}$ -diam filler. The filler sifted through the screen openings and became attached to the tape's adhesive. Inverting and tapping the disk removed excess filler. Figure 3 is a photomicrograph of a screen section after filling with spheres.

V. HOT-PRESSING

The sphere-filled screens were consolidated into filter vent frits by hot-pressing screen stackings of either 5, 7, or 10 layers in a die of Stackpole-type A-331 graphite. The screens were rotated angularly in the die; the amount of screen rotation was determined by dividing 360 by the number of screen layers. For example, in the 10-layer pressing, each screen was rotated 36° from the adjacent screen.

Fig. 3.

Section of a screen disk after filling with Pt-30 wt% Rh spheres.

Disks of Grafoil, a flexible graphite tape, were placed between the screen stack and the die punches to prevent sticking. The hot-pressing conditions and results are summarized in Table II with the following comments. Pressings 14 through 16 were made in air using a carbon black packing to protect the die, and a 75-kW motor generator was used to inductively heat the graphite susceptor die. Pressings 18 and 20 were hot-pressed in flowing argon and heated inductively with a 150-kV motor generator. Pressing loads were applied hydraulically. Because of material scarcity, preliminary development work was restricted. The data in Table II reflect this condition in that the pressing parameters changed in each run. Run 14, which was pressed in three stages, established the temperature and pressure conditions for producing a filter vent frit with the requisite helium leak. To conserve material, pressing 15 was made with five-layer stacking using the same temperature and pressure as in run 14 but for less time. For pressing 16, the pressure was approximately half that of pressing 14 because the graphite punches broke in run 14. In run 18 the temperature was decreased 100° because of the possibility of developing a large grain microstructure. In run 20, a 10-layer stacking was pressed for added strength and for welding considerations.

The pressed frits were fired in air to remove the carbon debris and were cleaned as outlined in steps 14 through 17 of the procedure listing. The hydrogen anneal, step 18, removed the surface discoloration, probably oxides, and returned the frit to a bright finish. Figure 4 is a photomicrograph of the frit cross section from pressing 20. After determining that the helium leak rate of the frit was within the specification (normalized to a 5.08-mm-diam insert), the frit was sectioned into filter vent inserts by electrical-discharge machining, and the inserts were machined to press-fit into the fuel vent holders. Figure 5 is a working drawing of the filter vent holder or fuel cell lid.

VI. ELECTRON-BEAM WELDING

The filter vent inserts were cleaned as described in steps 22 through 24 of the procedure listing, annealed sequentially in air, hydrogen, and vacuum (steps 25 through 27), and press-fitted into their

TABLE II
HOT-PRESSING DATA AND RESULTS

Pressing No.	Number of Screens	Pressure (MPa)	Pressure (psi)	Temperature (K)	Time (Ks)	Time (h)	Thickness (mm)	Leak Rate (cm ³ (STP)/s)
14*	7	12.64	1800	1373	9.0	2.5	0.77	---
		55.15	8000	1375	7.2	2.0	0.65	---
		66.19	9600	1573	21.6	6.0	0.46	0.001
15	5	66.19	9600	1523	18.0	5.0	---	0.004
16	5	38.64	5600	1523	39.6	11.0	0.37	0.001
18	5	44.12	6400	1423	50.4	14.0	0.38	0.002
20	10	55.10	8000	1473	28.8	8.0	0.62	0.0013

*Pressing No. 14 was pressed in three successive steps.

Fig. 4.

Cross section of a filter vent frit hot-pressed from a 10-layer screen stacking (pressing 20).

holders. Because of a lack of samples, weld development was performed on production components, and the unsatisfactory assemblies were reworked until weld procedures were developed. In the first welding attempts, cracks appeared in the insert, in the fusion zone, and in the heat-affected zone of the holder. Typical cracks in the fusion and heat-affected zones are shown in Figs. 6 and 7, respectively. The key to welding was to minimize the thermal stressing of adjacent material by using the lowest possible heat input required to obtain a 0.2-mm-wide weld bead.

Fig. 5.

RTG fuel can lid for mounting a filter vent.

The successful welding parameters using a Hamilton Standard machine are given in Table III. After welding, the helium leak of the assemblies was checked, the assemblies were cleaned by procedures 32 and 33 of the procedure listing, and a decontamination cover was welded over the top of the fuel vent opening by using the welding parameters given in Table III.

The helium leak rates of the completed assemblies are listed in Table IV. The two rates given for the 20-3 and -4 assemblies are measurements taken after

Fig. 6.
Typical welding crack formed in the fusion zone of the filter vent holder-insert.

Fig. 7.
Typical crack in the weld-heat-affected zone of the FV holder.

TABLE III

**WELDING PARAMETERS FOR FILTER VENT INSERT/FILTER VENT HOLDER
AND THE DECONTAMINATION COVER/FILTER VENT HOLDER**

<u>Parameter</u>	<u>Filter Vent Insert/ Filter Vent Holder</u>	<u>Decontamination Cover/ Filter Vent Holder</u>
Accelerating voltage (kV)	100	125
Beam current (mA)	1.2	2.0
Focus	Sharp	Sharp
Travel speed(mm/s)	1.6	1.7

the first and second weld passes; that is, rewelding the insert on the side opposite the first weld decreased the leak rate of the 20-3 assembly to an acceptable level; however, a second weld on the 20-4 assembly did not decrease the leak rate.

VII. CONCLUSIONS

Fabrication processes were developed for filter-vent assemblies of noble metal alloys using frits hot-pressed from sphere-filled screens and electron-beam-welding frit inserts into suitable holders.

Eight filter vent assemblies were prepared and processed into 25-W heat sources.

ACKNOWLEDGMENTS

The advice and suggestions of H. Sheinberg, the welding development by H. Casey, F. Flick, and V. Vigil, the hot-pressing operations by E. Velarde, and the suggestions and helium leak-rate measurements by LASL Group CMB-5 personnel are gratefully acknowledged.

TABLE IV
HELIUM LEAK RATES OF
FILTER VENT ASSEMBLIES

<u>Assembly No.</u>	<u>Helium Leak Rate</u> <u>[cm³ (STP)/s]</u>
14-2 ^a	0.005
18-6	0.0067
20-1	0.0011
20-2	0.0024
20-3	0.03
20-3 ^b	0.0012
20-4	0.015
20-4 ^b	0.019
20-5	0.0012
20-6	0.003
20-7	0.001

^aThe first number designates the frit number from which the filter vent insert was sectioned.

^bThe leak rate after rewelding the filter vent/filter vent holder on the side opposite the first weld.