40 JUN 18 1962

CONFIDENTIAL

MASTER FILED

NAA-SR-7064
COPY 183 OF 260
22 PAGES
SERIES A

UNCLASSIFIED

32989

ENCAPSULATION
OF
LEAD TELLURIDE
THERMOELECTRIC ELEMENTS
(Title Unclassified)

AEC Research and Development Report

~~RESTRICTED DATA~~

~~This document contains restricted data as defined in the Atomic Energy Act of 1954. Its transmittal or the disclosure of its contents in any manner to an unauthorized person is prohibited.~~

~~This document contains Confidential-Restricted Data relating to civilian applications of atomic energy.~~

ATOMICS INTERNATIONAL

A DIVISION OF NORTH AMERICAN AVIATION, INC.

UNCLASSIFIED

CONFIDENTIAL

CONFIDENTIAL

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

1 8407

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of 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. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

03165871000

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Printed in USA

Price \$0.50

Available from the

U. S. Atomic Energy Commission
Technical Information Extension,
P. O. Box 1001
Oak Ridge, Tennessee.

Please direct to the same address inquiries covering the procurement of other classified AEC reports.

DECLASSIFIED

DECLASSIFIED

~~CONFIDENTIAL~~

NAA-SR-7064
NUCLEAR TECHNOLOGY-
MATERIALS
M-3679 (25th Ed.)

UNCLASSIFIED

UNCLASSIFIED

Exempt from CCRP Re-review Requirements
(per 7/22/82 Duff/Caudle memorandum)

Classification cancelled (or changed to)

by authority of

H¹ 4/04

by GG

BTIE, date

5/24/73

ENCAPSULATION
OF
LEAD TELLURIDE
THERMOELECTRIC ELEMENTS
(Title Unclassified)

By

I. J. GROCE
E. L. REED

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, 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.

~~RESTRICTED~~

This document contains Restricted Data as defined in the Atomic Energy Act of 1954. Its transmittal or the disclosure of its contents in any manner to an unauthorized person is prohibited.

This document contains Confidential Restricted Data relating to civilian applications of atomic energy.

ATOMICS INTERNATIONAL

A DIVISION OF NORTH AMERICAN AVIATION, INC.
P.O. BOX 309 CANOGA PARK, CALIFORNIA

CONTRACT: AT(11-1)-GEN-8
ISSUED: JUNE 1, 1962

UNCLASSIFIED

~~CONFIDENTIAL~~

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

031507030

~~CONFIDENTIAL~~

DISTRIBUTION

Category: Nuclear Technology—
Materials
M-3679 (25th Ed.)

Copy No.

Aerojet-General, Azusa (BUWEPS)	1
Aerojet-General Corporation	2
Aerojet-General Nucleonics	3-4
Aeroprojects, Inc.	5
AiResearch Manufacturing Company of Arizona	6-7
Air Force Space Systems Division	8
Air Force Cambridge Research Laboratories	9
Air Force Special Weapons Center	10
Air Technical Intelligence Center	11
Allis-Chalmers Manufacturing Company	12
Allis-Chalmers Manufacturing Company, Washington	13
Allison Division — GMC	14
American-Standard	15
Argonne National Laboratory	16-17
Armour Research Foundation	18
Army Air Defense School	19
Army Chemical Center	20
Army Engineer Research and Development Laboratories	21
Army Medical Research Laboratory	22
Atomic Energy Commission, Washington	23-28
Atomic Power Development Associates, Inc.	29
Avco Corporation	30
Babcock and Wilcox Company	31-32
Battelle Memorial Institute	33
Bendix Aviation Corporation (ALOO-705)	34
National Distillers and Chemical Corp.	35
National Distillers and Chemical Corp., Ashtabula	36
Brookhaven National Laboratory	37
Bureau of Mines, Salt Lake City	38
Bureau of Naval Weapons	39-40
Bureau of Naval Weapons (SPO)	41
Bureau of Ships	42
Bureau of Yards and Docks	43
Carolinas-Virginia Nuclear Power Associates, Inc.	44
Central Intelligence Agency (NED)	45
Chicago Patent Group	46
Columbia University (NYOO-187)	47
Combustion Engineering, Inc.	48
Combustion Engineering, Inc. (NRD)	49-50
Convair Division, Fort Worth	51
Defense Atomic Support Agency, Washington	52
Denver Research Institute	53
Director of Defense Research and Engineering (OSD)	54
Division of International Affairs, Brussels	55
Division of International Affairs, Tokyo	56
Dow Corning Company (Rocky Flats)	57
duPont Company, Aiken	58-60
duPont Company, Wilmington	61
Edgerton, Germeshausen and Grier, Inc., Goleta	62
Edgerton, Germeshausen and Grier, Inc., Las Vegas	63
Electric Boat Division	64
Franklin Institute of Pennsylvania	65
General Atomic Division	66
General Electric Company (ANPD)	67-69
General Electric Company, Richland	70-81
General Nuclear Engineering Corporation	82
Gibbs and Cox, Inc.	83

NAA-SR-7064

031507030

~~CONFIDENTIAL~~

CONFIDENTIAL

DISTRIBUTION

	Copy No.
Goodyear Atomic Corporation	84
Grand Junction Operations Office	85
Hanford Operations Office	86
Iowa State University	87
Jet Propulsion Laboratory	88
Knolls Atomic Power Laboratory	89-93
Lockheed Missiles and Space Division	94
Los Alamos Scientific Laboratory	95-97
M & C Nuclear, Inc.	98
Mallinckrodt Chemical Works	99
Marquardt Corporation	100
Martin Company	101
Massachusetts Institute of Technology (Evans)	102
Mound Laboratory	103
NASA Ames Research Center	104
NASA Flight Research Center	105
NASA George C. Marshall Space Flight Center	106
NASA Langley Research Center	107
NASA Lewis Research Center	108
National Aeronautics and Space Administration, Washington	109
National Bureau of Standards	110
National Lead Company of Ohio	111-112
Naval Air Development Center	113
Naval Air Material Center	114
Naval Air Turbine Test Station	115
Naval Civil Engineer Corps Officers School	116
Naval Civil Engineering Laboratory	117
Naval Medical Research Institute	118
Naval Postgraduate School	119
Naval Radiological Defense Laboratory	120
Naval Research Laboratory	121
Naval Training Device Center	122
Naval Weapons Laboratory	123
New Brunswick Area Office	124
New York Naval Shipyard	125
New York Operations Office	126
United Nuclear Corporation (NDA)	127
Nuclear Materials and Equipment Corporation	128
Nuclear Metals, Inc.	129
Oak Ridge Operations Office	130
United Nuclear Corporation (OMC)	131
Patent Branch, Washington	132
Phillips Petroleum Company (NRTS)	133-136
Pratt and Whitney Aircraft Division	137
Princeton University	138
Public Health Service	139
Sandia Corporation	140
Sandia Corporation, Livermore	141
Sargent & Lundy	142
Savannah River Operations Office	143
Surgeon General	144
Sylvania Electric Products, Inc.	145
Union Carbide Nuclear Company (ORGDP)	146-147
Union Carbide Nuclear Company (ORNLI)	148-152
Union Carbide Nuclear Company (Paducah Plant)	153
Union Carbide Nuclear Company (Y-12 Plant)	154
University of California, Berkeley	155-156
University of California, Livermore	157-158
Walter Reed Army Medical Center	159
Westinghouse Bettis Atomic Power Laboratory	160-163
Westinghouse Electric Corporation	164
Westinghouse Electric Corporation (Biondi)	165
Aeronautical Systems Division	166-181
Yankee Atomic Electric Company (NYOO-222)	182
Division of Technical Information Extension	183-222
Library	223-260

NAA-SR-7064

CONFIDENTIAL

CONFIDENTIAL

0015587030

~~CONFIDENTIAL~~

CONTENTS

	Page
Abstract	6
I. Introduction	7
A. Encapsulation Requirements	7
II. Experimental Procedures	8
A. Research and Development Methods	8
1. Plasma Spray Coatings	8
2. Vapor Phase Coatings	8
3. Cements	9
4. Evaporated Coatings	10
5. Electrophoretically Deposited Coatings	10
6. Sleeve Encapsulation	11
7. Enamel Coatings	13
a. Ferro Al-2	13
b. Ferro Al-8	14
c. Corning Glass Compositions	14
d. Al Materials Development	14
e. Enamel 41	15
8. Fiber Wrapping	15
9. Glass Coated, Extruded PbTe	15
10. Swaged Elements	16
B. Reference Production Methods	16
1. PBX Cement	16
2. Enamel 41	16
III. Results	19
IV. Conclusions	22
References	22

0015587030

~~CONFIDENTIAL~~

REF ID: A66000

~~CONFIDENTIAL~~

TABLES

	Page
I. Expansion of Sleeve Materials	12
II. Weight Loss Tests	19
III. Resistivity of PbTe Elements Produced During December 1961	21

FIGURES

1. Sleeve Encapsulation.	11
2. Spray Equipment	18
3. Encapsulation Furnaces.	18

REF ID: A66000

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

ABSTRACT

One thermoelectric material that might be used in the Systems for Nuclear Auxiliary Power (SNAP 10A) converter was lead telluride (PbTe). In order to use PbTe in this converter, under the environmental conditions of 900°F and vacuum, it was necessary to prevent sublimation loss of the PbTe, by encapsulation or some other method, without exceeding a 5% heat shunt or a 1% electrical shunt through the encapsulation material. Several encapsulating methods were tried, including plasma flame spraying of ceramics, sleeves, vapor deposition of ceramics, electrophoretic deposition of ceramics, coating with heat curing cements, and spraying and firing of enamels. The spraying and firing of enamel onto the thermoelectric element proved to be the best method, although some promise was shown with sleeves.

Weight loss test data has shown that the fired enamel could be expected to protect the PbTe for 40,000 to 80,000 hr at 900°F in vacuum, before reaching a 5% PbTe sublimation loss. The goal was 10,000 hr.

Weight loss test data also indicated that sleeve encapsulation would improve sublimation protection. If the sleeve could also be used to hold the elements in compression, it might also prevent resistance degradation of the p-type PbTe elements. However, more research and development work would be required on this factor.

NAA-SR-7064

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

DECLASSIFIED

I. INTRODUCTION

At the outset of the Systems for Nuclear Auxiliary Power (SNAP 10A) thermoelectric converter program, one of the best thermoelectric materials available, from the standpoint of power output for a given weight, was lead telluride (PbTe). From the general operating concept developed in the design of such a converter, it was recognized that the PbTe would be subjected to an environment of space vacuum, and temperatures of 900°F at the hot end and 600°F at the cold (radiator) end. Since PbTe has a definite vapor pressure at these temperatures, some sort of encapsulation was required to prevent material loss, especially at the hot end.

A. ENCAPSULATION REQUIREMENTS

A number of requirements¹ were set forth as a guide for selecting a suitable encapsulation method:

- 1) The weight loss of an encapsulated element should be less than 0.5% per 1000 hr, when operated at 900°F in a vacuum (10^{-5} mm of Hg), or at 1000°F in an inert atmosphere.
- 2) The encapsulant could not have any detrimental effects on the thermal or electrical properties of the thermoelectric element material.
- 3) The heat flow through the encapsulant should be less than 5% of the heat flow through the thermoelectric element.
- 4) The electric loss through the encapsulant should be less than 1%.

DECLASSIFIED

~~CONFIDENTIAL~~

II. EXPERIMENTAL PROCEDURES

A. RESEARCH AND DEVELOPMENT METHODS

The problem of encapsulation was considered one of the most important ones in the converter development program, and many individuals were vitally concerned with its solution. As a result, many suggestions of methods to solve the problem were received, and as many of these were investigated as was practical. The methods that were investigated were:

- 1) Plasma spray coatings
- 2) Vapor phase coatings
- 3) Evaporated coatings
- 4) Electrophoretically deposited coatings
- 5) Sleeve encapsulation
- 6) Enamel coatings
- 7) Fiber wrapping
- 8) Glass coated, extruded PbTe
- 9) Swaged elements

1. Plasma Spray Coatings

An attempt was made to spray alumina and zirconia onto the contacted and uncontacted PbTe. This method was unsuccessful, primarily because the heat shock from the plasma flame caused the PbTe to crack and break.

PbTe pellets without contacts were successfully coated by Norton Refractories, using their "Rokide" process. Coatings of Al_2O_3 , MgO , Cr_2O_3 , and ZrO were applied over the entire surface of the pellets, so that there was no way to contact the PbTe for any resistance measurements, etc. It was observed also that some of the pellets were loose inside the coating, and could be "rattled-around," like a pea in a pod. Weight loss testing in vacuum at 900°F was performed on these, but the results were not felt to be worthwhile, inasmuch as the pellets could not be contacted and used in an element assembly.

2. Vapor Phase Coatings

The process involved in the vapor phase coatings is illustrated by the following chemical equation: $2\text{AlCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{HCl}$.

NAA-SR-7064

DECLASSIFIED

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

The chloride is volatilized in a stream of carrier gas which is directed at the object to be coated. The water is also introduced by volatilizing it into a second carrier gas medium. The two carrier gases, impinging on the surface of a PbTe element, formed the oxide coating on the surface and provided the sublimation barrier. Only two chlorides were used, TiCl_4 and AlCl_3 . None of the coatings made by this process were compact, hard, impervious, or adherent enough to provide protection for the PbTe. In addition to this, the wet HCl, formed in the process, reacted with the PbTe, yielding a dark colored product on the surface of the PbTe. One of the reaction products was definitely PbCl_2 , and efforts to prevent the reaction by using hydrogen gas were not successful.

3. Cements

Some of the industrial strain gage cements were used as encapsulation material, and most of these gave good appearing coatings. Quite a number of these were used, including:

<u>Name</u>	<u>Supplier</u>
Sauereisen Cement No. 1	Sauereisen Cements Co., Pittsburgh, Pennsylvania
PBX Cement	Baldwin-Lima-Hamilton Corp., Electronics and Instrumentation Div., Waltham, Massachusetts
Ecco Ceram	Trans-sonics, Inc., Burlington, Massachusetts
PT-209	
PT-404	Product Techniques, Inc. Los Angeles, California
PT-805	
Astroceram	American Thermocatalytic Corp., Mineola, New York

The PBX cement was used as the first reference process, and the coating was applied by dipping. The material in PBX is believed to be essentially Al_2O_3 powder with a phosphate binder. Weight loss tests gave an average of 5% weight loss in about 5000 hr, which was about half of the design requirement. Sauereisen cement gave similar average weight loss results; but the PT coatings were observed to lose excessively in the first 25 hr, before slowing the loss rate to a rate similar to that of PBX. On life tests, the PBX coated elements developed "whiskers" which contacted the conductor straps and shorted out the elements

NAA-SR-7064

0371291030

~~CONFIDENTIAL~~

03145087030

~~CONFIDENTIAL~~

after a few hours. Apparently, porosity within the refractory grains allowed PbTe vapors to come out to the surface, where they cooled and recondensed. Examination under a stereoscopic microscope also revealed the sandy nature of the cement coatings. These coatings were all rejected as encapsulation materials.

4. Evaporated Coatings

This process was accomplished inside a vacuum bell jar, where the materials were heated in a tungsten or molybdenum basket, or boat, to the temperature at which they vaporized. The elements to be coated were placed in such a position that the vapors could be condensed on the surface.

Titanium metal and silicon monoxide were the materials which were tried. After these materials were condensed onto the surface of the elements, the elements were heated to about 450°C in an oxidizing atmosphere to form the TiO_2 and SiO_2 . This method was abandoned for several reasons:

- a) The roughened surfaces of the PbTe did not allow complete coverage to fill the cracks and holes.
- b) Weight loss data showed that this method did not meet the requirements.
- c) The method was not readily adaptable for scaleup to production quantities.
- d) The materials and equipment are relatively expensive, and this is a time-consuming process.

5. Electrophoretically Deposited Coatings

This method was investigated primarily to get a uniform layer of encapsulating material on the surface of the element. PBX powder was deposited uniformly on the surfaces, and the curing liquid was then put on by dipping. The results were not as good as when the PBX powder was mixed with the curing liquid before the coating was applied.

The method consisted of fastening the element being encapsulated to an electrode and immersing it in a solvent in which the encapsulation material was suspended. A potential difference applied between this electrode and another one placed in the slurry imparted a charge to the suspended material, causing it to migrate to and be deposited on the element. Materials which could be deposited by this method were uniform and readily controlled. The method was never used,

NAA-SR-7064

03145087030

~~CONFIDENTIAL~~

DECLASSIFIED

CONFIDENTIAL

because the materials which gave good encapsulation could not be deposited by this method. Materials which were deposited included PBX powder (Al_2O_3 and Cr_2O_3), ZrO_2 , and glass.

6. Sleeve Encapsulation

A sleeve type of encapsulation appeared to offer promise, inasmuch as it would be possible to combine the encapsulation and the hot press bonding into a single operation. This type of approach was tried with Al_2O_3 , ZrO_2 , Supramica, Mykroy, Lavite, and Forsterite. Several methods of application were investigated. In one method, the sleeve was fitted into a die with the iron end caps and the PbTe pellet inside the sleeve. Figure 1 shows two Supramica sleeves. On the left, the sleeve, iron caps, and PbTe have not been hot pressed; while, on the right, the finished element has just been removed from hot pressing.

Figure 1. Sleeve Encapsulation
(Figure Unclassified)

7580-1858B

Weight loss test results varied, but it was apparent that a satisfactory sealant needed more than just a close tolerance, in order to stop PbTe vaporization losses. The problems involved in sleeve encapsulation are: (a) the ability to maintain required dimensions, and (b) the ability to make sleeves out of such brittle materials. It is relatively easy to make sleeves of 60-mil thicknesses of these materials, but using anything below 30 mils is similar to handling egg shells. The desired thickness of Supramica would be about 12 mil. Other materials should ideally be one third to one half this thickness, in order to be within the 5% heat shunt specification. Because of this thickness limitation, it does not appear practical to use anything but the mica type of materials, which have a very low heat conductivity, and therefore may be thicker.

NAA-SR-7064

DECLASSIFIED

CONFIDENTIAL

0310587030

~~CONFIDENTIAL~~

Another property which was found to be of paramount importance was the linear coefficient of expansion. The expansion of the sleeve should approximate the expansion of the PbTe, and very few of the normal refractory materials have coefficients of expansion close to that of PbTe. Table I illustrates this.

TABLE I
EXPANSION OF SLEEVE MATERIALS

Material	Linear Coefficient of Expansion [in. /in. /°C ($\times 10^{-6}$)]
PbTe	20 - 22
Li ₂ TiO ₃	18.1
MgO (95%)	12.8
Supramica	11.6
Forsterite	10.5
ZrO ₂	9.2
BeO (88%)	8.2
Al ₂ O ₃	7.2
Porcelain	6.0
Glasses	3.2 - 6.7
Fused Silica	0.55

A different method of application was attempted to bond the sleeves to metal, using one of the metal-to-ceramic seals. Titanium-cored brazing alloy, or titanium hydride powder, were materials which could accomplish metal-to-ceramic seals. The sleeves proved to be a very poor shape for this method; and, because of the difference in expansion coefficients, none of the sleeve materials were bonded without cracking. This is in contrast to the encapsulation method developed at G.E., which was probably accomplished with sleeves of much thicker cross section.²

Another method of application was to use a thin metallic sleeve, insulated from the PbTe with ceramic. One of the biggest problems in this method was to obtain metallic sleeves thin enough in cross section to stay below the 5% heat shunt requirement. To meet this requirement, a sleeve of stainless steel could be only 3/4 mil thick. The thinnest sleeves which were made were 1 mil.

CONFIDENTIAL

However, if the metal sleeve could serve to hold the element in compression, instead of using the stud which was later incorporated into the design, the 1 mil or 1.5 mil would probably not be unreasonable. Several elements were made, using 1 mil stainless steel sleeves with Solaramic No. 5210-C enamel coating as insulation. No weight loss or performance tests were made on these, but the method was demonstrated. One element was fabricated with a 2 mil stainless steel cup. A reference element (iron caps, hot-press loaded to PbTe at 1550°F and 5000 psi for 30 min) was brazed into the stainless steel cup insulated with Isomica. Seebeck measurements, after weight loss testing, were normal; and the resistance of the element showed approximately the usual rise. However, much more development work will be required, in order to make this a production method. For instance, the use of a brazing alloy inside the cup should be eliminated; and, if possible, the encapsulation should be combined into the hot pressing step.

7. Enamel Coatings

The enamel coatings have occupied most of the development efforts. Of particular interest were the enamels developed specifically for aluminum. Two of these, marketed by Ferro Corp.,* are called Al-2 and Al-8. It has been reported that phosphate glasses are being developed for aluminum coatings, but none of these were available commercially.

a. Ferro Al-2

Ferro Al-2 was first tried, in the manner specified for aluminum coatings, which called for firing in air to 1000°F. Under these conditions, the coating bubbled; but, by drying the coating at 212°F and firing in argon at 1000°F for 1 hr, a smooth adherent coating was obtained. The weight loss testing of the first few elements at 900°F indicated a survival time of 25,000 hr, which was well within the specified requirement of 10,000 hr. Some 2-element and 4-element modules were encapsulated with Al-2, and a 2-element module was tested for over 500 hr. The performance of the coating appeared to be excellent, until the controller allowed the temperature to exceed 900°F. The coating softened above 900°F, and bubbles formed near the high-temperature end of the elements. Examination under the microscope indicated a reaction with the iron end caps.

*Ferro Corp., Los Angeles, California

0345087030

~~CONFIDENTIAL~~

The Ferro Al-2 was analyzed and found to contain a large proportion of lead oxide (PbO). The reaction occurring with the iron was probably:

With any quantity of carbon present in the iron, an additional reaction of:

would occur. This would account for the formation of bubbles.

b. Ferro Al-8

The Ferro Al-8, when processed in a manner similar to Al-2, also gave an adherent and smooth coating, but it reacted with the PbTe, as well as with the iron end caps. Also, the Al-8 composition showed a high weight loss in vacuum at 900°F.

c. Corning Glass Compositions

In an effort to obtain an enamel with a higher softening point, several glass compositions were investigated. Most of the glasses had unfavorable coefficients of expansion and poor adherence to PbTe. Corning No. 1990, an iron sealing glass with a high PbO content, gave a fair coating, but there was very little difference in its softening point from that of Al-2.

d. AI Materials Development

Several compositions were formulated by the Materials Development Group, in an effort to obtain an enamel with better properties than Al-2. None of the silicate enamels had enough adherence to form a continuous coating over the PbTe. A fluoride salt mix and a phosphate glass were tried, but did not have sufficient adherence to PbTe, until MgO powder was fired on, prior to applying the enamels. This work is described in Reference 3. The fluoride salt mix had a rather sharp melting point, and was so fluid that it had a tendency to run off if the temperature overshot a few degrees in the firing cycle. It was abandoned in favor of the phosphate glass. Several phosphate-coated elements were tested in the weight loss testing apparatus; and, at 900°F, survival times of 109,000 hr were indicated. At 1000°F, the survival time dropped to about

0345087030

~~CONFIDENTIAL~~

CONFIDENTIAL

~~CONFIDENTIAL~~

8,000 hr. It was noted, however, that the adherence to the PbTe was not as good as with Enamel 41.

e. Enamel 41

Efforts were made to modify the Ferro Al-2, by making additions of some refractory oxides to it. Those tried were Al_2O_3 , SiO_2 , ZnO , and Li_2TiO_3 . The Al_2O_3 detrimentally changed the coefficient of expansion drastically. The SiO_2 lowered the melting point, instead of raising it. The ZnO improved the finished enamel for a time, but the shelf life of the raw mixture was shortened; and, after a few days, the enamel could not be fired to produce a continuous coating. The Li_2TiO_3 proved to be the best additive to the Ferro Al-2, and a ratio of four parts by dry weight of Al-2 to one part by dry weight of Li_2TiO_3 proved to be the optimum amount. Hence, the name, Enamel 41. Weight loss tests gave survivals of 68,000 hr at 900°F, and 8,000 hr at 1000°F. Because of the good adherence and the favorable weight loss tests, Enamel 41 was made the reference coating. However, this coating was not without its problems. The PbO was still reduced in the brazing cycle, either by hydrogen at 1200°F or by the iron end caps at 1350°F in argon. These cycles reduced the survival time, in either case, to about 8,000 hr. Fortunately, in the module assembly procedure, later brazing cycles were changed; so that a low temperature braze could be used, whereby the encapsulated elements were not required to exceed a temperature of 1100°F. Under these conditions, Enamel 41 encapsulated elements were expected to have a survival of about 68,000 hr at 900°F, based on weight loss considerations.

8. Fiber Wrapping

The objective of this method was to incorporate into the coating some fibrous material to give strength to the coating, as well as to the PbTe element. No compatible material was found.

9. Glass Coated, Extruded PbTe

This method has never gone beyond the idea stage. The equipment required for extrusion is complex, and not available within this organization; but the method is mentioned because of the high production rate which would be possible. It would also eliminate the necessity of pressing and sintering individual pellets.

NAA-SR-7064

~~CONFIDENTIAL~~

CONFIDENTIAL

0313507030

10. Swaged Elements

This method was used for the "Cylindrical Vacuum Design," TDR No. NAA-SR-6419, by G. W. Meyers.⁴ Several of these were made, and the design showed some promise. The exposed ends were coated with Enamel 41.

More development work should be done on this method, since it has the advantage of keeping the PbTe in compression and having a vapor barrier, for the most part composed of metal.

B. REFERENCE PRODUCTION METHODS

1. PBX Cement

Although the initial reference process chosen was the PBX Cement, no actual production was accomplished by this method. Weight loss tests showed, from the start, that this method would not meet the desired requirements; so no production was attempted.

2. Enamel 41

Soon after Enamel 41 was chosen as the reference process for production, the need for larger and larger quantities of encapsulated elements became evident. Life testing stations needed to be filled, and the brazing group needed experience on the assembly of finished modules. The encapsulation process was first developed for handling elements, one at a time; and, in order to meet production goals, some measure of improvement was needed. A brief description of the processing steps follows:

- a) Ferro Al-2 was purchased as a slip, suitable for brush or spray application to aluminum. The Li_2TiO_3 was obtained as -325 mesh powder.
- b) Small batches (about one quart per batch) were made, using 4 parts (dry weight) Al-2 to 1 part Li_2TiO_3 . This mixture was blended by ball milling for 4 hr, or by blending in a Waring Blender for 1 hr.
- c) Incoming PbTe elements were visually inspected, then degreased by spraying with acetone and wiping with a paper towel.
- d) The elements were placed on a rotating spindle in the direct rays of a heat lamp.

03158700

~~CONFIDENTIAL~~

- e) Enamel 41 was sprayed on, using a small pencil type H5 sprayer, made by Paasche Airbrush Company. Nitrogen at 40 to 50 psi was used as the propellant gas because it was convenient. Clean air would probably work as well.
- f) The operator's judgment determined the amount of slip to be sprayed on.
- g) The elements were allowed to rotate in the heat lamp rays until dry, then were transferred to a stainless steel tray and placed into a tube type furnace under flowing argon.
- h) The elements were first heated to 212°F for 20 min, followed by a curing temperature of 1100°F for 1 hr in flowing argon. This curing cycle was later altered to 1/2 hr at 1000°F and 1/2 hr at 1125°F, which produced smoother surfaces.
- i) The elements were then furnace cooled in flowing argon, until the temperature dropped to 400°F or below, before removal.
- j) The elements were cleaned before brazing or other processing by grit blasting the iron end caps with a fine alumina abrasive unit, to remove rust or excess enamel.

Figure 2 shows the spray gun, rotating spindles, and heat lamp. This is the large scale equipment, capable of spraying 35 elements at a time. The initial equipment could handle only one element at a time. Spraying was done in a hood, to prevent any possibility of personnel breathing any of the fine spray, since the Ferro Al-2 contained PbO as a primary constituent.

Figure 3 shows the development furnace (1-in. diameter quartz tube) and the production furnace (3-in. diameter Vycor tube), along with the firing trays. The small furnace was capable of holding 4 elements at a time, while the double-deck tray in the large furnace would hold approximately 125 elements. With two cycles per 8-hr day, the production capacity was increased from 8 elements per day to 250 elements per day, using a 2-man shift. Both furnaces were Hevi-Duty, hinged type, for visual access during the firing process. Temperatures were maintained by Wheelco controllers. The argon purge was from the house argon system, and the flow rate was established by needle valves and visual observation of a glass wash bottle. An alarm clock was used to time the steps of the process.

NAA-SR-7064

~~CONFIDENTIAL~~

03158700

7550-1858 C

Figure 2. Spray Equipment
(Figure Unclassified)

7580-1858 A

Figure 3. Encapsulation Furnaces
(Figure Unclassified)

NAA-SR-7064

III. RESULTS

The most important measurement for determining what process produced the better encapsulated elements was the weight loss of PbTe at the operating conditions. Table II gives the results of weight loss tests for the various encapsulation materials.

TABLE II
WEIGHT LOSS TESTS

Number	Encapsulation Material	Test Temperature (°F)	Vacuum (mm of Hg)	Number Tested	Hours on Test	Survival* Hours
1	None	900	1×10^{-3}	2	5	174
2	PBX	900	2×10^{-2}	3	50	5,000
3	PT-404	900	2×10^{-2}	2	50	1,500
4	Ferro Al-2	900	5×10^{-4}	2	60	25,000
5	Ferro Al-2	1000	2×10^{-2}	3	24	670
6	Sauereisen	900	3×10^{-5}	1	100	5,200
7	Enamel 41	900	3×10^{-5}	2	2208	68,000
8	Enamel 41 [†]	900	3×10^{-5}	4	150	9,000
9	Enamel 41	1000	3×10^{-5}	4	500	8,000
10	MgO-Phosphate	900	3×10^{-5}	2	160	109,000
11	MgO-Phosphate	1000	3×10^{-5}	2	160	8,000
12	Stainless Cup	900	3×10^{-5}	1	160	109,000
13	Stainless Cup	1000	3×10^{-5}	1	160	109,000

*Survival hours is the calculated time to reach a 5% weight loss of PbTe.

†Elements were subjected to braze cycles of 1350 and 1050°F, for 15 min each, before weight loss testing.

Many other weight loss tests were made which are not included in the table. Most of these confirmed the tabulated results, and were similar in value. Other tests were at intermediate temperatures. About 30 elements, rejected because of minor encapsulation flaws, were weight loss tested to aid the quality control group in establishing criteria for acceptance or rejection.

~~CONFIDENTIAL~~ ~~SECRET~~

These results definitely point out the superiority of the Enamel 41 encapsulant over the others, and of the MgO-phosphate over Enamel 41, especially at the 900°F temperature. However, a switch to MgO-phosphate was not made, for the following reasons:

- a) The complexity of handling the phosphate slip. The grain size was a critical factor in forming a good coating. The length of time the slip was made, before being used, was very critical; because the phosphate was soluble in water, and soon formed a thick solution which would not make good coatings.
- b) The adherence was not as good as with Enamel 41.
- c) Two firing cycles were necessary to produce adequate coatings, one for MgO and the second for the phosphate.
- d) Higher processing temperatures were required. This would probably produce greater degradation in the PbTe, and would increase the electrical resistance.

The best results, of course, were with the stainless cup encapsulation, which indicated survival times of 109,000 hr at 900, 950, and also 1000°F. Only one element was completed by this method of encapsulation, and more development work will be needed to adapt the method to large-scale production.

Other tests, performed on elements before and after encapsulation, were cap-to-cap resistance and Seebeck voltage. The Seebeck measurements were not felt to be accurate near room temperature, with small temperature differences. Also, elements put on performance tests under operating conditions indicated that the Seebeck voltage was not affected by the encapsulation process. Therefore, this test was not continued as a routine encapsulation check. However, the cap-to-cap resistance was observed to change considerably during encapsulation, and also during other testing. The data indicated that the lower the initial cap-to-cap resistance after hot press bonding, the less the resistance rise after encapsulation. The n elements changed very little during encapsulation, while the p elements changed to a much greater extent. Measurement of the cap-to-cap resistance was continued, as a routine check after encapsulation.

The three Sigma limits of resistance for elements produced during December 1961 are given in Table III.

0315087030

TABLE III
RESISTIVITY OF PbTe ELEMENTS
PRODUCED DURING DECEMBER 1961

PbTe Type	Three Sigma Limits of Resistance ($\mu\Omega$)	
	After Hot Pressing	After Encapsulation
n	115-137	124-188
p	257-305	336-446

A mean and average deviation of the p elements, produced in previous months, was $336 \pm 41 \mu\Omega$ after hot pressing and $461 \pm 55 \mu\Omega$ after encapsulation.

Results of life testing indicated that p element resistance increased with time at operating temperature, even though the initial resistance was low. Output power under operating conditions, with these p elements, dropped below the minimum allowable in about 1500 hr. Under these conditions, the p elements are not suitable for the SNAP-10A application. Just what part the encapsulant plays in the degradation, or how a different type of encapsulation might improve the stability of the elements, is not known.

DECLASSIFIED

CONFIDENTIAL

~~CONFIDENTIAL~~

REF ID: A6070311

IV. CONCLUSIONS

Encapsulation of PbTe thermoelectric elements can be performed to meet the requirements for SNAP-10A, using our Enamel 41. The encapsulation will not be adequate to withstand brazing cycles of 1325 to 1350°F in inert atmosphere, or 1200°F in hydrogen, but will withstand a brazing cycle of 1100°F in an inert atmosphere.

It is not known how much of a part the encapsulation plays in the resistance of p elements, during life testing; but the problem is presumed not to be chemical or metallurgical, since the Seebeck voltage is not changed. Therefore, a continued development of the metallic sleeve, or cup-type, encapsulation, where the sleeve could be used to keep the PbTe in compression, appears to be attractive.

REFERENCES

1. N. C. Miller (unpublished IOL to M. H. Binstock, Atomics International, Canoga Park, Calif., November 8, 1960)
2. E. Fischer, et al., "High Temperature Encapsulation of Thermoelectric Materials," R61ELS-28
3. D. O. Raleigh, "Ceramic Coatings for Lead Telluride," NAA-SR-6901 (March 1, 1962)
4. G. W. Meyers, "Cylindrical Vacuum Design," NAA-SR-TDR-6419 (May 17, 1961)

REF ID: A6070311

~~CONFIDENTIAL~~