FEB 6 1967

ALO-3633-3

UC 33

AEC RESEARCH AND DEVELOPMENT REPORT
SPECIAL

MASTER

GROUP PRICE

~~3.00~~ 65

AT(30-1)-3633
DEVELOP 1800F-400F FIBROUS-TYPE INSULATION
FOR RADIOISOTOPE POWER SYSTEMS

Third Quarterly Progress Report
Report No. ALO-3633-3

January 3, 1967

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.

Report Period: October 3, 1966 to December 30, 1966

J. O. Collins

RELEASED FOR ANNOUNCEMENT

IN NUCLEAR SCIENCE ABSTRACTS

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.

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 or contract with the Commission, or his employment with such Contractor.

Printed in U.S.A. Price Available from
The Office of Technical Services, Department of
Commerce, Washington 25, D.C.

iii

DISTRIBUTION

L. W. Oroski, Area Manager
Sandia Area Office
U. S. Atomic Energy Commission
Albuquerque Operations Office
Albuquerque, New Mexico 87115 (2 cys)

A. J. Clark, Manager
Isotope Power Department
Department 9330
Sandia Corporation
Post Office Box 5800
Albuquerque, New Mexico 87115 (1 cy)

R. T. Carpenter, Chief
Isotopic Power Branch
Division of Space Nuclear Systems
U. S. Atomic Energy Commission
Washington, D.C. 20545 (1 cy)

S. J. Seiken
Division of Reactor Development
and Technology
U. S. Atomic Energy Commission
Washington, D.C. 20545 (1 cy)

J. E. Konklin, Acting Chief
Technology Development Branch
Special Projects Division
U. S. Atomic Energy Commission
New York Operations Office
376 Hudson Street
New York, New York 10014 (1 cy)

L. Sisler, Isotope Power
Laboratory
Minnesota Mining & Manufacturing
Company
Space Center, 2501 Walnut Street
Roseville, Minnesota 55119 (2 cys)

J. F. O'Brien
Martin Marietta Corporation
Nuclear Products
Baltimore, Maryland 21203 (1 cy)

D. G. Harvey
Martin Marietta Corporation
Nuclear Products
Baltimore, Maryland 21203 (1 cy)

E. Ray
General Electric Company
Missile & Space Development
Valley Forge Space Technology
Center, P. O. Box 8555
Philadelphia, Pennsylvania 19101 (2 cys)

William Botts
Atomics International
Division of North American Aviation
P. O. Box 309
Canoga Park, California 91304 (2 cys)

P. Underhill, Project Manager
Large Milliwatt Program
Aerojet-General Nucleonics
Post Office Box 77
San Ramon, California (1 cy)

F. Hittman, General Manager
Hittman Associates, Inc.
4715 E. Wabash Avenue
Baltimore, Maryland 21215 (1 cy)

ALO-3633-3

UC-33

AEC RESEARCH AND DEVELOPMENT REPORT
SPECIAL

iv

J. Kenney, Program Manager
Compact Thermoelectric Converter
Westinghouse Electric Corporation
P. O. Box 10864
Pittsburgh, Pennsylvania 15213 (1 cy)

W. Kortier
Battelle Memorial Institute
505 King Avenue
Columbus, Ohio 43201 (1 cy)

J. Epstein
Goddard Space Flight Center
Greenbelt, Maryland (1 cy)

Capt. Morrow
Wright-Patterson Air Force Base
Dayton, Ohio 45433 (1 cy)

J. O. Collins
Johns-Manville Research &
Engineering Center
Manville, New Jersey 08835 (2 cys)

W. DeWitt
Union Carbide Corporation
Linde Division
P. O. Box 44
Tonawanda, New York 14152 (2 cys)

G. Rose
Radio Corporation of America
415 South Fifth Street
Building 10-2
Harrison, New Jersey (1 cy)

H. S. Potter, Chief
New York Patents Group
U. S. Atomic Energy Commission
Brookhaven Area Office
Upton, New York 11973 (1 cy)

J. Dunlay
Thermo Electron Engineering Corp.
Post Office Box 482
Waltham, Massachusetts 02154 (2 cys)

Harold Garber
NIMEC
600 North Warren Avenue
Apollo, Pennsylvania 15613 (1 cy)

U. S. Atomic Energy Commission
New York Operations Office
376 Hudson Street
New York, New York 10014
Attn: Reports Library (1 cy)

U. S. Atomic Energy Commission
Division of Technical Information
Extension
Post Office Box 62
Oak Ridge, Tennessee 37831 (3 cys
and one reproducible copy)

ALO-3633-3

UC 33

AEC RESEARCH AND DEVELOPMENT REPORT
SPECIAL

v

ABSTRACT

by

J. O. Collins

This is the Third Quarterly Report for AEC Contract AT(30-1)-3633 covering the period October 1966 through December 1966.

The physical properties (excluding thermal conductivity) of MICROTHERM made by Boucher & Co., England, were investigated. Formulations 1999 and 2002, developed for lead-telluride service, have been placed under prolonged compatibility tests, as have the fibrous candidates for the higher temperature silicon-germanium service. A complete evaluation of the stress-strain characteristic of Formulation 2002 and the effect of numerous variables on this characteristic has been completed.

Developmental efforts are concentrated upon a more thermally stable formulation for application in silicon-germanium systems.

TABLE OF CONTENTS

	<u>Page</u>
Legal Notice	ii
Distribution	iii
Abstract	v
I. Introduction	1
II. Final Screening	2
III. Detailed Evaluation	9
IV. Material and Process Development	25
V. Summary of Third Quarter Results and Conclusions	31
VI. Fourth Quarter Effort	33
VII. References	34
VIII. Appendix	35

LIST OF FIGURES

	<u>Page</u>
Figure 1. Stress-Strain Relationship of MICROTHERM	4
Figure 2. Stress-Strain Characteristics of Formulation 2002 in the "X" Direction (Room Temperature and 60 psi/min Loading Rate)	12
Figure 3. Stress-Strain Characteristics of Formulation 2002 in the "X" Direction (1400F Hot Face and 60 psi/min Loading Rate)	15
Figure 4. Combined Stress-Strain Characteristics for Formulation 2002 in the "X" Direction	16
Figure 5. Stress-Strain Characteristics of Formulation 2002 in the "Y" and "Z" Directions (Room Temperature and 60 psi/min Loading Rate)	17
Figure 6. Combined Stress-Strain Characteristics of Formulation 2002 in the "Y" and "Z" Directions (Room Temperature and 60 psi/min Loading Rate)	18
Figure 7. Load Relaxation of Formulation 2002 at 1400F Hot Face (50 and 100 psi Initial Stress)	20
Figure 8. Moisture Adsorption Rate of Formulation 2002 at Room Temperature and 27 Per cent RH	23

LIST OF TABLES

	<u>Page</u>
Table 1. MICROTHERM Shrinkage After 24 Hour Isothermal Exposure	2
Table 2. Modulus of Rupture of MICROTHERM	3
Table 3. Permanent Strain of Load Bearing Candidates After 168 Hours	7
Table 4. Formulation 2002 Stress-Strain Program	10
Table 5. Thermal Stability of Formulation 2002 at 1400F in Air Air	21
Table 6. Third Quarter Experimental MIN-K Formulations	26
Table 7. Properties of AEROSIL	25
Table 8. Thermal Conductivity of Formulations 2004, 2005, and 2006	27
Table 9. Thermal Stability of Formulations 2004, 2005 and 2006 After 24 Hours at 1800F	27
Table 10. Typical Firing Schedule of Silica	28

1. INTRODUCTION

The Second Quarter effort concluded that Formulations 1999 and 2002 would be satisfactory for service in PbTe RTG applications at maximum temperatures of 1000F and 1400F, respectively. These formulations were subsequently placed under more detailed and prolonged scrutiny involving stress-strain, load relaxation, and chemical compatibility with PbTe thermoelectric elements. The status and/or available test results for these evaluations are discussed.

A small specimen of MICROTHERM made by Boucher & Co., England, was previously analyzed for structure, composition, and weight loss using such tools as the light and electron microscopes, spectrographic and X-ray analysis, and thermogravimetric analysis. Receipt of additional material permitted a more thorough evaluation of MICROTHERM during the Third Quarter. These tests included modulus of rupture (breaking strength), stress-strain, thermal stability, and general observations.

Efforts to develop a MIN-K formulation(s) for continuous service in the 1600F to 1800F hot face temperature range for silicon-germanium RTG applications were initiated midway through the Third Quarter. Although the effort to date provided few positive conclusions, it did indicate the probable courses of action necessary to attain the desired product.

II. FINAL SCREENING

A. MICROTHERM

Three samples of MICROTHERM 12 x 12 x 1-in. were received from Boucher and Company, Kidderminster, England. These blocks represented additional material from that initially investigated for chemical composition.⁽¹⁾ Although one block had been cracked during shipment, sufficient material was available to perform the planned evaluations.

Thermal Stability

Specimens nominally 2 x 4 x 1-in. were subjected to isothermal conditions of 1600F, 1800F and 2000F for 24 hr each to establish comparative thermal stability data with MIN-K 1301 and 2000. Three specimens were subjected to 1600F for 24 hr and measured for shrinkage. The same three, plus an additional three (no previous thermal history) were subjected to 1800F for 24 hr. Likewise, the six which had been exposed to 1800F, plus an additional three were subjected to 2000F for 24 hr. In all instances, the previous thermal history had no effect upon the per cent shrinkage, based upon the original dimensions. Table 1 below summarizes the results.

TABLE 1.

MICROTHERM SHRINKAGE AFTER 24 HOUR ISOTHERMAL EXPOSURE

Temperature, °F	Number of Specimens	Average Shrinkage, %		
		Length	Width	Thickness
1600	3	2	2	2
1800	6	4	5	14
2000	9	35	35	45

These data show MICROTHERM to be less stable than MIN-K 2000, but more stable than MIN-K 1301.⁽²⁾ The comparison is somewhat academic, however, since the material appears to have little value for prolonged service above 1600F due to thermal instability.

Modulus of Rupture

The strength of MICROTHERM was evaluated in the same manner used to compare the strengths of the MIN-K formulations (see Appendix for the Modulus of Rupture test procedure). This evaluation was done on both the

⁽¹⁾ Numbers in parenthesis refer to references in Section VII.

"as received" material, and on material which had been exposed to 1400F for 2 hr (current manufacturing procedure for the experimental MIN-K formulations). Table 2 below summarizes the results.

TABLE 2.
MODULUS OF RUPTURE OF MICROTHERM

<u>Thermal History</u>	<u>Number of Specimens</u>	<u>Average MR, psi</u>
None	4	16.5
1400F, 2 hr	4	20.7

Although the number of test specimens was limited, the effect of the firing cycle appeared evident. However, the low strengths verified pretest impressions that the material was relatively fragile which could create handling problems during generator assembly.

Stress-Strain

Eight specimens, 4 x 4 x 1-in. were evaluated for stress-strain characteristics. Four were tested "as received", and four after 2 hr at 1400F. The tests were conducted on a Riehle Hydraulic Model KA-60 at a loading rate of 60 psi per minute, at room temperature, and with a 0.001 in. deflection dial gauge. The load was applied over the entire area with no lateral restraint provided the specimens during test. A static preload of 0.34 psi was applied to each specimen.

Figure 1 is a plot of the average stress-strain data obtained at 0.005 in./in. strain increments. In each group of four specimens, there was very little variation from the average, indicating good uniformity within a given 12 x 12 x 1-in. block. The curves appeared to consist of three straight-line segments. The first encompassed the 0 to 0.02 in./in. strain range, the second covered the 0.02 to 0.12 in./in. strain range, while the third went from 0.12 to 0.15 in./in. The first range was probably a result of thickness regain after molding, while the third may signify an internal fracture as experienced in MIN-K 1301 and Min-K 2000. The middle portion of the curve was used to calculate the modulus of elasticity values of 1000 psi and 1140 psi for unfired and fired specimens, respectively. These values were about half those for Formulation 2002 currently recommended for 1400F service.

Thermal Conductivity

Specimens have been prepared for thermal conductivity evaluation between 400F and 1200F mean temperature in air and vacuum. These tests will be

FIGURE 1.

STRESS-STRAIN RELATIONSHIP OF MICROTHERM

Loading Rate of 60 psi/min
Tested at Room Temperature

performed later in the program, however, as other materials which must undergo prolonged aging will be tested first.

General Comments

As previously mentioned, the handleability appeared to be poor, although no real test of its handleability was undertaken due to the relatively small amount of material available for the other physical evaluations. It was noted, however, that corners were easily chipped and broken, even with careful handling.

MICROTHERM has a strong dusting tendency as noted by an inability to "clean" cut edges of dust using a small, fine-haired brush.

The average density of the MICROTHERM blocks was slightly below 19 pcf, compared with 20 $\pm$ 0.5 pcf for the MIN-K formulations. This slightly lower density could account for a small per cent of the difference in physical properties between the Boucher and Johns-Manville products.

Boucher appears to have excellent control over the molded thickness, and the thickness regain (after molding). The nominal 1-in. thick blocks ranged from 0.988 in. to 1.011 in.

Fiber distribution within the blocks also appeared excellent with only a few scattered minute clumps visible to the eye. More evident, however, were small pockets of silica, indicating less efficient separation and subsequent mixing of the silica with the opacifier. However, neither of these small inconsistencies in distribution should affect the thermal efficiency of the product.

A cloth or fine mesh screen pattern was evident on both faces of the blocks, indicating that molding was not done directly against machined die surfaces as is the case with MIN-K.

It is recommended that no further evaluations be conducted on MICROTHERM (except for the programmed thermal conductivity measurements), since it appears to offer no advantage over the present MIN-K 1999 and 2002 formulations for 1400F service. It also appears, from the thermal stability data, that it would not be satisfactory for service at 1800F.

B. LOAD BEARING MATERIALS

Several materials have been evaluated as potential load-bearing candidates. They include:

CERABOARD (Johns-Manville) - a refractory fiber board containing an inorganic binder.

Thermal Conductivity: unavailable
Density: 40 - 50 pcf

GH BOARD (Carborundum) - similar to CERABOARD.

Thermal Conductivity: 0.9 Btu in./hr ft² °F at 1000F mean temperature
Density: 30 - 40 pcf

J-M 3000 INSULATING FIREBRICK (Johns-Manville) - 3000F refractory brick for furnaces, kilns, etcetera.

Thermal Conductivity: 3.3 Btu in./hr ft² °F at 1000F mean temperature
Density: 65 pcf

J-M 23 INSULATING FIREBRICK (Johns-Manville) - 2300F refractory brick for furnaces, kilns, etcetera.

Thermal Conductivity: 1.2 Btu in./hr ft² °F at 1000F mean temperature
Density: 31 pcf

GLASROCK NO. 25 (Glasrock Products Inc.) - open cell, pure fused silica foam.

Thermal Conductivity: approximately 1.0 Btu in./hr ft² °F at 1000F mean temperature
Density: 23 - 28 pcf

GLASROCK NO. 50 (Glasrock Products Inc.) - open cell, pure fused silica foam.

Thermal Conductivity: approximately 1.4 Btu in./hr ft² °F at 1000F mean temperature
Density: 44 - 50 pcf

(Above data supplied by the manufacturers.)

These materials were subjected to constant loads (50 to 300 psi) and hot face temperatures up to 1800F for periods of up to 168 hours to determine their creep tendencies (as established by the permanent strain

of the specimens). All specimens were 4 x 4 x 1-in. (approximately) with the exception of the GH board which consisted of several layers of 1/4-in. thick board. Table 3 summarizes the results.

TABLE 3.
PERMANENT STRAIN OF LOAD BEARING CANDIDATES
AFTER 168 HOURS

Material	Density pcf	Test Pressure psi	Hot Face °F	Permanent Strain in./in.
GLASROCK 25	24	150	1790	0.001
GLASROCK 25	24	200	1800	0.002
GLASROCK 25	24	200	1680	0.001
GLASROCK 25	24	200	1650	0.002
GLASROCK 25	24	200	1680	None
GLASROCK 50	50	200	1690	0.002
GLASROCK 50	50	200	1680	-0.002*
GLASROCK 50	50	200	1650	0.001
GLASROCK 50	50	200	1670	0.001
J-M 3000	67	50	1780	0.005
J-M 23	34	50	1800	0.017
J-M 23	34	300	1800	Crushed (24 hr)**
CERABOARD	45	100	1800	0.041
CERABOARD	45	200	1800	0.041 (96 hr)**
GH BOARD (3 pcs)	36	150	1800	0.321
GH BOARD (3 pcs)	31	200	1790	0.277
GH BOARD (4 pcs)	31	200	1800	0.424 (120 hr)**

*Measured thicker after test than before test.

**Tests aborted due to heater failure.

The more recent tests on GLASROCK were performed after a redesign of the heater plate and temperature control technique to eliminate heater burn-out. It then became impossible to achieve 1800°F hot face due to the relatively high heat loss through the specimen.

All measurements were made with a 0.001 in. dial gauge. In the case of one of the GLASROCK 50 specimens, the measurement after test of -0.002 in./in. permanent strain was an indication of the accuracy of measurement which could be expected. Thus, both GLASROCK No. 25 and No. 50 were

considered to have sustained the load without undergoing permanent strain, and hence, it could be assumed that there would have been no load-relaxation.

The only other material which approached GLASROCK in ability to carry load was J-M 3000 Insulating FIREBRICK. The high density and poor thermal conductivity, however, appear to make it less desirable than the GLASROCK materials. Samples of GLASROCK No. 25 and No. 50 will be tested for thermal conductivity at a later date.

III. DETAILED EVALUATION

A. MIN-K FORMULATION 2002

Stress Strain

A detailed program to evaluate the stress-strain characteristics of Formulation 2002 was completed. This program evaluated the following variables:

1. batch
2. blocks within a batch
3. specimens within a block
4. loading rate
5. test temperature
6. axial direction of loading

Table 4 details the schedule of specimen source and test conditions. Prime emphasis was given to the "X" axis (normal to the surface of the molded block).

Each batch was 2 lb, sufficient for two 9 x 9 x 1-in. blocks at 20 pcf. Each block was cut into four equal specimens (except for the 1400F hot face specimens which were trimmed to 4 x 4-in. to fit the apparatus). The "Y" and "Z" axis specimens were 4-1/2 x 1-1/2 x 1/2-in. The width of these specimens was limited by the thickness limitations encountered during molding.

Data on room temperature tests were taken at every 0.005 in./in. strain. However, since the hot face tests involved furnace deflection as well as specimen strain (furnace deflection determined before and after each test), total strain readings were taken at every 100 lb total load (6.25 psi increments), and the furnace deflection subsequently subtracted from the total strain readings to obtain the true specimen strain. The maximum stress applied to the hot face specimens was 200 psi (equipment limitation).

All room temperature test specimens had an initial static preload of 0.3 psi, whereas the hot face test specimens had an initial static preload of 3 psi. Although the lower preload (0.3 psi) would have been preferred, a 3 psi preload on the hot face compression units was necessary to insure proper nesting of the heater plate, thermocouple, and specimen assembly within the body of the furnace.

Figure 2 represents the average stress-strain curve for the thirty specimens tested at room temperature and at a loading rate of 60 psi/min. The dash lines represent the standard deviation (68% limits), while the dotted lines represent twice the standard deviation (95% limits).

TABLE 4.

FORMULATION 2002 STRESS-STRAIN PROGRAM

Batch	Block	Specimen	Room Temp	Test Conditions				
				1400F Hot Face	60 psi/ min	180 psi/ min	"1Y" Direct.	"2Y" Direct.
A	1	a	*		*			
		b	*		*			
		c	*		*			
		d		*	*			
	2	a	*		*			
		b	*		*			
		c	*		*			
		d	*			*		
B	1	a	*		*			
		b	*		*			
		c	*		*			
		d		*	*			
	2	a	*		*			
		b	*		*			
		c	*		*			
		d	*			*		
C	1	a	*		*			
		b	*		*			
		c	*		*			
		d		*	*			
	2	a	*		*			
		b	*		*			
		c	*		*			
		d	*			*		
D	1	a	*		*			
		b	*		*			
		c	*		*			
		d		*	*			
	2	a	*		*			
		b	*		*			
		c	*		*			
		d	*			*		

Continued

TABLE 4. (Continued)

Batch	Block	Specimen	Room Temp	Test Conditions				
				1400F Hot Face	60 psi/ min	180 psi/ min	"Y" Direct.	"Z" Direct.
E	1	a	*		*			
		b	*		*			
		c	*		*			
		d		*	*			
	2	a	*		*			
		b	*		*			
		c	*		*			
		d	*			*		
F	1	a	*		*		*	
		b	*		*		*	
		c	*		*		*	
		d	*		*		*	
		e	*		*		*	
		f	*		*		*	
		g	*		*			*
		h	*		*			*
		i	*		*			*
		j	*		*			*
		k	*		*			*

SUMMARY:

Total number of specimens in "X" direction, at room temperature and 60 psi/min	30
Total number of specimens in "X" direction, at room temperature and 180 psi/min	5
Total number of specimens in "X" direction, at 1400F and 60 psi/min	5
Total number of specimens in "Y" direction	6
Total number of specimens in "Z" direction	5

FIGURE 2.

STRESS-STRAIN CHARACTERISTICS OF FORMULATION 2002
IN THE "X" DIRECTION

An analysis of variance indicated that a significant difference existed between batches as well as between blocks, and hence, separate curves should be plotted for each of these variables. However, practical considerations dictated that all the data should be combined, and a standard deviation calculated for all specimens as shown in Figure 2.

The equation for the stress-strain curve between 0.02 and 0.15 in./in. strain was:

$$\text{Stress} = -11.04 + (2002)(\text{strain})$$

The non-linear portion of the curve (below 0.02 in./in.) was not considered in the calculations, and hence, a negative stress intercept was obtained.

The 95 per cent confidence limits were calculated to be +3.7 psi at 0.02 in./in., +13.4 psi at 0.08 in./in., and +26.8 psi at 0.14 in./in. Previous data on MIN-K 1301 by Martin Company⁽³⁾ resulted in 90 per cent confidence limits of +16 psi at 0.02 in./in. These early tests were conducted on specimens cut from the same block, thus eliminating two of the potential sources of variability (between blocks, and between batches) which were included in the present curve. Consequently, it would appear that the estimate of uniformity made following the machining evaluation of Formulation 2002⁽¹⁾, has been verified; namely, that Formulation 2002 is superior in uniformity to MIN-K 1301.

The preliminary stress-strain data for Formulation 2002⁽¹⁾ indicated that a change in slope of the curve at the 0.11 to 0.12 strain level may occur. This was not evident in the more detailed evaluation. However, minute edge fractures were first noted between 0.08 in./in. and 0.11 in./in. strain. The significance of these fractures is unknown since their effect could not be detected on the stress-strain curve.

Five specimens, one from each batch, were subjected to room temperature loading at a rate of 180 psi/min. The equation for these data was:

$$\text{Stress} = -11.84 + (2052)(\text{strain})$$

It will be noted that this equation does not significantly differ (on a practical basis) from that derived from the previous data taken at the lower loading rate.

Likewise, five specimens, one from each batch, were subjected to 1400F hot face, and 60 psi/min loading rate. The equation derived from these data was:

$$\text{Stress} = 8.33 + (2116)(\text{strain})$$

As previously noted, the preload for the hot face tests was greater than that for the room temperature tests, and thus the apparent positive stress intercept. This curve is plotted in Figure 3. The 68 per cent and 95 per cent confidence limits are also plotted.

The adjustment of the stress intercept of the hot face curve, the combination of all room temperature data, and the rounding off of the equation constants in keeping with practical engineering and design requirements resulted in the following equations:

Room Temp

$$\text{Stress} = -11 + (2000)(\text{strain})$$

Hot Face

$$\text{Stress} = -11 + (2100)(\text{strain})$$

These equations are plotted in Figure 4.

The calculated modulus of elasticity at room temperature was 2000 psi, whereas the modulus of elasticity at 1400F hot face was 2100 psi. These values are considerably less than the 5000 psi determined by Martin Company (3) for MIN-K 1301.

All of the above data was obtained on Formulation 2002 in the "x" direction (normal to the molded surface). The results of the "y" and "z" directions are plotted in Figure 5 from the following equations:

"y" Direction

$$\text{Stress} = -3.9 + (240)(\text{strain}) + (6009)(\ln \text{strain})$$

"z" Direction

$$\text{Stress} = -3.7 + (286)(\text{strain}) + (6078)(\ln \text{strain})$$

Within practical engineering limits, these two equations may be combined into one as follows:

$$\text{Stress} = -4 + (260)(\text{strain}) + (6040)(\ln \text{strain})$$

This equation is plotted in Figure 6 together with the 95 per cent (2 σ) confidence limits. It is interesting to note that these data were more consistent than those in the "x" direction.

FIGURE 3.

STRESS-STRAIN CHARACTERISTICS OF FORMULATION 2002
IN THE "X" DIRECTION

1400F Hot Face
Loading Rate of 60 psi/min

FIGURE 4.

COMBINED STRESS-STRAIN CHARACTERISTICS
FOR FORMULATION 2002
IN THE "X" DIRECTION

FIGURE 5.

STRESS-STRAIN CHARACTERISTICS OF FORMULATION 2002
IN THE "Y" AND "Z" DIRECTIONS

Room Temperature
Loading Rate of 60 psi/min

FIGURE 6.

COMBINED STRESS-STRAIN CHARACTERISTICS
OF FORMULATION 2002 IN THE "Y" AND "Z" DIRECTIONS

Room Temperature
Loading Rate of 60 psi/min

As expected, the "Y" and "Z" directions did not have the same load carrying ability of the "X" direction. Stresses between 50 and 75 psi resulted in obvious delamination cracks and a lateral "spreading" of the specimen in the test fixture. As the test progressed, specimens were delaminated such that two or three individual pieces were frequently evident. No side restraint was provided for the specimens.

This phenomenon was characteristic of MIN-K 1301, and hence was expected in the new formulations. Thus, it may be concluded that Formulation 2002 should not carry a primary stress parallel to the molded surfaces, but that secondary stresses (such as vibrational loadings) on a reasonably well contained block could probably be tolerated.

From these evaluations, it may be concluded that the stress-strain characteristics of Formulation 2002 are independent, for all practical consideration, of the variables investigated except for the axial loading direction. As mentioned previously, the modulus of elasticity of Formulation 2002 is considerably lower than that for MIN-K 1301. Other tests are currently under way to determine the effect this may have on the dynamic properties of the material.

The stress-strain characteristics are the only properties found to date which have been compromised during the development of the improved formulations. It shall be proposed as part of Phase II that consideration be given to the development of a heavier density product having greater load bearing capability. However, such a program would necessarily include reformulation investigations to minimize the increase in thermal conductivity which must be anticipated.

Load Relaxation

The load relaxation test procedure (see Appendix) requires that the furnace deflection be considered together with a constant specimen strain when determining the load which the specimen will sustain at any given time. Although the furnace is calibrated both before and after each test, the amount of creep within the furnace at any given time cannot be determined during the test. Consequently, after the specimen is removed from the furnace, it will be placed in a room temperature compression fixture having zero deflection and creep under load. The final load reading during the hot face portion of the test will be applied and the specimen strain noted. If it is less than the calculated strain established at the start of the hot face test, additional load will be applied until the proper strain is attained. This new load would then more nearly represent the load which the specimen would sustain after the extended test period.

Formulation 2002 specimens have attained over 1300 hours of test at 1400°F hot face. Figure 7 is a log-log plot showing the general pattern

FIGURE 7.

LOAD RELAXATION OF FORMULATION 2002 AT 1400F HOT FACE

of the individual tests. None of the data have been corrected for possible furnace creep as described above since the tests are still in progress. It appears that the rate of load relaxation is independent of the initial load (50 or 100 psi), but is related to the per cent of initial load. Initial loadings of 150 psi will be initiated during the fourth quarter.

Thermal Stability

The thermal stability testing of Formulation 2002 in air at 1400F for 2000 hr has been completed. The test will be continued during the next quarter to include 100 hr at 1500F and 48 hr at 1600F.

Twelve 6 x 3 x 1-in. specimens were measured for length, width, thickness, and weight, and placed into a large furnace in a random manner. After 500 hr, specimens 1, 2, and 3 were removed (while the furnace was at 1400F), measured, and re-inserted into the hot furnace. At 1000 hr, specimens 1 through 6 were removed, measured, and re-inserted. A similar procedure was followed for 1500 hr and 2000 hr exposure. In all instances, the per cent change was based on the specimen dimensions prior to the prolonged exposure. Measurements were made with a 0.001 in. dial gauge.

The results indicated no apparent difference between those specimens which were removed periodically, and those which remained heated for 2000 hr. Likewise, the shrinkage after 500 hr was indicative of the shrinkage after 2000 hr, except in the width direction. An abrupt increase in shrinkage from 0.4 per cent to 0.8 per cent was noted for all twelve specimens. A review of the test procedure and technique, the temperature recording charts, formulation chemistry, and a check of the temperature distribution within the furnace failed to yield a reason for this change. Table 5 below summarizes the results.

TABLE 5.

THE THERMAL STABILITY OF FORMULATION 2002 AT 1400F IN AIR

Time at 1400F, hr	No. of Specimens	Shrinkage, Per cent			Weight Loss, Per Cent
		Length	Width	Thickness	
500	3	0.3	0.3	0.7	0.1
1000	6	0.4	0.4	0.8	0.2
1500	9	0.3	0.4	0.7	0.2
2000	12	0.4	0.8	0.8	0.2
Estimated accuracy		+0.03	+0.07	+0.2	+0.1

It should be stressed that all shrinkage values were based upon isothermal exposure to a temperature fluctuation of 1395F to 1425F. In service, a specimen subjected to 1400F hot face, and a gradient of 800F or more would show considerably less shrinkage.

Moisture Adsorption Rate

A test series has been initiated to determine the moisture adsorption rate of various thicknesses of a MIN-K type when exposed to low, medium and high humidity room temperature conditions. The program will also include the rate at which moisture is desorbed in a still air atmosphere at 110C (230F). Information of this nature will indicate the extent of the precautions necessary to prevent this insulation from coming in contact with atmospheric conditions during generator assembly, and also the time required to remove the moisture should exposure occur.

To determine the adsorption rate, specimens of Formulation 2002 were subjected to drying conditions of 110C (230F) for 24 hr. The specimens were then placed into plastic bags, sealed and cooled to room temperature. They were then placed on a balance in a controlled humidity chamber, and the change in weight of the specimens was recorded at various time intervals.

To date, only the adsorption rate at 27 per cent RH has been completed. The results for 1/4-in., 1/2-in., and 1-in. thick 4 x 4-in. specimens are shown in Figure 8. The curves followed the anticipated time-per cent pickup relationship. Similarly, the relationship between thicknesses was as expected.

Note that the equilibrium points for the 1/4-in. and 1-in. specimens were 0.55 per cent after 960 min, and 0.66 per cent after 2880 min, respectively.

It is apparent that MIN-K (the name used to include all formulations) readily adsorbs moisture from the air, and that only a few minutes' exposure to atmospheric conditions is necessary to pick up significant amounts of moisture.

B. CHEMICAL COMPATIBILITY OF FORMULATION 1999 AND 2002 WITH PbTe ELEMENTS

The 2000 hr PbTe compatibility tests in argon at 1000F began December 1, 1966 (see Appendix for test procedure). The first set of elements were

FIGURE 8.

MOISTURE ADSORPTION RATE OF FORMULATION 2002 AT ROOM TEMPERATURE
AND 27 PER CENT RH

removed on December 22, 1966 after 500 hr of exposure. These elements have been delivered to Martin Company for retest of Seebeck voltage and resistivity to determine the effect of the intimate contact with the insulation on the performance of the elements. The results of these retests were not available within this reporting period.

C. CHEMICAL COMPATIBILITY OF FIBROUS CANDIDATES WITH SiGe ELEMENTS

MICRO-QUARTZ, ASTROQUARTZ, DYNAQUARTZ, and Irish REFRASIL high temperature fibrous insulations have been selected for chemical compatibility tests with SiGe elements (in pellet form) at 1600F in both air and vacuum. These tests (see Appendix) were devised to determine by spectrographic analysis the change in chemical composition of the surface of the element as a result of intimate contact with the insulations.

The compatibility test in air with the four fibrous candidates was initiated this quarter and has passed the 500 hr mark. The analyses, however, were not completed for this report. The compatibility test in vacuum was also initiated, but did not pass the 500 hr mark before the end of the quarter.

In addition to the above tests, SiGe N and P bars, 1/4-in. square in cross-section and 1-3/4-in. long, will be embedded into Formulation XXXX and Irish REFRASIL, and subjected to 1600F in air and vacuum. The measure of performance will be room temperature Seebeck voltage and resistivity tests before and after exposure. Bars embedded in MICRO-QUARTZ will be used for comparison purposes. This test has the advantage of measuring bulk properties of the elements rather than surface properties as in the tests currently in progress. These tests are scheduled to begin during the next quarter.

IV. MATERIAL AND PROCESS DEVELOPMENT

A. SILICA EVALUATIONS FOR HIGH TEMPERATURE USE

The prime concern in upgrading the temperature limit of the developmental formulations is the thermal stability of the silica material itself. For example, MIN-K 2000 is considerably more stable than MIN-K 1301 because CAB-O-SIL M5 has greater thermal stability than SANTOCEL A.

The upgrading of Formulations 1999 and/or 2002 can be achieved in two ways:

- a. use a more stable silica,
- b. prefire the silica to elevated temperatures prior to formulating the mix.

Method (a) is far more advantageous since it requires no additional processing steps, and insures a uniform raw material. Both techniques are under investigation, however. Table 6 (see Page 26) lists the formulations investigated during the third quarter pertaining to an 1800F material.

Three new (to this program) silica materials were investigated for thermal stability. They were AEROSIL uncompressed, AEROSIL 2491-380, and AEROSIL 2491, distributed by Degussa Inc., Pigments, Division, Kearny, New Jersey. Typical property data on each are given in Table 7. The main differences between these products lie in the particle size and surface area. By comparison, CAB-O-SIL M5 has a surface area of 200 m²/gm, thus indicating that these materials would be as good, if not better than CAB-O-SIL from a thermal efficiency standpoint.

TABLE 7.

PROPERTIES OF AEROSIL (MANUFACTURER'S DATA)

Property	AEROSIL Uncompressed	AEROSIL 2491-380	AEROSIL 2491
SiO ₂ , per cent	>99.8	>99.8	>99.8
Particle size, m μ	10-40	3-15	5-20
BET Surface Area, m ² /gm	200 $\pm$ 25	380 $\pm$ 40	300 $\pm$ 30
Bulk Density, lb/ft ³	2.5-3.5	2.5-3.5	2.5-3.5
HCl, per cent	<0.025	<0.025	<0.025
Al ₂ O ₃ , per cent	<0.05	<0.05	<0.05
TiO ₂ , per cent	<0.03	<0.03	<0.03
Fe ₂ O ₃ , per cent	<0.003	<0.003	<0.003

TABLE 6.

THIRD QUARTER EXPERIMENTAL MIN-K FORMULATIONS (1)

Number	Silica			Fiber			TAM -5 μ TiO ₂	BRP 5095 Binder	Comments
	CAB-O-SIL M5	AEROSIL Uncompr.	AEROSIL 2491-380	AEROSIL 2491	ASTRO- QUARTZ 1/2"	ASTRO- QUARTZ 1/4"	MICRO- QUARTZ AA		
2004		75			5		4	16	0
2005			75		5		4	16	0
2006				75	5		4	16	0
2007	75(2)				5		4	16	0
2008	75(2)				5		4	16	0
2009	75(3)				5		4	16	0
2010	75(3)					1	8	16	0
2011	73(2)					1	8	16	2
2012		75(4)				1	8	16	0
2013		73(4)				1	8	16	2

CAB-O-SIL premilled in
Henschel 5 min.

AEROSIL premilled in
Henschel 5 min.

AEROSIL premilled in
Henschel 5 min.

(1) All numbers represent per cent by weight.

(2) Prefired 2 hr at 1850F.

(3) Prefired to 1850F.

(4) Prefired to 1820F.

B. THERMAL CONDUCTIVITY

Formulations 2004, 2005, and 2006, similar to Formulation 2002, but containing the AEROSIL products, were molded and tested for thermal conductivity on the rapid heat meter apparatus. Table 8 summarizes the results.

TABLE 8.

THERMAL CONDUCTIVITY OF FORMULATIONS 2004, 2005, AND 2006

<u>Formulation</u>	<u>Density, pcf</u>	<u>Mean Temp, °F</u>	<u>Thermal Conduct., Btu in./hr ft² °F</u>
2004	19.7	1017	.24 (2)
2005	20.4	1017	.22 (6)
2006	20.3	1017	.23 (5)

The above data indicated that each silica provided excellent thermal efficiency, and should be considered further.

C. THERMAL STABILITY

Each of the AEROSIL formulations was fired to 1800F for 24 hr. The results are summarized in Table 9.

TABLE 9.

THERMAL STABILITY OF FORMULATIONS 2004, 2005, AND 2006 AFTER 24 HOURS AT 1800F

<u>Formulation</u>	<u>Shrinkage, %</u>			<u>Weight Loss, %</u>
	<u>Length</u>	<u>Width</u>	<u>Thickness</u>	
2004	1.0	1.3	6.9	1.0
2005	1.9	2.4	14.7	2.5
2006	1.7	2.6	13.7	2.1

Formulation 2004 containing AEROSIL uncompressed had half the linear shrinkage of the other two formulations, and was similar to the shrinkage of MIN-K 2000(2). However, it failed to approach the desired thermal stability for an 1800F bulk insulation. AEROSIL uncompressed and CAB-O-SIL M5 were selected for further evaluation incorporating a silica prefiring step into the manufacturing process.

D. PREFIRING CAB-O-SIL AND AEROSIL

The purpose of prefiring the silica (prior to incorporation into the formulation) was to initiate the sintering process within the silica, and thus reduce the amount of sintering which would normally occur in the product at elevated temperatures. This could be a relatively delicate process, since prefiring at too low a temperature may have little advantage, whereas prefiring at too high a temperature may seriously degrade the thermal conductivity of the product. These extremes may be separated by only 50 to 100 degrees F.

Prefiring of the silica was done in a 14 x 14 x 12-in. Inconel sheet metal container capable of holding approximately 4 lb of silica. The container was placed into a gas fired kiln and instrumented with a thermocouple placed in the center of the container. The reported thermal history for each firing was based on the readings taken from this thermocouple.

A typical firing schedule is shown in Table 10 below. The desired silica temperature (in this case CAB-O-SIL) was 1850F as indicated by the thermocouple within the container. Note that the temperature lag between the kiln and the silica was not serious, and that a kiln setting of 1870F was required to achieve 1850F within the silica.

TABLE 10.

TYPICAL FIRING SCHEDULE OF SILICA

<u>Time, hr</u>	<u>Silica Thermocouple Reading, °F</u>	<u>Kiln Temperature °F</u>
0	105	100
1	1665	1850 - 1870
2	1785	1850 - 1870
3	1820	1850 - 1870
4	1850	1850 - 1870
6	1850	1850 - 1870

In several instances such as Formulations 2007 and 2008, the silica temperature was held at 1850F for 2 hr. For Formulations 2009 and 2010, the kiln was turned off just as the temperature of the silica reached 1850F. Similar procedures were conducted for AEROSIL uncompressed, except that the maximum silica temperature was 1820F.

It became apparent that the time at temperature also had an effect upon the resultant silica. For example, the first silica firing was initiated with a maximum kiln temperature of 1850F. After several hours, it became obvious that the kiln temperature had to be increased to about 1870F before the silica temperature would reach 1850F. These additional few hours resulted in a "gritty" feel to Formulation 2007, indicating noticeable sintering of the silica particles. In contrast, the firing of a second batch of CAB-O-SIL for Formulation 2008 did not have this "gritty" feel, probably because the total time at the elevated temperature was considerably less. Similarly, the silicas fired for Formulations 2009 through 2013 did not have a "gritty" feel, although a 5-min premill of the silica alone in the Henschel mixer was adopted as a means of minimizing the possibility of fused silica particles in the formulation.

E. MOLDING CHARACTERISTICS

Formulations 2004, 2005, and 2006 had satisfactory, although not outstanding molding characteristics. Each 9 x 9 x 1-in. block had many hairline delamination cracks on all four edges. However, they were shallow, and the remainder of each block was solid and uniform.

Blocks 9 x 9 x 1-in. made from Formulations 2007 through 2010 were very poor, showing many delamination cracks, excessive thickness regain, and a dull "ring" which is characteristic of a block with internal delaminations. It was apparent that the prefiring step was detrimental to the "self-bonding" characteristics of the CAB-O-SIL M5.

Formulation 2011 containing 2 per cent powdered phenolic binder (same as in MIN-K 1301 and MIN-K 2000) resulted in a good, solid block free from delaminations. Ignition of this block at 1400F for 2 hr (to remove the binder) did not alter the condition of the block, indicating that although some binder may be required during the molding step to insure a satisfactory part, it can be subsequently removed without harmful effects.

Formulation 2012 containing prefired AEROSIL uncompressed molded satisfactorily, although many hairline cracks were evident as in Formulations 2004, 2005, and 2006. The prefiring of the AEROSIL uncompressed to 1820F apparently did not significantly alter its molding characteristics.

Formulation 2013 (containing 2 per cent binder) was made as insurance against Formulation 2012 failing to mold satisfactorily. It will be retained for possible use in the future.

F. THERMAL STABILITY OF FORMULATIONS CONTAINING PREFIRED SILICA

A program to determine the thermal stability of several of the formulations containing prefired silica was initiated just prior to the close of this quarter. Consequently, the results are incomplete at this writing. Indications are, however, that Formulations 2010 or 2011 (identical except for the binder) may have sufficient thermal stability for 1600F service around the SiGe thermoelectric elements.

V. SUMMARY OF THIRD QUARTER RESULTS AND CONCLUSIONS

A. FINAL SCREENING

1. MICROTHERM was more stable to shrinkage at elevated temperatures than MIN-K 1301, but less stable than MIN-K 2002.
2. The modulus of rupture (breaking strength) of MICROTHERM was only 16 to 20 psi.
3. MICROTHERM has a modulus of elasticity of approximately 1110 psi. This is about one-fifth that of MIN-K 1301 and one-half that of Formulation 2002.
4. MICROTHERM has a strong dusting tendency, and appears to be relatively fragile.
5. Unless thermal conductivity measurements scheduled for the fourth quarter yield unexpectedly low results, MICROTHERM appears to offer no advantage over Formulations 1999 and 2002.
6. The GLASROCK 25 and GLASROCK 50 products are the only materials tested to date that can withstand 200 psi loading without creep or permanent deformation.

B. DETAILED EVALUATION

1. The stress-strain characteristics of Formulation 2002 are, for all practical purposes, independent of batch, blocks within a batch, specimens within a block, loading rate, and test temperature.
2. The modulus of elasticity in the "X" direction was 2000 psi for the room temperature tests, and 2100 psi for the 1400F hot face tests.
3. Formulation 2002 had poor stress-strain characteristics in the "Y" and "Z" directions.
4. Formulation 2002 should not carry a primary stress in the "Y" or "Z" directions (parallel to the molded surfaces). However, secondary stresses on a reasonably well contained block could probably be tolerated.
5. After 1300 hours at 1400F hot face, Formulation 2002 supported approximately 50 per cent of its initial loading (50 or 100 psi).
6. The linear and thickness shrinkage of Formulation 2002 was less than 1 per cent after 2000 hours isothermal exposure to 1400F in air.

7. Formulation 2002 rapidly adsorbs moisture in a 27 per cent RH, room temperature atmosphere, and achieves equilibrium at about 0.6 per cent moisture pickup at this humidity level.
8. All test results to date have indicated that Formulations 1999 and 2002 are satisfactory for service in PbTe RTG applications.

C. MATERIAL AND PROCESS DEVELOPMENT

1. AEROSIL uncompressed, 2491-380, and 2491 provide essentially the same insulating effectiveness as CAB-O-SIL M5.
2. Formulation 2004 made with AEROSIL uncompressed had the same linear shrinkage as MIN-K 2000 at 1800F.
3. Prefiring CAB-O-SIL M5 to 1850F hindered its ability to mold satisfactorily without binder.
4. The prefiring step appears to improve the thermal stability of the formulation.

VI. FOURTH QUARTER EFFORT

1. Continue compatibility tests already in progress:
 - a. PbTe - Formulations 1999 and 2002 in argon at 1000F,
 - b. SiGe - fibrous candidates in air at 1600F,
 - c. SiGe - fibrous candidates in vacuum at 1600F.
2. Complete Formulation 2002 load relaxation tests.
3. Initiate SiGe compatibility tests using Seebeck voltage and resistivity measurements as the criteria for compatibility.
4. Initiate Formulation 2002 outgassing tests.
5. Initiate dynamic testing of Formulation 2002.
6. Continue formulation development for 1800F service.

VII. REFERENCES

1. Develop 1800F - 400F Fibrous Type Insulation for Radioisotope Power Systems, Second Quarterly Progress Report, Report No. ALO-3633-2, October 3, 1966, under AEC Contract AT(30-1)-3633.
2. Develop 1800F - 400F Fibrous Type Insulation for Radioisotope Power Systems, First Quarterly Progress Report, Report No. ALO-3633-1, July 1, 1966, under AEC Contract AT(30-1)-3633.
3. Structural Evaluation of MIN-K 1301, Report No. NMD-3169-45, January 1965, under AEC Contract AT(30-1)-3169.

VIII. APPENDIX

MODULUS OF RUPTURE OF EXPERIMENTAL MIN-K FORMULATIONS

1.0 Purpose

The purpose of this test is to determine the flexural strength of preformed block-type thermal insulations such as MIN-K, experimental formulations and MICROTHERM. This test does not necessarily yield an absolute value, but is useful in determining relative changes and/or the effect of formulation modifications upon:

- a. handleability
- b. fiber distribution
- c. fiber openness
- d. fiber reinforcing efficiency.

2.0 Equipment

The equipment shall consist of the following:

2.1 Any form of testing machine capable of applying and measuring the required load. Load application shall consist of a single, self-aligning bearing edge approximately 1/2 in. diameter and 6 in. long.

2.2 Parallel, self-aligning cylindrical bearing edges approximately 1/2 in. diameter and 6 in. long whose distance between centers can be adjusted and accurately set to provide a given specimen span.

3.0 Specimens

The test specimens shall be nominally 4-1/2 x 4-1/2 x 1 in. in size, cut from any sized slab or block which is nominally 1 in. thick.

The width and thickness of the specimen shall be measured to the nearest 0.001 in.

4.0 Test Procedure

- 4.1 Adjust the parallel bearing edges so as to provide a specimen span of 4.0 ± 0.05 in.
- 4.2 Place the specimen on the parallel bearing edges such that the width dimension is parallel to the edges.
- 4.3 Center the loading edge such that it contacts the specimen midway (± 0.05 in.) between the bearing edges.
- 4.4 Counter-balance the scale to read zero load.
- 4.5 Apply the load at a rate not to exceed 250 lb/min.
- 4.6 Continue loading until a maximum load in pounds is indicated by the test equipment, indicating a failure of the specimen.
- 4.7 Record the maximum load attained in Step 4.6.
- 4.8 The Modulus of Rupture shall be calculated as follows:

$$MR = \frac{3Wl}{2bt^2}$$

Where: MR = Modulus of Rupture in psi,

W = maximum load in pounds,

l = span (in this case, 4 in.),

b = width of specimen in inches, and

t = thickness of specimen in inches.

5.0 General Comments

This test is designed after ASTM C 203-58. The ASTM procedure specifies a 10-in. span, a 6-in. specimen width, and a 1-1/2-in. specimen thickness as preferred dimensions. It will be noted that although the span to thickness, and the span to width ratios have been altered slightly, the span to thickness ratio is the same. Nonetheless, the ASTM procedure does allow for dimensional modifications, but stipulates that "numerical values should be compared only when determined on materials of similar composition and physical properties." The above specified dimensions have been in use for MIN-K products since their inception with satisfactory results.

LOAD-RELAXATION OF MIN-K 2002 AT
50, 100, AND 150 PSI INITIAL LOADING
Revision A dated December 12, 1966

1.0 Purpose

The purpose of this test is to evaluate the relaxation tendencies of experimental MIN-K under load. Since the furnace also experiences deflection under load, it is necessary to calibrate the furnace, and make subsequent pressure adjustments during the test (on a trial and error basis) to maintain a constant sample deflection. (Deflection readings combine both furnace and sample deflections.)

At the conclusion of the test, each specimen is subjected to the same calculated deflection and the same final loading under cold, rigid fixture conditions as a check of the terminal test conditions.

2.0 Samples

The samples shall be approximately 4 x 4 x 1-in. and loaded normal to the molded faces of the MIN-K block.

3.0 Furnace Calibration

3.1 Load furnace with 1-in. dummy specimen and heat to 1800 - 1900F (control temperature) for a minimum of 2 hr. (Note: This step is necessary only following a rebuild of the furnace unit.) Apply 3200 lb gauge pressure and hold.

3.2 Cool furnace (if necessary) to hot face test temperature and apply 200 psi load. Hold these conditions for a minimum of 72 hr, adjusting pressure as necessary.

- 3.3 Cool furnace to room temperature, replace dummy specimen with steel plates.
- 3.4 Load furnace to test pressure and hold for 24 hr (minimum).
- 3.5 Release load, reload to 50 lb (approximately 3 psi), and adjust dial gauge to zero.
- 3.6 Calibrate furnace at 100 lb increments up to test pressure.
- 3.7 Release load, reapply 50 lb, zero dial gauge, and repeat calibration.
- 3.8 Repeat 3.6 and 3.7 until a total of 5 calibrations have been run.
(Read the 0.001 dial gauge to the nearest 0.0005 in.)
- 3.9 Release load, reapply 50 lb, zero dial gauge, and hold under this load, for 24 hr (minimum).
- 3.10 Recalibrate per 3.6, 3.7 and 3.8.

4.0 Test Procedure

- 4.1 Premeasure the test specimen (approximately 4 x 4 x 1-in.) for length, width, thickness, and weight.
- 4.2 Place specimen in furnace. Slowly increase load to 300 lb and immediately release. Reset dial gauge to zero under 50 lb load. Repeat until dial returns to zero under 50 lb load three successive times.
(This is to insure proper seating of the sample, thermocouple wires, etc.)

- 4.3 Load to 50 lb (3 psi) and heat to the desired hot face temperature.
- 4.4 Hold temperature and load conditions for 24 hr, adjusting load as necessary during heat-up and stabilization.
- 4.5 Zero gauge at 50 lb load (if not already done so).
- 4.6 Increase load to test pressure at a rate of approximately 100 lb per 5 seconds, with the 50 to 100 lb range requiring 5 seconds.
- 4.7 Read gauge deflection every 100 lb (i.e., at 100, 200, 300 lb etc.) until test pressure is reached.
- 4.8 Read deflection at test pressure, and subtract from this the calibrated furnace deflection at the test load. This calculation represents the initial sample deflection.

Note: From this point on, the dial gauge should not show any additional deflection for the duration of the test. Likewise, test load should never exceed the initial loading.

- 4.9 Procedure for adjusting load:
 - 4.9.1 Read and record load and deflection.
 - 4.9.2 Determine furnace deflection at the load in paragraph 4.9.1 (from calibration curve), and subtract it from the deflection reading in paragraph 4.9.1.
 - 4.9.3 If the sample deflection calculated in paragraph 4.9.2 equals the initial sample deflection (paragraph 4.8), no pressure adjustment is necessary, and the load and deflection readings should be recorded as "corrected" readings.

- 4.9.4 If the calculation in paragraph 4.9.2 does not equal the initial sample deflection, adjust the pressure (less pressure if the sample deflection is greater, more pressure if it is lower), and proceed as in paragraph 4.9.2. Repeat as necessary until initial sample deflection is attained.
- 4.9.5 When initial sample deflection is attained, read pressure and deflection and record as "corrected" readings.
- 4.10 Specimen should be checked at least daily, and more frequently during the first week of test.
- 4.11 Pressure and deflection readings should be recorded:
- a. whenever a pressure adjustment is required; or
 - b. at least every 72 hr (approximate) whether a pressure change is necessary or not.
- 4.12 Record hot and cold face temperatures whenever loads and deflections are recorded.
- 4.13 At completion of test, release pressure and reset pressure to 50 lb.
- 4.14 Record dial reading.
- 4.15 Cool furnace and remove sample.
- 4.16 Remeasure sample for length, width, thickness and weight.
- 4.17 Place sample in room temperature compression-deflection unit, zero dial gauge with only the weight of the compression jig applied.

- 4.18 Load to 50 lb, hold for 1 minute, and record deflection. Rezero dial gauge.
- 4.19 Apply load to specimen slowly until either the final load or calculated sample deflection per the hot face test is achieved. Hold condition of interest constant for 1 minute and record load and deflection.
- 4.20 Continue loading until the other factor is attained (final load or calculated sample deflection). Hold condition of interest constant for 1 minute and record load and deflection.

5.0 Furnace Recalibration

- 5.1 Repeat steps 3.3 through 3.10.

CHEMICAL COMPATIBILITY OF MIN-K FORMULATIONS 1999
AND 2002 AND PbTe ELEMENTS

Revision B, November 10, 1966

1.0 Purpose

The purpose of this test is to determine the chemical compatibility of MIN-K Formulation 1999 and 2002 and PbTe thermoelectric elements, when exposed to 1000F in 1 atmosphere argon. The MIN-K specimens will be outgassed as much as can be tolerated by the PbTe elements prior to the initiation of the long term tests so that a differentiation can be made between chemical compatibility and effects due to outgassing products, should they exist.

Prime emphasis will be placed upon compatibility with Formulation 1999 since this was the formulation developed for this specific service. However, 1500 and 2000 hr exposures will also include Formulation 2002.

2.0 Equipment

The equipment will consist of four ceramic tubes nominally 4-3/8-in. diameter by 30-in. long, each having the following attachments:

1. Viton or similar gasket and flange assembly for sealing tube.
2. Valved gas inlet port (for introduction of argon) with a 0 to 2 atmosphere gauge attached for reading positive pressure within the tube.
3. A 1-1/2-in. diameter vacuum valve with flange for connecting to vacuum pump system.
4. Argon bottle and copper manifold system leading to gas inlet port (item 2).

The four tubes will be placed into a single box furnace per the original equipment designs.

3.0 Samples

Samples of Formulation 1999 and 2002 approximately 3 x 6 x 1-in. will be drilled to accept the PbTe elements. All elements will have been tested for Seebeck voltage and room temperature resistivity prior to this test.

4.0 Test Procedure

4.1 Preliminary Conditioning

4.1.1 Place predrilled blocks of MIN-K into the tubes as follows:

Tube 1 - Formulation 1999

Tube 2 - Formulation 1999

Tube 3 - Formulation 1999 and Formulation 2002

Tube 4 - Formulation 1999 and Formulation 2002

4.1.2 Seal tubes, heat to 1400F $\pm$ 20F under active vacuum and continue evacuation for a minimum of 24 hr.

4.1.3 Cool to 225F under active vacuum. Backfill with argon to 50 mm Hg above 1 atmosphere pressure.

4.1.4 Open each tube and insert the PbTe elements into the predrilled holes according to the following schedule.

Tube	Formulation	Exposure Time	Element Number			
			<u>2N</u>	<u>2P</u>	<u>3N</u>	<u>3P</u>
1	1999	500 hr	1	1	1	1
1	Blanks*	500 hr	2	2	2	2
2	1999	1000 hr	3, 4	3, 4	3, 4	3, 4
2	Blanks	1000 hr	5	5	5	5
3	1999	1500 hr	6, 7	6, 7	6, 7	6, 7
3	2002	1500 hr	8, 9	8, 9	8, 9	8, 9
3	Blanks	1500 hr	10	10	10	10
4	1999	2000 hr	11, 12, 13	11, 12, 13	11, 12, 13	11, 12, 13
4	2002	2000 hr	14, 15, 16	14, 15, 16	14, 15, 16	14, 15, 16
4	Blanks	2000 hr	17, 18	17, 18	17, 18	17, 18

*Blanks to be placed individually in small glazed crucibles atop the MIN-K blocks.

Each tube is to be loaded in sequence, and the elements must be placed in the proper premarked hole in the MIN-K.

4.1.5 Close and seal each tube when loaded.

4.1.6 Evacuate each tube to ≤ 5 microns at 250F. Leak check by closing vacuum line and note pressure rise (5 microns/hr maximum allowable).

4.1.7 Actively evacuate while heating tubes to $400 \pm 20^\circ\text{F}$. Continue evacuation for 24 hr.

4.1.8 Backfill with argon to 1 atmosphere.

4.1.9 Evacuate each tube to 5 microns or less and backfill with argon to 1 atmosphere.

- 4.1.10 Repeat 4.1.9.
- 4.1.11 Actively evacuate while heating tubes to $600 \pm 20^\circ\text{F}$. Continue evacuation for 24 hr.
- 4.1.12 Backfill with argon to 1 atmosphere.
- 4.1.13 Evacuate each tube to 5 microns or less and backfill with argon to 1 atmosphere.
- 4.1.14 Repeat 4.1.13.
- 4.1.15 Heat tubes to $1000 \pm 20^\circ\text{F}$ maintaining approximately 50 mm above 1 atmosphere pressure. Evacuate at 1000°F to < 20 microns, or for five minutes, whichever occurs first.
- 4.1.16 Backfill with argon to a pressure of 50 mm Hg above 1 atmosphere.
- 4.1.17 Repeat 4.1.15 and 4.1.16 until 20 microns is achieved, or total pumping time reaches 30 minutes.

4.2 Prolonged Testing

- 4.2.1 Maintain $1000 \pm 20^\circ\text{F}$ and 50 mm Hg above 1 atmosphere argon pressure for 500 hr.
- 4.2.2 Slowly (over a period of several hours) remove No. 1 tube from furnace protecting it with insulation felts as necessary to reduce thermal shock.
- 4.2.3 Bleed air into tube 1 after tube has cooled to 150°F , remove seal, and return each T/E to its original container.*

*Retest the T/E elements from each tube for Seebeck voltage and room temperature resistivity as soon as possible.

4.2.4 Repeat steps 4.2.2 and 4.2.3 at each 500 hr interval
until tube 4 has completed 2000 hr.

CHEMICAL COMPATIBILITY OF PACKED FIBERS WITH SiGe ELEMENTS
Revision C, December 13, 1966

1.0 Purpose

The purpose of this test is to determine the chemical compatibility between N and P SiGe elements and candidate insulations at 1600F and in air and/or vacuum. The criteria for compatibility shall be the change in chemical composition of the cylindrical surface of the elements as determined by spectrographic analysis.

2.0 Sample Preparation

- 2.1 Shred a sufficient amount of fiber for packing at a density of 10 pcf into a 2-in. diameter x 6-in. high ceramic crucible. (Shredding may best be done by placing small quantities of hand shredded felt into a Waring Blender, and blending for 10 to 15 seconds. The intent is not to chop the fiber, but rather to separate them as much as possible.)
- 2.2 Pack 41 gm of fiber to within 1/2-in. of the top of the crucible, compressing the mass periodically during this step to insure greater uniformity throughout the mass.
- 2.3 Drill 4 holes in the top surface of the packed fiber, three approximately 1-in. deep, and one approximately 2-1/2-in. deep, and all slightly undersized to the diameter of the element. (Drilling with a No. 7 cork borer to accept an element 0.444-in. diameter is satisfactory.)

- 2.4 Hole (or position) No. 1, so marked on the outside of the crucible will receive one N and P element for 500 hr exposure. This is repeated for holes 2 and 3, for 1000 and 1500 hr exposure, respectively. Hole 4 will receive three N and three P elements for 2000 hr exposure.
- 2.5 After insertion of all elements, flatten top surface of the packed fiber, and measure and record the distance between the rim of the crucible and the fiber.

3.0 Test Procedure for Air Exposure

- 3.1 Place crucibles into a furnace, and heat to $1600 \pm 20^\circ\text{F}$.
- 3.2 After approximately 500 hr at $1600 \pm 20^\circ\text{F}$, cool furnace, and remove crucibles.
- 3.3 Measure and record the distance between the top of the crucible and the packed felt.
- 3.4 Remove the elements from position No. 1 of each crucible, and return them to their original containers.
- 3.5 Return the crucibles to the furnace and reheat to $1600 \pm 20^\circ\text{F}$.
- 3.6 Repeat steps 3.2 through 3.5 at 500 hr intervals.
- 3.7 Each element will be analyzed spectrographically following removal from test.

4.0 Test Procedure for Vacuum Exposure

- 4.1 Insert each crucible into a vacuum tube furnace.

- 4.2 Seal furnace and actively evacuate to ≤ 2 microns for 24 hr.
- 4.3 Leak check each tube by closing vacuum valve leading to each tube and noting the rate of pressure rise. This should not exceed 5 microns/hr. Record rate of pressure rise.
- 4.4 Heat tube furnaces to $1600 \pm 20^\circ\text{F}$ under active vacuum (should achieve ≤ 2 microns within 24 hr).
- 4.5 After 24 hr at 1600°F (assuming pressure ≤ 2 microns), leak check per 4.3 above. If pressure exceeds 2 microns, or if the leak rate of ≤ 5 microns/hr cannot be achieved, make necessary equipment alterations.
- 4.6 Return each tube to active vacuum and hold the ≤ 2 microns and $1600 \pm 20^\circ\text{F}$ conditions for 500 hr.
- 4.7 Cool furnace under active vacuum to room temperature.
- 4.8 Allow tube to come to atmospheric pressure and open tube (steps 4.8 through 4.10 to be done on first tube before progressing to second tube, etc.).
- 4.9 Remove crucible, measure and record distance between top of crucible and packed fibers.
- 4.10 Remove pertinent elements, and replace crucible into tube furnace, reseal and evacuate.
- 4.11 After all samples have been removed and the tubes resealed, repeat steps 4.2 through 4.6.

4.12 Repeat steps 4.7 through 4.11 at 500 hr intervals.

4.13 Each element will be analyzed spectrographically following removal from test.

CHEMICAL COMPATIBILITY OF BLOCK INSULATIONS WITH SiGe ELEMENTS

December 13, 1966

1.0 Purpose

The purpose of this test is to determine the chemical compatibility between N and P SiGe elements and candidate insulations at 1600F and in air and/or vacuum. The criteria for compatibility shall be the change in chemical composition of the cylindrical surface of the elements as determined by spectrographic analysis.

2.0 Sample Preparation

2.1 Cut the insulation specimen to 6 x 3 x 1-in. (approximate) and drill (No. 7 cork borer is satisfactory) two (2) rows of 4 holes each.

2.2 Measure and weigh specimen.

2.3 Insert one N element into one hole, and one P element in the corresponding hole in the other row. These elements will be exposed for 500 hr. Repeat for 1000 hr and 1500 hr exposure. Insert 3 N and 3 P elements into the last pair of holes for 2000 hr exposure.

2.4 Mark the side of the insulation specimen with the corresponding element type and number.

3.0 Test Procedure for Air Exposure

3.1 Place insulation specimen into furnace and heat to 1600 $\pm$ 20F.

3.2 After approximately 500 hr at 1600 $\pm$ 20F, cool furnace and remove specimen.

- 3.3 Measure and record length, width, thickness and weight.
- 3.4 Remove the first pair of N and P elements and return to their original container.
- 3.5 Return the specimen to the furnace and reheat to $1600 \pm 20^\circ\text{F}$.
- 3.6 Repeat steps 3.2 through 3.5 at 500 hr intervals.
- 3.7 Each element will be analyzed spectrographically following removal from test.

4.0 Test Procedure for Vacuum Exposure

- 4.1 Insert the specimen into a vacuum tube furnace.
- 4.2 Seal furnace and actively evacuate to < 2 microns for 24 hr.
- 4.3 Leak check each tube by closing vacuum valve leading to each tube and noting the rate of pressure rise. This should not exceed 5 microns/hr. Record rate of pressure rise.
- 4.4 Heat tube furnaces to $1600 \pm 20^\circ\text{F}$ under active vacuum (should achieve < 2 microns within 24 hr).
- 4.5 After 24 hr at 1600°F (assuming pressure < 2 microns), leak check per 4.3 above. If pressure exceeds 2 microns, or if the leak rate of < 5 microns/hr cannot be achieved, make necessary equipment alterations.
- 4.6 Return each tube to active vacuum and hold the < 2 microns and $1600 \pm 20^\circ\text{F}$ conditions for 500 hr.

- 4.7 Cool furnace under active vacuum to room temperature.
- 4.8 Allow tube to come to atmospheric pressure and open tube (steps 4.8 through 4.10 to be done on first tube before progressing to second tube, etc.).
- 4.9 Remove specimens, measure and record the length, width, thickness and weight.
- 4.10 Remove pertinent elements, and replace specimen into tube furnace, reseal and evacuate.
- 4.11 Repeat steps 4.2 through 4.6.
- 4.12 Repeat steps 4.7 through 4.11 at 500 hr intervals.
- 4.13 Each element will be analyzed spectrographically following removal from test.