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LEAD TELLURIDE NON-MAGNETIC BONDING RESEARCH STUDY

Fourth Quarterly Report
for period December 1, 1965
through February 28, 1966

Contract Number NAS5-9149

Prepared for

National Aeronautics and Space Administration
Goddard Space Flight Center
Greenbelt, Maryland

Tyco Laboratories, Inc.
Bear Hill
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by
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ABSTRACT

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The purposes of this study are (1) to define the most appropriate system and process for the reproducible fabrication of low-resistance high-strength bonds of nonmagnetic electrodes to PbTe and PbTe-SnTe thermoelectric alloys, (2) to study degradation processes in these materials, and (3) to study the junctions of these materials with their electrodes. Equilibria between Ta , PbTe , and SnTe and between W and PbTe were investigated, along with diffusion bonding of W to powdered and sintered PbTe materials. The diffusion bonding process for 3N and 3P thermoelements was scaled up for increased production of bonded elements.

I. INTRODUCTION

This program comprises an investigation of the bonding of PbTe and PbTe-SnTe thermoelements to nonmagnetic electrodes, and a study of the physical and chemical factors contributing to the degradation and failure of such thermocouples during extended operation. The bonding studies are directed toward the optimization of procedures for diffusion- and braze-bonding of W and Ta electrodes to n- and p-type PbTe and PbTe-SnTe. The studies of degradation and failure are aimed at elucidating the processes involved in the long-term deterioration of bulk thermoelement properties and of the element-electrode junction. Studies of the kinetics of these processes and of the chemical equilibria involved at the element-electrode interface should make possible some predictions of the long-term behavior of bonded thermoelements.

Work during this quarter was involved with study of PbTe-W and PbTe-Ta, SnTe-Ta equilibria, with bonding to sintered pellets of pure PbTe and 3N powder, and with design and construction of equipment.

II. BONDING STUDIES

A. Bonding of Pressed and Sintered Pellets

Experiments with bonding of W to dense PbTe and $Pb_{.7}Sn_{.3}Te$ materials were discussed in the Third Quarterly Report. The line of investigation which was begun there has been continued during this quarter. Powders were made by ball-milling several different materials: pure $Pb_{.5}Sn_{.5}Te$ (made by reacting the elements in the liquid state and then quenching), PbTe + 0.03% PbI_2 and $Pb_{.7}Sn_{.3}Te$ (originally made by an ultrasonic casting process under Contract Nobs-86015 Bureau of Ships, Department of the Navy), and 3M's 3N and 3P powder. These latter materials were pressed in the as-received condition (a mixture of widely differing particle sizes), and after ball-milling to a fine, fairly uniform powder.

Pellets 0.250 in. by approximately 0.32 in. were cold-pressed from the various powders in a hand press whose maximum pressure was estimated at 25,000 - 30,000 psi. The green compacts were sintered in hydrogen up to 500°C, then in argon for 30 minutes at 600°C and 15 minutes at 700°C. Densities of sintered pellets showed only slight increases over green densities, even in the case of PbTe pellets sintered at 850°C for 30 minutes. Green and sintered densities of PbTe and $Pb_{.7}Sn_{.3}Te$ pellets were approximately 89% of theoretical; $Pb_{.5}Sn_{.5}Te$ elements were approximately 83 - 84% dense. Sintered pellets of 3N powder with and without ball-milling and of PbTe + .03% PbI_2 were prepared in the standard manner for bonding. Electrode and pellet surfaces were lapped to 1800 grit. The standard n-type bonding treatment of 850°C for 30 minutes failed to produce any bonding of the pellets. (The same boat was used immediately after to bond a batch of 3M's pressed- and sintered-3N elements as a check on the system. These gave entirely satisfactory bonds.)

This result, taken with the previous experiments on dense PbTe, seems to imply that the bonding of pressed-and sintered-3N elements to W is a unique process, dependent on some factor or impurity introduced during the fabrication of the elements. We have not been able, apparently, to reproduce this factor in fabricating elements from what is assumed to be the identical starting material. Samples of all the materials used in these experiments are currently being checked for oxygen content to determine the amounts present at various stages in the fabrication of the elements.

B. Equipment

A considerable amount of time was spent during this quarter in building and setting up equipment for the increasing activity in the program. To increase the production of bonded elements for testing, two things were done. A motorized precision lapping machine was refurbished in order to automate partially the lapping of electrode and element contact surfaces. With this device approximately 80 electrodes can be lapped to 1800 grit in a day; thirty-five elements can be lapped to 1800 on both ends within a half hour. Secondly, a large, Globar-heated tube furnace was built to accommodate a level hot zone approximately 10 inches long. The 3.75 inch ID quartz tube extends 14 inches from the furnace at one end. A water cooled coil provides a zone for holding the bonding jigs before insertion to the hot zone. A vacuum tight brass cover over the tube is fitted with seals for a push-rod (for moving the jig into the furnace)and for the gas-vacuum line. Currently a jig which accommodates 36 elements is in use. This jig is made up of three high-purity graphite blocks held rigidly together at the end of a stainless steel tube. (See Fig. 1) The jig may be held in the cold zone until the furnace is at temperature, in which case the elements heat from approximately 50°C to 850°C in fifteen minutes; or the jig may be placed in the hot zone and heated with the furnace from 25° to 850° in about 100 minutes. (a rate similar to that of the previous furnace). The cooling rate of the Globar furnace is approximately the same as those previously experienced: 10°/min the first 10 minutes, 6°/min the second 10 minutes, and 5°/min the third 10 minutes and thereafter.

C. Recent Bonding Experiments

Three runs have been made thus far in the large bonding furnace described above. The first two were made with n-type elements. The average contact resistivity for the seven elements of the first run was 19 $\mu\,\Omega\text{-cm}^2$; the average resistivity of forty contacts in the second run was 13 $\mu\,\Omega\text{-cm}^2$; and the highest resistivity measured was 22 $\mu\,\Omega\text{-cm}^2$. The apparatus was not particularly gas tight during these runs and despite (or possibly as a result of) high argon flow rates, the tungsten weights were oxidized considerably. The bottom electrodes also showed some oxidation. It is uncertain what effect this had on the contact resistivities. Some experiments are planned to assess the effect of oxygen on the bonding process by introducing controlled amounts of oxygen into the argon stream.

Subsequent to the first two runs, the system was made tight and provision was made for evacuating with a mechanical pump before starting

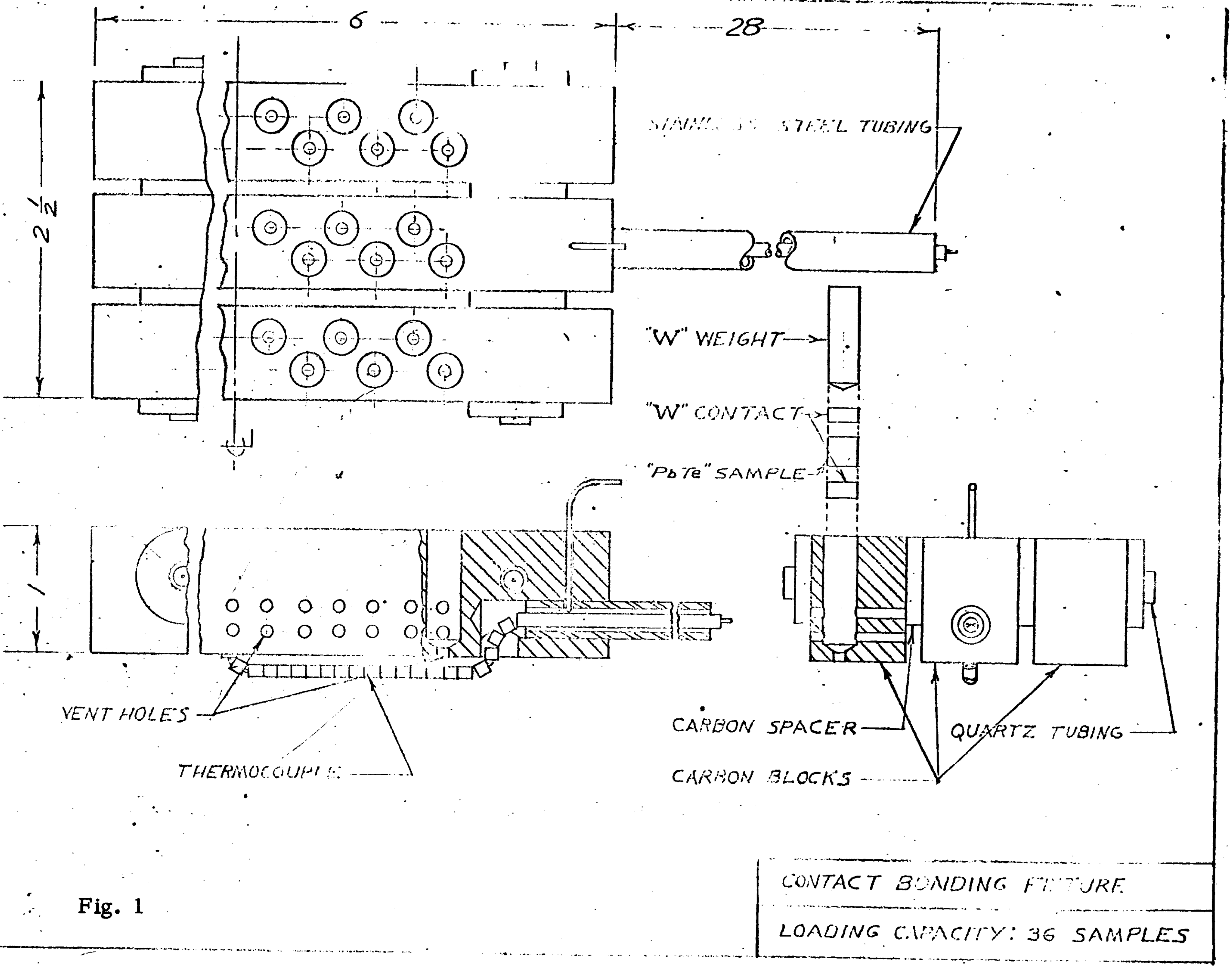
6
28
2 1/2
1
STAINLESS STEEL TUBING
"W" WEIGHT
"W" CONTACT
"PbTe" SAMPLE
VENT HOLES
THERMOCOUPLE
CARBON SPACER
CARBON BLOCKS
QUARTZ TUBING
CONTACT BONDING FIXTURE
LOADING CAPACITY: 36 SAMPLES

Fig. 1

a run. Twenty p-type (Pb-Sn) elements were used for the third run. Four elements did not bond, while the average contact resistivity of the remainder was 54 $\mu \Omega\text{-cm}^2$. The average resistivity of the twenty contacts less than or equal to 35 $\mu \Omega\text{-cm}^2$ (i.e. 100 $\mu \Omega$) was 25 $\mu \Omega\text{-cm}^2$. There were no signs of oxidation in this run; however, it was found that most of the electrodes, which had been ground flat with a surface grinder before lapping, had a small burr on the edge of the contact face left apparently from the grinding. It is felt that these burrs contributed in large part to the poor results in this case by catching on the sides of the holes in the jig and thus holding the electrode at an angle off the element surface. The burr is now removed by tumbling the electrodes before lapping. Further runs, basically experimental in nature, are planned for the p-type material to assess primarily the effects of pressure and time on the bonding to tungsten.

III. CONSTITUTIONAL STUDIES

Investigations on the constitution of ternary systems M-Pb-Te and M-Sn-Te were started in this quarter using the "Klarkreuz" Method of Guertler as outlined in the last report.

A. Tungsten-Lead Telluride

It has already been shown that tungsten does not dissolve in liquid lead telluride. Investigations were continued by annealing a pressed powder compact of 80 mol % PbTe and 20 mol % W for 4 weeks at 850°C. After this time the compact was removed from the furnace and was well sintered. The pill was crushed and ground into a fine powder which was filled in a 0.2 mm glass capillary for X-raying in a 114.59 mm diameter Philips Debye-Scherrer camera. Exposure was for 6 hours with Ni-filtered Cu radiation.

All lines found in the powder pattern could be assigned to PbTe and W according to the ASTM-X-ray powder data file (1, 2). The lines of PbTe and W were both extrapolated to $\theta = 90°$ using the Nelson-Riley function. Lattice parameters were calculated from the plots by a least squares method.

Lattice parameters found were:

PbTe: 6.466 ± 0.001 Å

W: 3.166 ± 0.001 Å

The lattice parameter of PbTe is increased about 0.005 Å if compared with the latest values in the Pb-Te system (3). This would indicate some solid solubility in the PbTe. It is difficult to say at this time, though, if W is dissolved in PbTe (which could cause the bond) or if oxygen, which is very likely present on the surface of the W-powder, diffused into PbTe during annealing. It is difficult, in any case, to perceive how dissolved tungsten could increase the lattice parameter of PbTe since its atomic radius is smaller than that of Pb .

B. Tantalum-Lead Telluride

In this system three alloys have to be prepared according to the cross points of three $TaTe_x$-Pb sections with the PbTe-Ta line. Three compounds - $TaTe_3$, $TaTe_2$, and TaTe (4, 5) - have been reported in the system. The latter one also is reported to exist only at high temperatures (~ 900°C); at low temperatures it decomposes and compounds of stoichiometries $TaTe_{0.85}$ and $TaTe_{0.72}$ form. Patterns for these latter two, which are taken from (4), are given in Tables I and II. These compounds, particularly $TaTe_{0.85}$, should then be found in our alloy of the TaTe-Pb section if a reaction between PbTe and Ta occurs. Two series of 3 alloys were made; they are designated as follows:

P1 - Ta , A-1 - Ta: Cross point PbTe - Ta and $TaTe_3$ - Pb

P2 - Ta , A-2 - Ta: Cross point PbTe - Ta and $TaTe_2$ - Pb

P4 - Ta , A-4 - Ta: Cross point PbTe - Ta and TaTe - Pb

TABLE I

$TaTe_{0.72}$ (After 4)

Line #	I (0 - 10)	d (PT)*
1	2	3.29
2	3	3.16
3	3	2.800
4	10	2.636
5	5	2.530
6	1	2.425
7	8	2.376
8	1	2.316
9	6	2.265
10	4	2.205
11	4	2.149
12	3	1.689
13	1.5	1.507
14	1.5	1.472
15	8	1.413
16	3	1.378
17	1	1.336
18	2	1.294
19	2	1.273
20	3	1.231

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*PT = Values taken from "Data for X-ray Analysis, Vol. I," Philips Technical Library

TABLE II

$TaTe_{0.85}$ (After 4)

Line #	I (0 - 10)	d (PT)
1	6	7.10
2	3	3.37
3	2	3.08
4	10	2.578
5	1	2.538
6	6	2.355
7	3	2.222
8	2	2.144
9	1.5	2.100
10	1.5	2.019
11	3	2.005
12	5	1.911
13	2	1.801
14	8	1.755
15	2	1.598
16	1.5	1.551
17	5	1.443
18	4	1.401
19	2	1.356
20	3	1.326
21	2	1.315
22	1.5	1.281
23	1.7	1.258
24	1.5	1.231
25	3	1.177

P are powder compacts pressed from PbTe and Ta powder and annealed for 10 days at 850°C. A are alloys prepared from pieces of PbTe and Ta reacted for 20 hrs at 965°C (above the melting point of PbTe). Figures 2, 3, and 4 show the three A alloys. It is clearly visible that tantalum was attacked and formed two reaction products. Nevertheless, the alloys are not at all in equilibrium: quantitative conclusions are, therefore, difficult to draw. The columnar phase, however, is quite clearly identifiable as the same one frequently found in brazed PbTe-Ta junctions.

The alloys obviously have to be reacted much longer in order to achieve equilibrium.

The same considerations apply to the powder compacts. Although the X-ray spectrum of the P4-Ta-alloy shows clearly PbTe and Pb (6) (Table III) a number of lines cannot be assigned to any of the tantalum tellurides or to Ta itself, which seems to be entirely absent. This situation forces longer annealing times as well as an investigation of the solubility of Pb in TaTe (or $TaTe_{0.85}$) in order to clearly define the reactions in the system. The presence of lead in the reaction products, however, if confirmed, (i.e. by thermal analysis) excludes any direct contacting of PbTe and Ta .

All alloys in the Pb-Te-Ta system will, therefore, be prepared again and reacted to equilibrium before any final conclusions are drawn.

C. Tantalum-Tin Telluride

Studies in this system were postponed somewhat after the experiences in the Ta-PbTe-system. We felt it is imperative to anneal these alloys much longer than even the PbTe-Ta alloys since, owing to the lower melting point of SnTe , the powder compacts have to be annealed at lower temperatures. Only qualitative results could be obtained showing that apparently Ta reacts slowly with liquid SnTe . (Figure 5.)

IV. INVESTIGATIONS ON JUNCTIONS

Some junctions were investigated again by electron microprobe analysis in order to check the reaction zones.

Fig. 2 Alloy A-1-Ta (see text) PbTe and Ta held at 965°C for 20 hours. X 200

Fig. 3 Alloy A-2-Ta; 20 hours at 965°C. X 200

Fig. 4 Alloy A-4-Ta; 20 hours at 965°C. It should be noted that the Ta content increases in going from A-1 to A-4. X 200

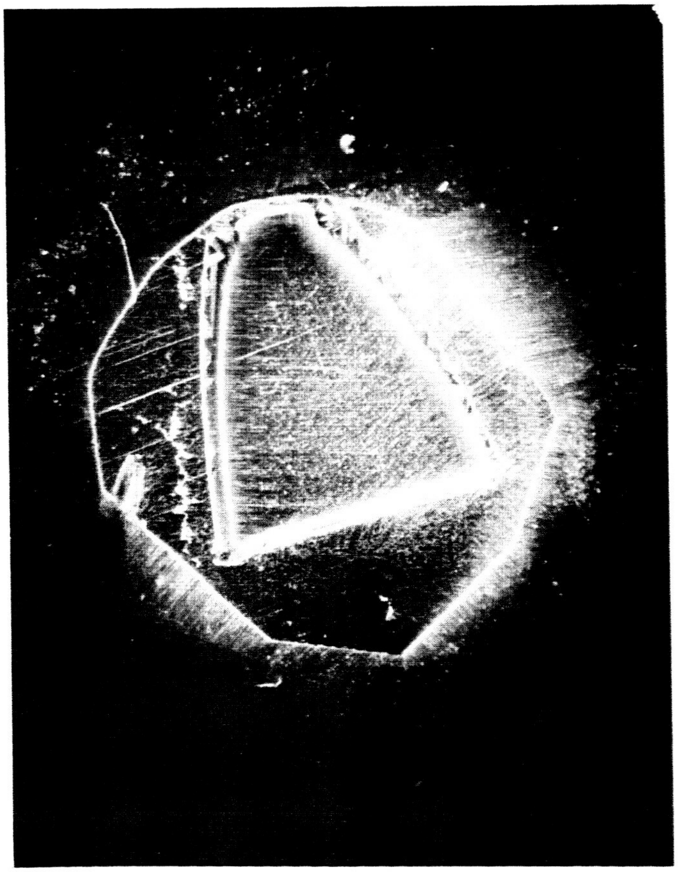

Fig. 5 A-2-Ta-SnTe section of Ta held in SnTe 18 hours at 855°C, note reaction zone and large precipitates within it. X 25

TABLE III

PbTe P4-Ta

$$\theta_1 = \frac{70.40 + 125.80}{2} = 98.10$$

$$\theta_2 - \theta_1 = 179.85 \qquad S_{corr} = \frac{180.00}{179.85} = 1.000834$$

$$\theta_2 = \frac{229.15 + 326.75}{2} = 277.95$$

Line	I	S_1	$S_1 - \theta_1$	S_1 corrected	d (PT)	Assigned	d (ASTM)
1	W	122.05 mm	23.95 mm	23.97	3.71	PbTe 111	(3.74)
2	S	125.75	27.65	27.67	3.22	PbTe 200	(3.23)
3	M	129.50	31.40	31.43	2.845	Pb 111	(2.855)
4	VW	132.50	34.40	34.43	2.605		
4A	VW	133.55	35.45	35.48	2.530		
5	MW	134.45	36.35	36.38	2.471	Pb 200	(2.475)
6	VW	135.25	37.15	37.18	2.418		
7	VW	136.40	38.30	38.33	2.348		
8	S	137.60	39.50	39.53	2.279	PbTe 200	(2.28)
9	MW	138.45	40.35	40.38	2.234		
10	VW	140.50	42.40	42.44	2.130		
11	VW	144.75	46.65	46.69	1.945		
12	M	147.00	48.90	48.94	1.862	PbTe 222	(1.858)
13	MW	150.40	52.30	52.34	1.748	Pb 220	(1.750)
14	MW	155.20	57.10	57.15	1.612	PbTe 400	(1.609)
15	W	156.45	58.35	58.40	1.580		

TABLE III (Cont.)

Line	I	S_1	$S_1 - \theta_1$	S_1 corrected	d (PT)	Assigned	d (ASTM)
16	MW	160.35	62.25	62.30	1.490	Pb 311	(1.493)
17	M	162.65	64.55	64.60	1.442	PbTe 420	(1.442)
18	W	163.35	65.25	65.30	1.429	Pb 222	(1.429)
19	M	169.60	71.50	71.56	1.319	PbTe 422	(1.314)
20	MW	171.30	73.20	73.26	1.292		
21	?						
22	VW	175.10	77.00	77.06	1.238	Pb 400	(1.238)
23	W	183.15	85.05	85.12	1.140	PbTe 440	(1.138)
24	W	183.55	85.45	85.52	1.136	PbTe 440	(1.138)
25	W	185.10	87.00	87.07	1.119	Pb 331	(1.135)
26	W	186.30	88.20	88.27	1.107	Pb 420	(1.069)
27	?						
28	MW	189.40	91.30	91.38	1.078	PbTe, 600, 244	(1.072)
29	MW	196.05	97.95	98.03	1.021		
30	W	197.30	99.20	98.28	1.019	PbTe 620	(1.019)
31	W	198.65	100.55	100.63	1.002	Pb 422	(1.0105)
32	W	202.65	104.55	104.64	.974		
33	VW	202.90	104.80	104.89	.973	PbTe 622	(.970)
34	VW	206.05	107.95	108.04	.952	Pb 511	(.9526)
35	VW	209.55	111.45	111.54	.933		
36	VW	212.80	114.70	114.80	.916		
37	VW	216.70	118.60	118.70	.897	PbTe 640	(.896)

TABLE III (Cont.)

Line	I	S_1	$S_1 - \theta_1$	S_1 corrected	d (PT)	Assigned	d (ASTM)
38	VW	221.60	123.50	123.60	.875	Pb 440	(.8752)
39		224.30	126.20	126.30	.864	PbTe 642	(.862)
40α_1	M	229.00	130.90	131.01	.846		
40α_2	W	229.70	131.60	131.71	.846		
41	W	232.10	134.00	134.11	.837	Pb 531	(.8369)
42	split?	235.90	139.80	137.91	.825	Pb 600	(.8251)
43	?						
44	W	251.45	153.35	153.48	.792		
45	?	256.60	158.50	158.63	.785		

TABLE IV

Determine Phase Chemistries (w/o)*

Area		Ta	Pb	Sn	Te
(1)	Columnal Growth*	35 - 37	1.5 - 2.5	6 - 8	55 - 57
	Grey Precipitate**	33 - 36	~ 0	0.15 - 1.5	63 - 65
	Matrix around Precipitates	6 - 8	20 - 22	24 - 26	46 - 48
(2)	Band	~ 0	33 - 35	20 - 22	43 - 46
	$Pb_{.5}Sn_{.5}Te$ (matrix)***	~ 0	35.7	20.4	43.9

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* Range of precision due to surface roughness. However actual concentrations may vary ± 10% of the amount present since no calibration data were available in these alloy systems.

** Appears to be a $TaTe_2$ phase.

*** Calculated stoichiometric composition.

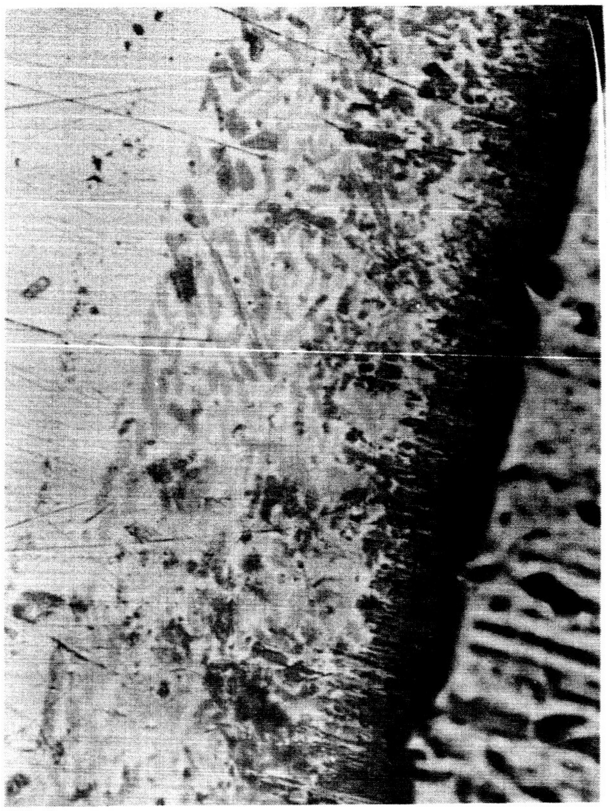


Fig. 6a Precipitation in SnTe braze layer on Ta electrode (top right). X 500

Fig. 6b Same as 6a; note similarity of precipitates to those of Fig. 4.

In the case of PbTe-W bonds it could be confirmed that within the limits of accuracy of the microprobe, there is no diffusion of either junction partner in the other. Also a tin telluride brazed $Pb_{0.7}Sn_{0.3}Te$ to tantalum-element was investigated. (Figure 6.) The results are shown in Table IV.

To draw conclusions here is somewhat difficult. In the most simplified case (assuming that the microprobe did not include any two phase material) it seems that the layer immediately adjacent to Ta consists of $TaTe_2$ which has a considerable solubility for both lead and tin. The grey precipitate is then to be thought of as the same compound with some solubility for lead only. The matrix around the precipitate would consequently appear to be lead-tin-telluride which contains Ta in solid solution.

The band seems to be slightly shifted composition of (Pb-Sn)-Te . However, this explanation seems rather unlikely except for the fact that extensive solid solutions in the pseudo-binary systems of the tantalum tellurides and lead, respectively, tin telluride existed. This would be rather interesting from the viewpoint of the thermoelectric materials themselves, since such solid solutions could have favorable thermoelectric properties. On the other hand, it is quite possible, that in the reaction zone a very fine two phase structure existed, which could not be resolved by the microprobe.

The constitutional studies now in progress on the systems concerned should provide the necessary information to resolve these questions.

V. LIFE TESTING

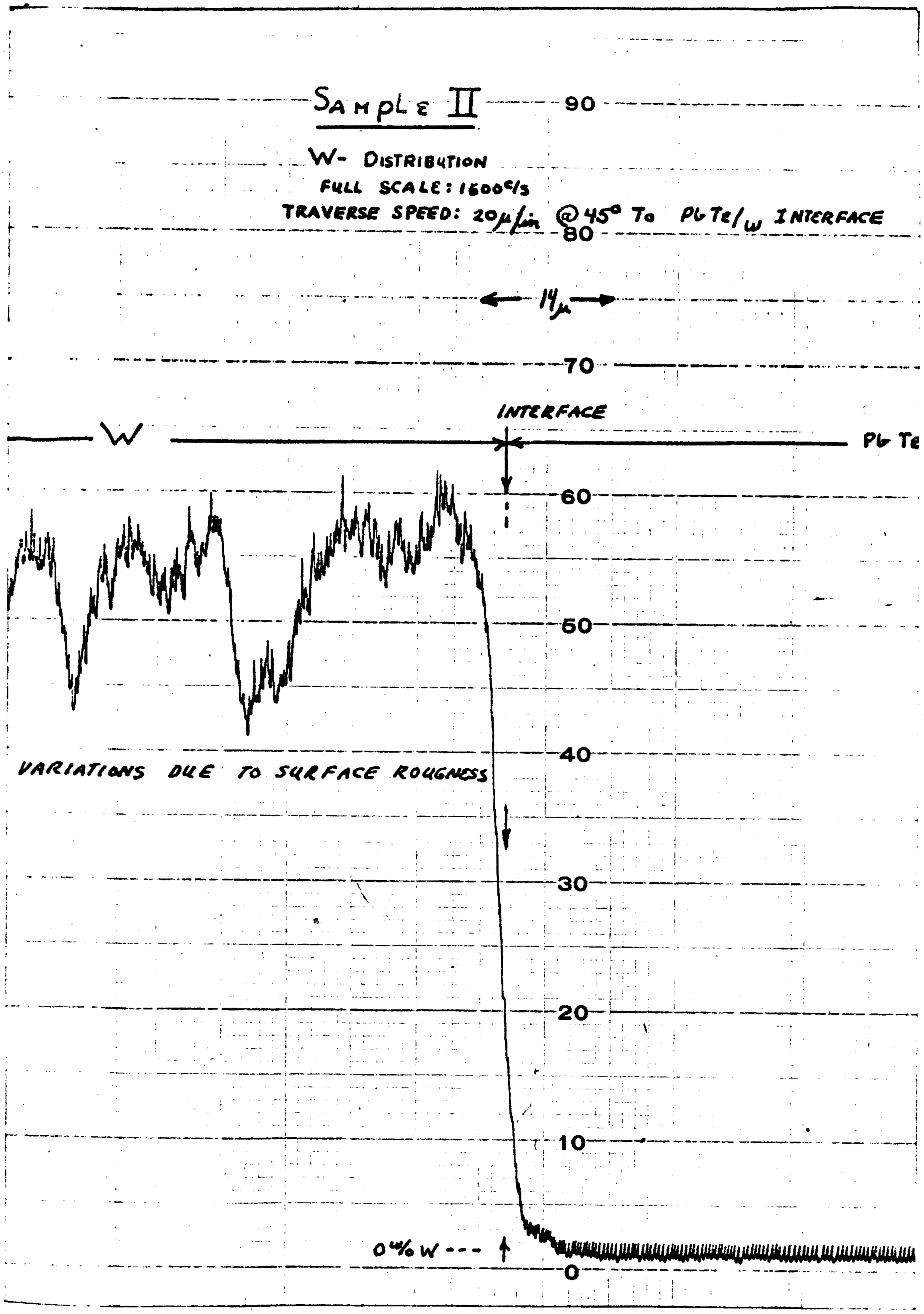
Eight n- and p-type elements bonded to tungsten electrodes were tested at 500° and 600°C for 1000 hours. The three n-type elements tested - two at 500° , one at 600°C - showed an increase in average contact resistivity from 3 $\mu\,\Omega\text{-cm}^2$ to 16 $\mu\,\Omega\text{-cm}^2$. The top contacts (designation from position in bonding fixture) averaged only 10 $\mu\,\Omega\text{-cm}^2$ after testing, compared to 21 $\mu\,\Omega\text{-cm}^2$ for the bottom contacts. Average bulk resistivity of the elements decreased from 0.328 to 0.308 m Ω-cm. Three p-type elements were tested at 600°, two at 500°. Four of the five bottom-end contacts failed during the test. The element and electrode surfaces of three of these were severely discolored. The average initial contact resistivity of the five bonds which survived was 26 $\mu\ \Omega\text{-cm}^2$. This increased to 87 $\mu\ \Omega\text{-cm}^2$ after testing. Three p-type specimens which had been tested to 2000 hours at 600° were found partially melted in the ampoules. These specimens were measured after their first 500 hours and removed from the furnace for inspection at 1500 hours, at which time the bonds were still intact. Apparently the furnace temperature was increased briefly by accident, probably short circuiting of the control thermocouple.

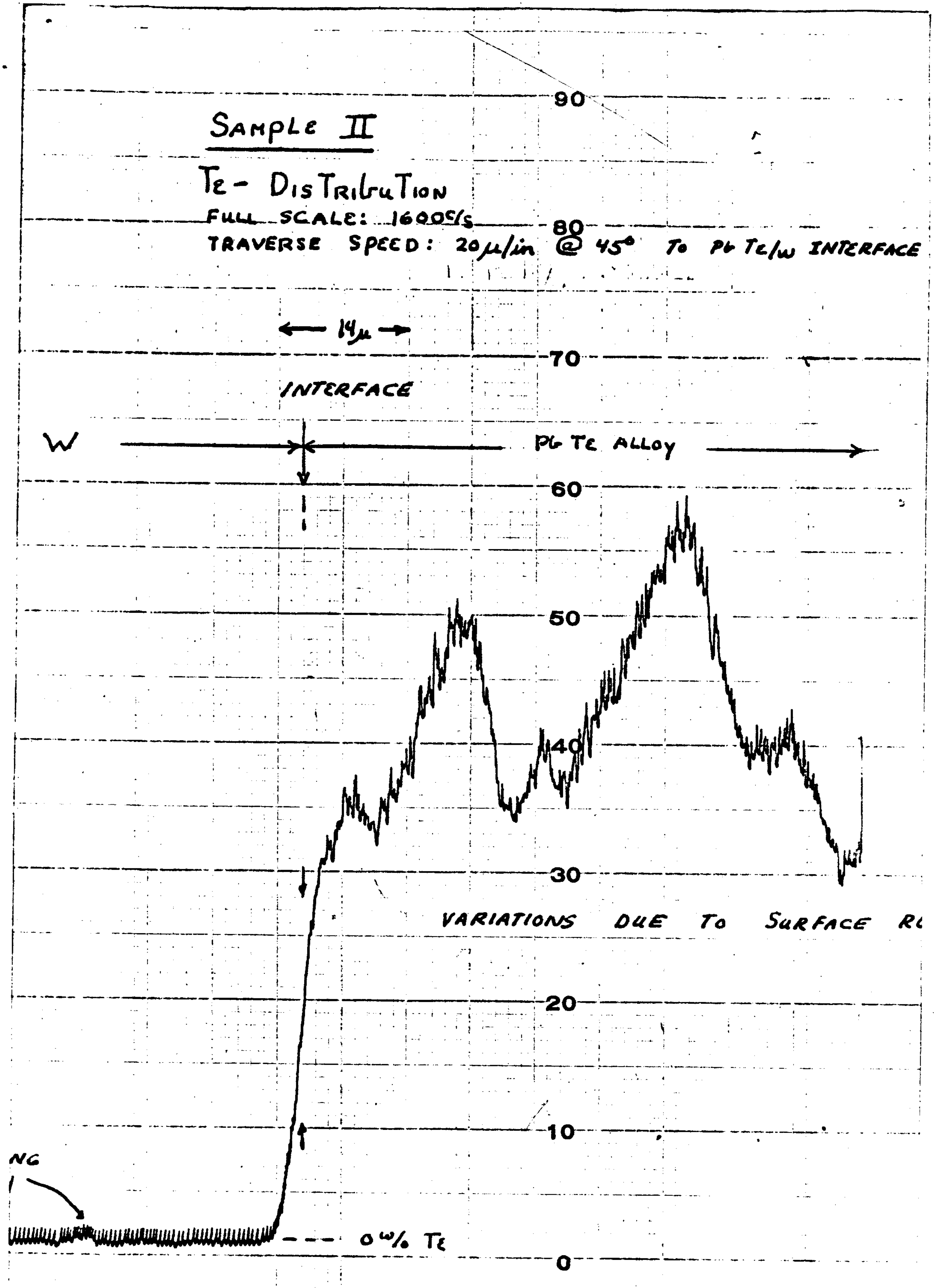
A tungsten-bonded, n-type element held 500 hours at 600° was examined with an electron beam microprobe. (A companion element with the same history had been examined previously; however, the traces were difficult to interpret because of the surface preparation of the element.) The traces for the three major constituents are reproduced in Figs. 7-9. It is obvious that interdiffusion is very limited, if indeed any has occurred. These traces should be compared to those made on an as-bonded element and shown in Figs. 10-11 of the Second Quarterly Report.

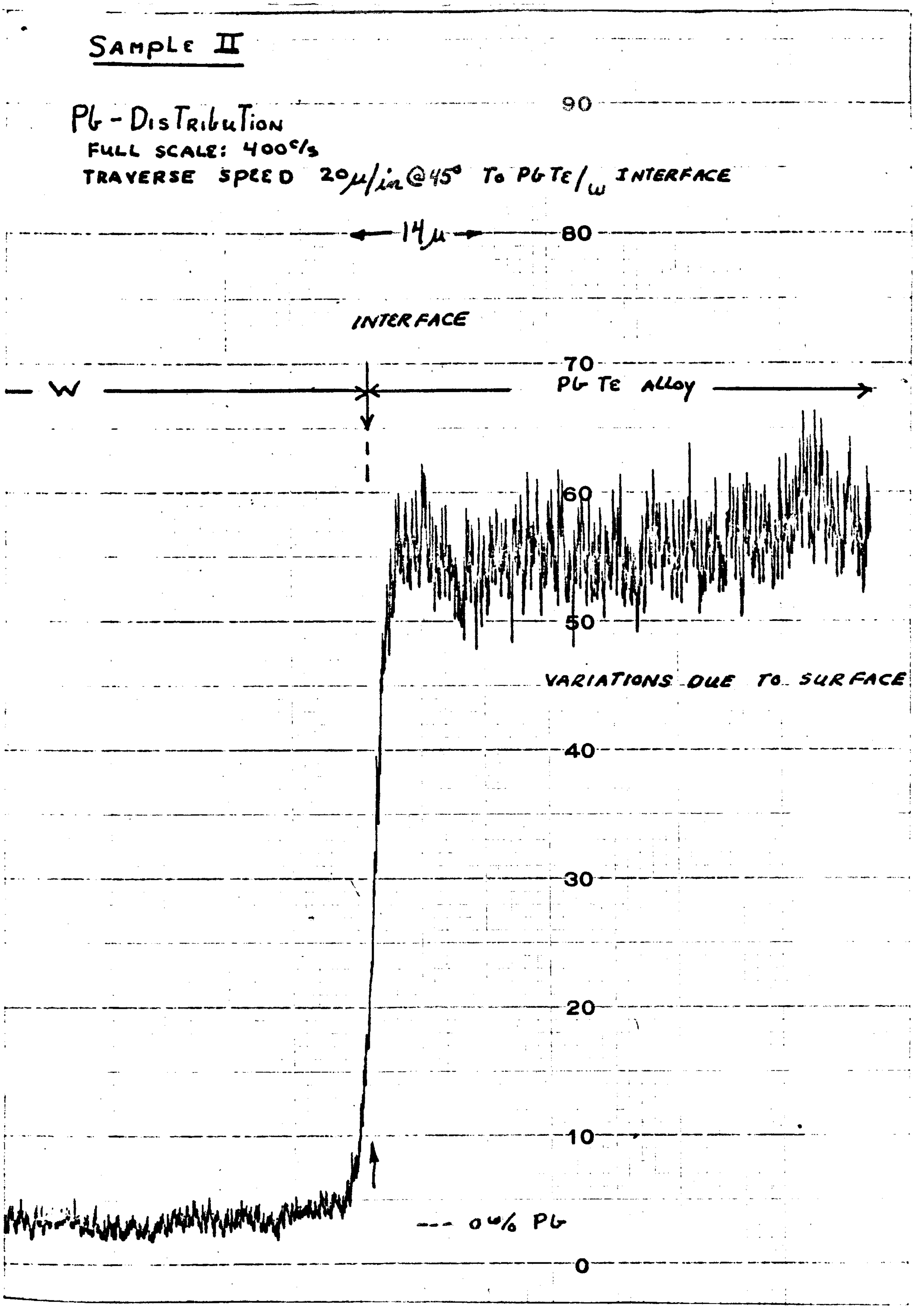
VI. CONCLUSIONS

During the fourth quarter the reactions of Ta with PbTe and SnTe and W with PbTe were studied, bonding to sintered PbTe materials was investigated, and scale-up of the diffusion bonding process was accomplished. The following conclusions may be made from these studies:

1. Both PbTe and SnTe react rather extensively with Ta. The exact stoichiometries of the equilibrium phases have not yet been determined.


SAMPLE II
W- DISTRIBUTION
FULL SCALE: 1600c/s
TRAVERSE SPEED: 20µ/in @ 45° To PbTe/W INTERFACE
90
80
← 14µ →
70
INTERFACE
W
PbTe
60
50
40
VARIATIONS DUE TO SURFACE ROUGNESS
30
20
10
0% W ---
0


SAMPLE II
Te - DISTRIBUTION
FULL SCALE: 1600c/s
TRAVERSE SPEED: 20μ/in @ 45° TO Pb Te/W INTERFACE
← 14μ →
INTERFACE
W
Pb Te ALLOY
VARIATIONS DUE TO SURFACE R
NG
0 w/o Te
90
80
70
60
50
40
30
20
10
0



SAMPLE II

Pb - DisTribuTion
FULL SCALE: 400c/s
TRAVERSE SPEED 20µ/in @45° To PbTe/W INTERFACE

2. The absence of a reaction between PbTe and W has been confirmed, although a slight increase in the PbTe lattice parameter was found in a sample annealed with W .

3. Production of much larger quantities of bonded thermoelements is now possible with semiautomation of some preparation processes and direct scale-up of the bonding process.

4. Bonding of W to 3N thermoelements seems to be the result of a condition or impurity which we have not been able to reproduce either in pellets of 3N material or other essentially pure PbTe compositions.

VII. FUTURE WORK

During the next quarter the following will be undertaken:

1. Studies of bonding process variables, particularly for p-type (Pb-Sn) elements
2. Study of the bonding of p-type PbTe to tungsten
3. Fabrication of SiGe-PbTe segmented couples
4. Continued constitutional studies of the stoichiometries of the reactions of Ta-SnTe , PbTe , of W-SnTe , and of the reactions of Fe with SnTe and PbTe .
5. Study of the effect of oxygen level on the bonding process
6. Construction of life-test module.

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