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E. I. DU PONT DE NEMOURS & COMPANY, INC.

EXPERIMENTAL STATION

PIGMENTS DEPARTMENT

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THERMOELECTRIC PROPERTIES OF SELENIDES AND TELLURIDES
OF GROUPS VB AND VIB METALS AND THEIR SOLID SOLUTIONS

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Seventh Quarterly Report
by
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approved by

D. G. Kelemen

This report covers the period January 1, 1963 to March 30, 1963.
Calculations have been made of idealized efficiencies for various operating conditions and geometries of thermoelectric modules with segmented elements of Ta-doped WSe₂ with Na-doped PbTe, encapsulated in constantan as the n-element. An efficiency of 9.6% was calculated for the combination W₀.₉₆Ta₀.ₐ₄Se₂ and PbTe + 0.₃ at. % Na in the gradient 1000°C to 25°C. The power per unit volume is 0.₄₇ watts cm⁻³ compared with 0.₁₉ watts cm⁻³ for PbTe-based modules. Studies of preparative techniques have continued, and doped PbTe specimens have been obtained for direct experimental measurements of efficiencies.

Development of test modules has continued with particular attention to hot junction problems. Bonding through a new phase is under particular study. Observations on the thermal decomposition of WSe₂ indicate a measurable pressure of Se at 400°C, which remains considerably below 1 atm at 1100°C.

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>1</td>
</tr>
<tr>
<td>I. MATERIAL RESEARCH</td>
<td>2</td>
</tr>
<tr>
<td>II. DEVELOPMENT OF THERMOELECTRIC MODULES</td>
<td>23</td>
</tr>
</tbody>
</table>
Calculations have been made of idealized efficiencies for various operating conditions and geometries of thermoelectric modules with segmented elements of tantalum-doped tungsten diselenide in combination with sodium-doped lead telluride, encapsulated in constantan cylinders serving as the n-type element. These calculations followed a 704-Computer program developed in another organization. An efficiency of 9.6% was calculated for the combination W_{0.98}Ta_{0.02}Se_2 and PbTe + 0.3 at.% Na operating in the gradient 1000°C to 25°C. The power per unit volume is 0.47 watts cm\(^{-3}\) compared with 0.19 watts cm\(^{-3}\) for PbTe-based modules.

Studies of improved preparative techniques for the diselenides have continued, and doped lead telluride specimens have been obtained for assembly into test modules for direct experimental measurement of efficiencies in an apparatus now completed.

Development of test modules has continued with particular attention to the Achilles's heel of all such devices, the hot junction. Bonding the thermoelement to the constantan through a new phase is under particular study; a combination of a Mo disc welded to the constantan by sintered Cu powder appears most promising.

Observations on the thermal decomposition of WSe_2 indicate a measurable pressure of Se at 400°C, which remains considerably below 1 atm at 1100°C.
Further studies have been done on preparative techniques for the system $W_{1-x}Ta_xSe_2$ in order to improve thermoelectric properties and their reproducibility. Work has been done on the effects of stoichiometry and tungsten quality for the particular composition, $W_{0.99}Ta_{0.01}Se_2$. The effect of varying the final reaction temperature was also studied. New preparations of this series with values of $x$ ranging from 0.005 to 0.05 have been made using improved techniques.

Several types of lead telluride were ordered from the Minnesota Mining and Manufacturing Co. for use in the p-leg, low-temperature segment of thermoelectric modules. The electrical properties claimed for these materials were remeasured as functions of temperature and substantiated.

The 704-Computer program supplied by Texas Instruments Corporation was used to calculate the ideal efficiencies and other operating parameters of thermoelectric modules containing tungsten diselenide in order to determine what combination of materials and dimensions may give the greatest efficiency.

Material Improvement

Effects of Stoichiometry and Tungsten Source

In the preceding Quarterly Report, measurements showing the effect of varying stoichiometry and the source of
tungsten used in producing the composition $W_{0.99}Ta_{0.01}Se_2$ were presented, but the results were somewhat ambiguous. In this last period, more samples of this composition were produced and their electrical properties were measured up to 600°C. A set of samples with $y = 1.998, 2.000$ and 2.002, where $y$ represents the number of atoms of selenium, were made using two sources of tungsten, Wah Chang Corporation and General Electric Co., which were shown to be best in the last report. In the preparation of the samples thorough mechanical mixing was given the powders while still in sealed quartz tubes after the initial reaction. Table I summarizes the resulting electrical properties at 600°C. These results illustrate that, for the materials made from General Electric tungsten, slight metal excess or selenium excess yielded somewhat better Figures of Merit. However, the effects of stoichiometry are not nearly so clear for the materials made from Wah Chang tungsten. The stoichiometric and selenium-excess samples appear slightly better than those with excess metal. In any case, all the samples made from Wah Chang tungsten are clearly superior to those made from General Electric tungsten when all the samples are prepared by exactly the same technique and reacted at exactly the same temperatures. The superiority of the Wah Chang tungsten may be due to its lower oxygen content. According to the manufacturer's analyses, the oxygen content of the Wah Chang tungsten
was 230 ppm, while that of General Electric tungsten was 490 ppm. It is concluded that for the present Wah Chang tungsten be preferred for preparation of these materials, and a value of $y = 2.002$ should be used. Even if there is a slight loss of selenium during the reaction, the stoichiometric composition should still have equally good properties.

Effects of Final Reaction Temperature

The preparative technique for samples used in this work has been described in detail in previous reports. Briefly, the correct amount of the elements are weighed into quartz tubes which are evacuated and sealed; and an initial reaction is carried out at around $600^\circ$C for an overnight period. The optimum temperature for this initial reaction is presently being determined. After this initial reaction, a loose powder product is obtained which is thoroughly mixed by agitation on a mechanically vibrated table. The samples are then given a final homogenizing reaction at temperatures around $1100^\circ$C. A series of samples has been made where this final reaction temperature was varied, but otherwise all the samples were prepared in the same manner. The samples were prepared from General Electric tungsten, had the stoichiometric composition $W_{0.99}Ta_{0.01}Se_2$, and were initially reacted at $650^\circ$C.
The electrical properties of these samples at 600°C are summarized in Table II. From this table, it appears that the final reaction temperature should be 1000°C. However, during the reaction of these samples there were some errors in temperature measurement of about 50°C, and although the temperatures in the table are corrected, the results are in some doubt, and are being checked. All previous samples were reacted finally at temperatures of 1100°C or higher.

Remeasurement of the Electrical Properties of W_{1-x}Ta_xSe_2

In the preceding Quarterly Report, the effect was discussed of more thorough mixing of the reacted powders on the final electrical properties of the composition W_{0.99Ta_{0.01}Se_2}. In addition, careful remeasurements of Seebeck coefficient were shown to give somewhat lower results than those previously reported. It was considered worthwhile to resynthesize and evaluate the electrical properties of the entire series W_{1-x}Ta_xSe_2, x varying from 0 to 0.05. The results of these measurements at 600°C are summarized in Figure 1 where the Seebeck coefficient, resistivity and truncated Figure of Merit are shown as a function of x. These samples were all made from Wah Chang tungsten and with a value of 1.998 atoms of Se per atom of combined metals. It is felt that the thermal conductivities
given for this series in the preceding Quarterly Report would not be affected by changes in the recent preparative techniques, since for these materials the thermal conductivity varies only slightly with \( x \). Thus, the quantity, \( S^2/\rho \), is a good indication of their relative Figures of Merit. It is seen in Figure 1 that there is a broad maximum in Figure of Merit ranging from \( x = 0.01 \) to \( x = 0.03 \) with a slightly higher Figure of Merit at \( x = 0.01 \) to 0.015. However, since compositions at lower values of \( x \) may tend to show intrinsic effects at lower temperatures than those at higher \( x \), it is expected that this maximum in the Figure of Merit will shift to slightly higher values of \( x \), possibly 0.02 or 0.03, at temperatures above 600°C. In addition, as will be shown in a later section of this report, this maximum is sufficiently flat that other considerations may indeed lead to a choice of values of \( x \) higher than 0.01 when these compositions are actually used in a thermoelectric module.

**Data for Module Construction**

**Properties of PbTe**

Three compositions of PbTe were ordered from Minnesota Mining and Manufacturing Co. in the form of sintered 1/4" x 1/4" x 2" bars. The first is p-type, was labeled TEG #2P, and is nominally lead telluride with \( J \) at 3% Na. The second is a p-type...
PbTe-SnTe solution labeled TEG #3P which has poorer thermoelectric properties than the Na-doped material but is reputed to have better durability than the Te-excess, Na-doped materials. The third was TEG #3N which is an n-type material and is nominally PbTe-0.1 mol % PbI₂. The Minnesota Mining and Manufacturing Co. kindly supplied curves giving thermoelectric properties versus temperature for the three materials, TEG #2P, TEG #3P, and TEG #3N, which are made to meet electrical rather than composition specifications. They also supplied curves based on earlier measurements by Fritts and Richards for 0.1, 0.3 and 1 at % Na and 0.01, 0.03, 0.055 and 0.10 mol % PbI₂ doped PbTe. Table III compares the thermoelectric properties of the three types of PbTe supplied by the supplier along with the equivalent sodium- or PbI₂-doped materials at the temperatures where the maximum Figures of Merit occur for the respective materials. An improvement is noted in the recent products over the original properties claimed for sodium- and PbI₂-doped materials.

The electrical properties of the three trade materials were checked in measurements up to 500°C and the results are shown in Figures 2, 3 and 4. For the samples TEG #2P and #3N, good agreement is found between our measurements and the curves supplied with the material by Minnesota Mining, especially if one considers that their curves were based on typical properties.
In the case of the sample TEG #3P, the electrical properties measured in this laboratory yield a Figure of Merit lower than that supplied by Minnesota Mining and Manufacturing.

Calculation of Module Efficiency

Texas Instruments Co. has graciously supplied us with a 704 Computer program developed by R. G. Moore\textsuperscript{1}. The program calculates efficiency, optimum area ratio, optimum load resistance, current and other parameters for segmented thermoelectric modules by three methods as follows:

(1) The thermoelectric parameters, Seebeck coefficient, resistivity, and thermal conductivity are averaged over the whole temperature range of the thermoelectric module as if each leg were composed of a single thermoelectric material with equivalent average properties. No heat balance is applied at the boundaries between the segments in the legs. This is a relatively simple calculation and can be done on a desk computer.

(2) The thermoelectric parameters are averaged for each segment over the particular temperature interval of that segment. Conditions of heat balance are imposed at the boundaries. This procedure is a good approximation to the true efficiency of the module but requires a number of special approximations with a high-speed computer.

\textsuperscript{1} R. G. Moore, Advanced Energy Conversion 2, 183-195 (1962).
The third method takes into account the temperature dependence of the parameters for each segment as well as applying heat balance conditions at the boundaries. This method yields an exact solution to the efficiency of the module, but requires a great deal more time on the IBM 704 Computer.

In the case of single component legs, methods (1) and (2) give identical results. For segmented legs, method (1) sometimes is misleading.

By all methods, the calculations ignore contact resistance, and, of course, heat which passes through thermal insulation or encapsulation materials and is wasted. Furthermore, in a complete thermoelectric generator, not all the energy in the source is converted into heat and supplied to the thermoelectric modules; heat is lost through exhaust and incomplete combustion. In most generators described to date, only about 50% of the calculated efficiency for a module is actually realized in a complete generator. With the tungsten selenides, we would hope to attain to a greater percentage of the ideal efficiency because of better heat transfer at the higher temperatures of operation our materials permit.

In the following calculations, it was assumed that the semiconductor materials, WSe$_2$, PbTe or the combination thereof, were encapsulated with suitable insulation in a constantan can having appropriate thickness to yield the area ratio for highest...
efficiency, unless otherwise stated. The use of a constantan can was suggested in the previous Quarterly Report. It was assumed that the $W_{1-x}Ta_xSe_2$ bar will be used in the a-axis direction of the component crystallites; that is, perpendicular to the pressing direction. The Seebeck coefficient and resistivity have been measured up to 1000°C for the composition $x = 0.01$ as described in the previous Quarterly Report. For higher values of $x$, the properties recently measured and illustrated in Figure 1 of this report were used up to 600°C. Above 600°C, the resistivity was extrapolated from the lower temperature curve. The Seebeck coefficient was extrapolated to 800°C and then a constant value was assumed from 800°C to 1000°C.

Seebeck coefficients$^2$ and thermal conductivities$^3$ are reported in the literature for constantan metal as a function of temperature, and are summarized in Figure 5. The Figure of Merit was calculated assuming a constant resistivity value of 50 $\mu\Omega$-cm from 25 to 1000°C. Stainless steel properties were taken from the "Landolt-Börnstein Tabellen" and Silverman.$^3$

All results presented in this report were calculated by Method Two discussed above, since the more exact solutions of Method Three did not converge in a reasonable time. According to

R. G. Moore's paper the results of Method Three are not significantly different from those of Method Two, but some Method Three solutions will be attempted in the future.

For comparison with more complex modules, efficiencies for modules with single component legs are shown in Table IV with various hot- and cold-junction temperatures. As expected, the module involving WSe$_2$ alone as the p-type leg would not be satisfactory for use in a thermoelectric generator and this material must be used in segmented leg construction at higher temperatures with PbTe as the thermoelectric segment for lower temperatures.

Table V summarizes the efficiency of a more complex module where the p-leg is segmented and consists of $W_{0.99}Ta_{0.01}Se_2$ as the high-temperature segment and PbTe TEGS-2P as the low-temperature segment, as a function of various hot and cold junction temperatures and two different boundary temperatures. Some improvement is seen in using lead telluride up to 550°C instead of simply to 500°C with this particular doping level for the semiconductors. It also may be seen that raising the cold junction temperature from 25 to 100°C, which is a more likely cold junction temperature in an air-cooled generator, does not decrease the efficiency substantially. Lowering the hot junction temperature from 1000°C to 900°C, which may be necessary for a long
generator lifetime, results in a more serious degradation of the efficiency.

Table V shows the efficiency calculated with different combinations of WSe$_2$ and PbTe having various doping levels. For these calculations a cold junction temperature of 25°C, a hot junction temperature of 1000°C, and a boundary temperature of 500°C were assumed. The average thermoelectric parameters, Seebeck coefficient, resistivity, thermal conductivity and Figure of Merit are listed with the materials for their particular temperature intervals. These values illustrate that the best efficiency is obtained with a composition of PbTe having an inferior Figure of Merit but which has electrical resistivity and thermal conductivity values which better match the average values of those of WSe$_2$ in its temperature interval.

The highest efficiency, 9.6%, was obtained with the composition W$_{0.98}$Ta$_{0.02}$Se$_2$ as the higher temperature segment and PbTe-0.3 at % Na as the low temperature segment of the p-leg. This particular module, operating over the above mentioned temperatures, with a semiconductor leg 1/2" dia and 2 cm long contained in an encapsulating constantan can with a wall 2.7 mils thick to give the optimum area ratio, would have the following operating parameters: current, 11.6 amp; ratio of load resistance to interior resistance, 1.177; load resistance, 0.0142 ohms;
open circuit voltage, .306 volts; and the high-temperature WSe$_2$ segment should be 1.151 cm long.

This efficiency is slightly lower than that given for matched PbTe legs given in Table IV above operating at a lower temperature. However, the power per area, power per volume, and power per weight value of this thermoelectric module would be more than two times higher than those of the matched PbTe module. For the segmented module, the power-to-area ratio is 1.19 watts/sq.cm, the power-to-volume ratio is 0.47 watts/cm$^3$ and the power-to-weight ratio is 0.056 watts/gram. In comparison, for the matched PbTe thermoelectric module operating between 25 and 550°C the power-to-area ratio is 0.49 watts/sq.cm, power-to-volume ratio is 0.19 watts/cm$^3$ and the power-to-weight ratio is 0.024 watts/gram. Furthermore, the actual efficiency of constantan-jacketed thermoelements, with a thin ceramic coating to serve as electrical insulation, is likely to be closer to the calculated efficiency than the actual efficiency of all-semiconductor modules, where heat flow through heavy ceramic encapsulation frequently represents a substantial loss.

In addition, it is possible that better heat transfer occurring at the higher junction temperature will favor the actual efficiency of the complex module over that of the matched PbTe module. Furthermore, as illustrated in Table III, the properties of the more recent preparation TEGS-2P are better than the earlier
results measured for PbTe-1 at % Na. A similar improvement in properties for a recent preparation of Pb-0.3 at % Na would yield an efficiency higher than 9.6% for the complex module.

The thickness of the constantan shell given above, which gives the optimum area ratio for maximum efficiency of the module, is too thin to have sufficient rigidity for mechanical strength and long durability of the module. Thus, efficiencies were also calculated for thicker constantan shells; these are summarized in Table VI. It is seen that increasing the thickness from the optimum 2.7 mils to 5 mils causes a slight reduction in the efficiency. By the time the shell thickness has been increased to 10 mils, the reduction in efficiency is greater than desirable.

Since constantan has a tendency to oxidize in long exposures at 1000°C a calculation was also made for "446" stainless steel. Since the steel has a very low Seebeck coefficient and is p-type, opposing the p-type semiconductor leg, resulting efficiency is much too low.

Measurement of Module Efficiency

The furnace has been constructed for delivering a measured heat input into a thermoelectric module. This furnace has been insulated on all sides with approximately 6" of "Tipersul"* insulation. The furnace required 30 watts to hold

* Registered Du Pont Trademark.
its center heating coil at 1000°C with no module in place. This may be compared with an additional 5 to 10 watts which should be required to hold the heater at 1000°C when a module is in place. Power meters of sufficient accuracy should be available to measure this difference in power input to the furnace, which is equal to the power input to the module. The heat going through the module will also be measured by a water circuit which passes over the cold end of the module. This circuit is now being constructed and tested.

Acknowledgment

Sample preparation and electrical measurements were carried out by A. R. Sohodski.

We are indebted to the Texas Instruments Co. for the use of the program developed by R. G. Moore during his employment with them. Paul Carnahan of the Texas Instruments Data Processing Section provided considerable help to us in adopting the program so that it could be run on computers available to us.

Mrs. R. M. Stanley of the Engineering Service Department of this Company adapted and supervised the operation of the program for us.
TABLE I
EFFECT OF TUNGSTEN SOURCE AND STOICHIOMETRY ON ELECTRICAL PROPERTIES OF W_{0.99Ta_{0.01Se_0.3}} AT 600°C

<table>
<thead>
<tr>
<th>W Source</th>
<th>y</th>
<th>S(μv/deg)</th>
<th>ρ(mΩ-cm)</th>
<th>S^2/ρ(μV/deg·cm·10^5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GE</td>
<td>1.998</td>
<td>299</td>
<td>9.4</td>
<td>0.95</td>
</tr>
<tr>
<td>GE</td>
<td>2.000</td>
<td>309</td>
<td>10.6</td>
<td>0.90</td>
</tr>
<tr>
<td>GE</td>
<td>2.002</td>
<td>324</td>
<td>11.1</td>
<td>0.95</td>
</tr>
<tr>
<td>Wah Chang</td>
<td>1.998</td>
<td>297</td>
<td>9.1</td>
<td>0.97</td>
</tr>
<tr>
<td>Wah Chang</td>
<td>2.000</td>
<td>296</td>
<td>8.7</td>
<td>1.01</td>
</tr>
<tr>
<td>Wah Chang</td>
<td>2.002</td>
<td>299</td>
<td>8.7</td>
<td>1.03</td>
</tr>
</tbody>
</table>
TABLE II
EFFECT OF FINAL REACTION TEMPERATURE ON ELECTRICAL PROPERTIES OF $W_{0.99}Ta_{0.01}Se_2$ MEASURED AT 600°C

<table>
<thead>
<tr>
<th>$t_f$ (°C)</th>
<th>$S$(μV/deg)</th>
<th>$\rho$(mΩ-cm)</th>
<th>$S^2/\rho$(w/deg²-cm)·10⁵</th>
</tr>
</thead>
<tbody>
<tr>
<td>950</td>
<td>291</td>
<td>11.8</td>
<td>0.72</td>
</tr>
<tr>
<td>1000</td>
<td>324</td>
<td>9.7</td>
<td>1.08</td>
</tr>
<tr>
<td>1050</td>
<td>293</td>
<td>9.8</td>
<td>0.88</td>
</tr>
<tr>
<td>1100</td>
<td>290</td>
<td>10.6</td>
<td>0.79</td>
</tr>
<tr>
<td>1165</td>
<td>295</td>
<td>11.0</td>
<td>0.79</td>
</tr>
</tbody>
</table>
### TABLE III

**Thermoelectric Properties of Several Types of PbTe at Temperature of Maximum Figure of Merit**

<table>
<thead>
<tr>
<th>Material</th>
<th>$tZ_{\text{max}}$ (°C)</th>
<th>$S(\mu V/\text{deg})$</th>
<th>$\rho(\Omega \cdot \text{cm})$</th>
<th>$k(\text{mw/deg-cm})$</th>
<th>$Z_{\text{ma}}: (\text{deg}^{-1}) \cdot 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3 at % Na</td>
<td>170</td>
<td>232</td>
<td>2.3</td>
<td>17.5</td>
<td>1.36</td>
</tr>
<tr>
<td>1 at % Na</td>
<td>300</td>
<td>239</td>
<td>3.1</td>
<td>16.3</td>
<td>1.18</td>
</tr>
<tr>
<td>TEGS-2P</td>
<td>350</td>
<td>281</td>
<td>3.2</td>
<td>11.4</td>
<td>1.83</td>
</tr>
<tr>
<td>0.1 mol % PbI$_2$</td>
<td>320</td>
<td>-154</td>
<td>0.95</td>
<td>24.5</td>
<td>1.00</td>
</tr>
<tr>
<td>TEGS-3N</td>
<td>345</td>
<td>-211</td>
<td>1.87</td>
<td>13.5</td>
<td>1.82</td>
</tr>
<tr>
<td>p-Leg Material</td>
<td>n-Leg Material</td>
<td>$t_c$ (°C)</td>
<td>$t_h$ (°C)</td>
<td>$\eta$ (%)</td>
<td></td>
</tr>
<tr>
<td>---------------------</td>
<td>---------------------</td>
<td>------------</td>
<td>------------</td>
<td>------------</td>
<td></td>
</tr>
<tr>
<td>W$<em>{0.99}$Ta$</em>{0.01}$Se$_2$</td>
<td>Constantan</td>
<td>25</td>
<td>1000</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td>PbTe (TEGS-2P)</td>
<td>Constantan</td>
<td>25</td>
<td>550</td>
<td>6.9</td>
<td></td>
</tr>
<tr>
<td>PbTe (TEGS-2P)</td>
<td>Constantan</td>
<td>100</td>
<td>550</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>PbTe (TEGS-2P)</td>
<td>PbTe (TEGS-3N)</td>
<td>25</td>
<td>550</td>
<td>10.0</td>
<td></td>
</tr>
<tr>
<td>PbTe (TEGS-2P)</td>
<td>PbTe (TEGS-3N)</td>
<td>100</td>
<td>550</td>
<td>9.7</td>
<td></td>
</tr>
</tbody>
</table>

$tc$ is cold junction temperature.

$th$ is hot junction temperature.
**TABLE V**

**EFFECT OF BOUNDARY TEMPERATURES ON SEGMENTED MODULE EFFICIENCY**  
**W₀.9₈Te₀.0₁Se⁻ PLUS PbTe (TEGS-2P) VS. CONSTANTAN**

<table>
<thead>
<tr>
<th>t₀(°C)</th>
<th>tₐ(°C)</th>
<th>tₜ(°C)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>500</td>
<td>1000</td>
<td>8.21</td>
</tr>
<tr>
<td>25</td>
<td>550</td>
<td>1000</td>
<td>8.50</td>
</tr>
<tr>
<td>100</td>
<td>550</td>
<td>1000</td>
<td>8.23</td>
</tr>
<tr>
<td>100</td>
<td>550</td>
<td>900</td>
<td>7.86</td>
</tr>
</tbody>
</table>

\[ t_b \] is temperature of boundary between WSe₂ and PbTe.
### Table VI

**Effects of Matching Conductivities on Efficiency of Segmented Module**

\( t_c = 25^\circ C; \ t_b = 500^\circ C; \ th = 1000^\circ C. \) Constantan N-leg.

| \( W_{1-x}Ta_xSe_2 \) Segment | \( W_{1-x}Ta_xSe_2 \) Segment | \( S \) (\( \mu V/\text{deg} \)) | \( \rho \) (\( m\Omega\cdot \text{cm} \)) | \( k \) (\( \text{mw/deg-cm} \)) | \( Z_{av} \) (\( \text{deg}^{-1} \)) | 10^3 | \( Z_{av} \) (\( \text{deg}^{-1} \)) | \( \eta \) (%) | \( Z_{av1} \) (\( \text{deg}^{-1} \)) | \( \eta \) (%) |
|-----------------------------|-----------------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| 0.01 | 317 | 10.7 | 20.4 | 0.46 | 0.3 at.%Na | 268 | 5.1 | 16.2 | 0.87 | 8.99 |
| 0.01 | 317 | 10.7 | 20.4 | 0.46 | 1 at.%Na | 202 | 2.7 | 19.1 | 0.78 | 8.03 |
| 0.01 | 317 | 10.7 | 20.4 | 0.46 | TEGS-2P | 203 | 2.4 | 18.1 | 0.96 | 8.64 |
| 0.02 | 235 | 5.5 | 20.4 | 0.49 | 0.3 at.%Na | 268 | 5.1 | 16.2 | 0.87 | 9.63 |
| 0.02 | 235 | 5.5 | 20.4 | 0.49 | 1 at.%Na | 202 | 2.7 | 19.1 | 0.78 | 8.58 |
| 0.02 | 235 | 5.5 | 20.4 | 0.49 | TEGS-2P | 203 | 2.4 | 18.1 | 0.96 | 8.93 |
| 0.03 | 194 | 4.2 | 20.4 | 0.44 | 0.3 at.%Na | 268 | 5.1 | 16.2 | 0.87 | 9.43 |
| 0.03 | 194 | 4.2 | 20.4 | 0.44 | 1 at.%Na | 202 | 2.7 | 19.1 | 0.78 | 8.58 |
| 0.03 | 194 | 4.2 | 20.4 | 0.44 | TEGS-2P | 203 | 2.4 | 18.1 | 0.96 | 8.93 |
TABLE VII
EFFECT OF VARYING THICKNESS OF CONSTANTAN AND STAINLESS STEEL N-LEG SHELLS.

$W_{0.28Ta_0.02Se_2}$ PLUS PbTe-0.3 at \% Na P-LEG. $t_c = 25^\circ C$; $t_b = 500^\circ C$; $t_h = 1000^\circ C$.

<table>
<thead>
<tr>
<th>N-Leg Material</th>
<th>Thickness (mils)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constantan</td>
<td>2.7 (opt)</td>
<td>9.59</td>
</tr>
<tr>
<td>Constantan</td>
<td>5</td>
<td>8.95</td>
</tr>
<tr>
<td>Constantan</td>
<td>10</td>
<td>7.03</td>
</tr>
<tr>
<td>446 Stainless Steel</td>
<td>5.4 (opt)</td>
<td>3.02</td>
</tr>
</tbody>
</table>
FIGURE - 1
Electrical Properties vs x for W_{1-x}Te_xSe_2
at 600° C
FIGURE 2
Electrical Properties of TEGS-2P (sintered PbTe) vs Temperature
FIGURE - 3
Electrical Properties of TEGS-3N (sintered PbTe) vs Temperature

- $S (\mu V/deg)\n
- $P (m A-cm)\n
- $\frac{\alpha^2}{\phi} (V/cm^2.cm) \times 10^5$
FIGURE 4
Electrical Properties of TEGS-3P (sintered PbTe) vs Temperature

- THIS LABORATORY
- 3M Co. CURVES

vs Temperture (°C)

S (μV/°K)

J(μA/cm²)

$S^2/Av$ (deg²-cm) / $10^5$
FIGURE 5
Thermoelectric Properties vs Temperature for Constantan

$S$ (µV/deg)

$K$ (W/(deg·m))

$Z$ (deg$^{-1}$)·10³
II. DEVELOPMENT OF THERMOELECTRIC MODULES - H. Valdsaar

1. Encapsulation in Metal Cans

Development of the metal can concept for tungsten selenide encapsulation was continued. Practical testing was carried out with constantan and stainless steel cans. The choice was made to standardize at 1/2" diameter for the inner, p-type thermoelement. This dimension permits a direct comparison between tungsten selenide and lead telluride (which is not readily available at larger diameters); and furthermore, permits use of these materials in series for improved efficiency over a wide temperature range.

The intended design features are as follows:

Metal Can - constantan 3/4"-1" long, outside diameter 5/8", wall thickness 10 mils or less, suitable protective coatings inside and outside for the hot end.

Thermoelement - tantalum-doped (1-3%) tungsten selenide by itself, or combined with p-type lead telluride at the low-temperature end; total length about 3/4", common diameter 1/2".

Wall Insulation - ceramic less than 1/16" thick, plasma sprayed or brush applied; edge insulation at the cold open end by high-temperature resin.

Contacts - at the hot end a pressure contact with a diffused band, or through a new phase established by addition of
other components. The latter possibility is presently under active study. At the cold end, standard techniques will be sufficient.

2. **Powder Compaction**

Powder compaction will be standardized with the use of the specially selected short mold of 1" x 1/2" cross-section and variable thickness. The particular stainless steel mold construction allows compaction pressures up to 100 tsi.

The heat flow and electrical current direction in the module is to follow the crystallographic a-direction (which is perpendicular to the pressing direction).

Until the high-pressure mold becomes available, the 1/2" dia., 1/2" long elements, used in standard testing (a-crystallographic direction) have been cut from cylindrical 3/4" dia. pellets compacted at 40 tsi.

In preliminary tests, a larger (1-1/4" dia., 1/2" thick) tungsten selenide (1% Ta) disc was successfully compacted in a cylindrical mold under 70 tsi. The compact had 93.5% of the theoretical density. Electrical resistivity was about 8 milliohm-cm in a-direction and at least twice the value in c-direction.

A hydrostatically compacted pellet, also at 70 tsi, had a multitude of cracks which made it unusable.
3. **Experimental Results**

Most of the testing was done with 3/4" dia. cans using sections of ceramic tubing for inside wall insulation. Module #24 had plasma-sprayed zirconia on the inside wall. Tungsten selenide compacts were installed in either α or γ crystallographic direction. The main objective was not the optimization of the thermoelectric performance, but rather observation of the stability of the module and study of the bonding of end contacts.

As expected, the hot end contact at about 1000°C presents a major problem in the formation of a stable low-resistivity bond, which should retain its desirable characteristics through multiple heating cycles. The metal bottom of the can, whether constantan, nickel or stainless steel, has to be protected from exposure to selenium vapors. A plasma-sprayed molybdenum coating is somewhat porous and does not completely hinder selenium penetration to the metal underneath the protective layer. Furthermore, some cracking and flaking of the sprayed molybdenum layer was evident. In contrast, a thin molybdenum disc (8 mils) cut from a solid sheet remained unaffected and seemed to offer satisfactory protection against direct attack by selenium vapors. When a little fine copper dust was left between the molybdenum disc and the constantan bottom, they bonded rather well to each other under slight pressure at 1000°C.
The weld of the constantan can between the 25 mil thick bottom section and the 10 mil wall proved to be weak during a longer heating period. A thick bottom (1/4") section allowed a better distribution of strains on the weld. In an ultimate design, the weld would be unnecessary, because the metal cans could be preformed from one piece into the desired shape.

In Modules #27 and #28, sections of lead telluride (Minnesota Mining & Manufacturing Co., Code No. TEGS-2PB) were included at the low-temperature end. The average resistivity of this material is about 3 milliohm-cm, and for good power performance it should be matched with lower resistivity tungsten selenide, which is planned for modules to be studied. These tests showed, however, that PbTe and WSe$_2$ in direct contact under operating conditions form a firm low-resistivity bond between them.

With constantan cans, the measured constantan contribution to the module voltage was close to that of the expected value, about 60 mV at 975°C, open circuit. Resistance of the constantan can was between 1-2 milliohm usually, less than 10 percent of the total module resistance. The power contribution of constantan walls to the module, however, was close to 35 percent of the total power with a matched load.
4. Material Combinations in Individual Modules

Module #24 - Constantan can with thin bottom (25 mils), plasma-sprayed niobium layer on the bottom and zirconia layer on the inside wall, both layers 7 mils thick. A single piece of tungsten selenide 3/4" dia. and 7/8" long, current flow in c-crystallographic direction. After 7 hours of heating, cracks in the bottom weld became evident. There was some flaking of the niobium layer at the bottom. Zirconia on the walls seemed unaffected.

Module #25 - Constantan can with thin bottom (25 mils), a loose disc of molybdenum sheet at the bottom, ceramic tube as wall insulation. Tungsten selenide pellet, 5/8" dia., 3/4" long, was cut from a 1" dia. pellet in a-crystallographic direction. The bottom of the can separated after the first heating cycle (7 hours), because of the weakened weld. No adverse reaction with the molybdenum disc.

Module #26 - Constantan can with heavy (1/4") bottom, a loose molybdenum disc (8 mils) at the bottom, ceramic tube as wall insulation. Two identical tungsten pellets, 1/2" dia. and 1/2" long, in c-crystallographic direction. Three heat cycles, a total of 20 hours, had caused severe wall corrosion from the inside near the hot end, where the ceramic tube did not exclude selenium vapors from contacting the wall.
Module #27 - Constantan can with heavy (1/4") bottom, molybdenum spray coat (16 mils) inside over the bottom and 1/4" up the wall. Ceramic tube as wall insulation. A 1/2" dia. and 1/2" long tungsten selenide pellet, cut in a-crystallographic direction from a larger pellet, placed next to a 1/2" dia. and 1/2" long lead telluride pellet. Two heating cycles with time total of 15 hours. Resistance remained almost constant, voltage dropped about 10 percent. The WSe$_2$ and PbTe had formed a single solid piece. The molybdenum layer showed several cracks, and evidently some reaction had taken place on either side of it.

Module #28 - Stainless steel can with heavy (1/4") bottom, molybdenum spray coat (12 mils) on the bottom with another coat of nickel (7 mils). Ceramic tube as wall insulation. A 1/2" dia. and 5/8" long tungsten selenide pellet with 1/2" dia. and 5/16" long lead telluride section. No indication of wall deterioration after one heating cycle. The WSe$_2$ and PbTe again had formed a strong bond to each other.

5. Decomposition Pressure of Tungsten Selenide

The true decomposition pressure of tungsten selenide as a function of temperature has not yet been determined. A few tests were performed with the material W$_{0.99}$Ta$_{0.01}$Se$_2$, which is usually encapsulated in the modules.
1. A small amount of powder, 0.2 grams, was degassed at 200°C and 10^{-5} mm for two hours inside a narrow quartz tube. Then the tube was sealed off under vacuum and gradually heated to 1500°C. The walls of the quartz tube softened and collapsed without breakage.

2. The test was repeated with a larger sample, 1.226 g., in the same volume, 12 cc. The powder had been degassed for an hour at 160°C and 7 microns Hg pressure, then sealed under vacuum. First the tube was heated to 1350°C and cooled. There was no obvious change in the appearance of the powder. Then the tube was gradually heated to 1500°C and held there for half an hour before cooling. The tube was completely flattened without breakage. The tungsten selenide powder seemed unchanged.

3. A standard compact of a tungsten selenide bar, 19.5 grams, was sealed under vacuum in a volume of 5 cc without preliminary degassing at elevated temperatures.

   The sample was heated gradually to 1350°C. The quartz tube expanded and broke at this temperature due to internal pressure.

4. Another small sample was sealed under vacuum into a 6 mm I.D. x 33 cm long quartz tube. The end of the tube containing the tungsten selenide powder was placed in the center of a tube furnace, with the other end near room temperature, outside the furnace. As the temperature increased to 400°C in the furnace,
a very slight selenium mirror condensed at the cooler end. It did not change appreciably until 1000°C was reached when a black selenium deposit grew into sizeable needles and platelets over a 40-hour period.
# TABLE VIII

**CHARACTERISTICS OF METAL ENCAPSULATED MODULES**

<table>
<thead>
<tr>
<th>Module No.</th>
<th>#24</th>
<th>#25</th>
<th>#26</th>
<th>#27</th>
<th>#28</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner Element</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cross-section, cm²</td>
<td>2.7</td>
<td>2.0</td>
<td>1.2</td>
<td>1.2</td>
<td>1.24</td>
</tr>
<tr>
<td>Length, cm</td>
<td>2.3</td>
<td>1.8</td>
<td>2.51</td>
<td>2.53</td>
<td>2.34</td>
</tr>
<tr>
<td>Crystallographic Direction</td>
<td>c</td>
<td>a</td>
<td>c</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>Total Resistance, at 950°C, mΩ</td>
<td>29</td>
<td>17</td>
<td>140²</td>
<td>18</td>
<td>28</td>
</tr>
<tr>
<td>Temperature Interval Hot-Cold, °C</td>
<td>962-50</td>
<td>975-100</td>
<td>987-50</td>
<td>950-75</td>
<td>950-50</td>
</tr>
<tr>
<td>Open Circuit Voltage, mV</td>
<td>226</td>
<td>277</td>
<td>262</td>
<td>253</td>
<td>214</td>
</tr>
<tr>
<td>Average Seebeck Coefficient, µV/°C</td>
<td>248</td>
<td>316</td>
<td>280</td>
<td>289</td>
<td>238</td>
</tr>
<tr>
<td>Maximum Power, mW</td>
<td>600</td>
<td>1146</td>
<td>114</td>
<td>812</td>
<td>408</td>
</tr>
</tbody>
</table>

1) Two pellets, each 1/2" long, both tungsten selenide.
2) Includes the contact resistance between the two pellets.
3) Two pellets, each 1/2" long, one tungsten selenide, the other lead telluride.
4) Two pellets, tungsten selenide 5/8" long, and lead telluride 5/16" long.
Tungsten selenide element, 3/4" diam. and 7/8" long, soldered to a copper cooling block. The empty constantan can shown next to it has a narrow copper clamp around its open end during operation which serves as the second power lead. The can is sealed at the cold end with resin.
Figure 7. Module # 25 Opened After Seven Hours of Operation

The bottom is removed at the welded joint. The smaller cross-section shows the thin outside wall, the ceramic spacer, and the tungsten selenide element. The larger cross-section shows a molybdenum disc on constantan bottom with some selenide deposit on it but otherwise quite unaffected.
Figure 8. Module #27 Opened After 15 Hours of Operation

Plasma-sprayed molybdenum coating (1 mils thick) showed cracks and material loss on both sides of the coating. The nickel heat shield is visible below the bottom of the module. Thermocouple wire is located between the bottom of the module and the heat shield.