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

EXPERIMENTAL STATION

PIGMENTS DEPARTMENT

October 31, 1962

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

NObs-84824 Index No. SR-007-12-01 Task 802

Fifth Quarterly Report

by

W. T. Hicks, H. Valdsaar

approved by

D. G. Kelemen

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This Report Covers the Period July 1, 1962 to September 30, 1962.

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ABSTRACT

The study of the tantalum-doped solid solutions of the compounds WSe_2, WTe_2, $MoSe_2$ and $MoTe_2$ was continued. To date, these complex materials showed no practical advantage over tantalum-doped tungsten diselenide. Incidental observations made in the course of this study have revealed occasional difficulties in reproducing earlier data.

Hall coefficient data were obtained on several $W_{1-x}Ta_xSe_2$ compositions at temperatures up to 600°C and were interpreted to yield information on the scattering mechanism at various doping levels and on the relation between chemical dopant concentration and carrier density. Hall effect measurements were also made on rhenium-doped molybdenum diselenide.

A number of niobium and tantalum tellurides and selenides were synthesized in exploratory work. They show no promise of practical value as thermoelectric materials.

Several test modules utilizing tantalum-doped tungsten diselenide were constructed; the results suggest that this p-type material may be useful in cascaded generators between 500 and 1000°C.

Experiments on melting tungsten diselenide at high pressures are in progress.

A. INTRODUCTION - D. G. Kelemen

Following the pattern established earlier in this project, this report consists of two major sections: a detailed study of selected compositions by Dr. W. T. Hicks and an account directed toward their practical application by Dr. Herbert Valdsaar.

Dr. Hicks has continued his work in exploring some of the more complex derivatives of tungsten diselenide. The general formula of these tantalum-doped compositions is $W_{(1-w)(1-x)}Mo_{w(1-x)}Ta_xSe_{2(1-y)}Te_{2y}$, where for compositions of potential practical interest x is the range of a few atom percent and w and y may be in the order of 50 atom percent. Confirming data obtained earlier, these complex compositions show no advantage over simple $W_{1-x}Ta_xSe_2$, primarily because the hoped-for reduction in thermal conductivity due to the isoelectric substitutions manifests itself only at room temperature, but not in the 600-900°C region where the Figures of Merit of these materials are relatively favorable.

Hall effect measurements carried out by Dr. Hicks at temperatures up to 600°C clarified the scattering mechanism in $W_{1-x}Ta_xSe_2$. The nominally undoped (high resistivity p-type) material seems to exhibit the scattering mechanism of an atomic lattice. The carrier concentration increases at temperatures in excess of 400°C with a slope corresponding to an energy gap of 1.4 eV. The mobility vs. temperature plot of preparations doped with 1% Ta suggests impurity scattering, while 3% Ta substitution leads to the type of temperature dependence conventionally attributed to an ionic lattice. In these heavily doped specimens the carrier concentration is independent of temperature.

Dr. Hicks has also interpreted his Hall effect measurements in terms of carriers contributed by the dopant in terms of its chemically established concentration. The number of holes contributed per added tantalum atom in the range x = 1% to 5% in $W_{1-x}Ta_xSe_2$ increases gradually from 0.4 to 0.7.

Dr. Valdsaar's work continues to broaden our background for the eventual construction of practical generators. Contact resistances in potentially durable encapsulated modules utilizing tantalum-doped tungsten diselenide with dimensions appropriate for practical applications are in the order of 20% of the total resistance; we shall endeavor to reduce this value further.

Dr. Valdsaar has also carried out some initial experiments toward melting tungsten diselenide under pressure. This technique promises to be helpful in the fabrication of modules and may also result, as suggested earlier, in better material properties than we have observed to date with pressed samples.

In earlier reports, we have indicated that Dr. Valdsaar planned to examine some silicide-germanide solid solutions suitable for temperatures in excess of 1000°C in cascaded thermoelectric generators. Partly because these materials turned out to be less efficient than we expected, and partly because we have come to consider the practicality of operating at such high temperaturs questionable on general grounds, we have discontinued this work.

In the future, we propose to recess gradually all further work on the basic properties of tungsten diselenide and its derivatives. We believe that tantalum-doped p-type tungsten diselenide may have practical merit in the 500-1000°C section of cascaded thermoelectric generators operating between room temperature and 1000°C. Both Dr. Hicks and Dr. Valdsaar will devote themselves mainly to the problems connected with the development of complete modules for such generators.

B. THERMOELECTRIC PROPERTIES OF SELENIDES AND TELLURIDES OF GROUPS VB AND VIB METALS AND THEIR SOLID SOLUTIONS - W. T. Hicks

The study of the complex family of solid solutions made from varying ratios of WSe_2, WTe_2, $MoSe_2$, and $MoTe_2$ doped with a constant level of tantalum has been continued. As shown in the previous report, the complex solid solutions show no decrease in thermal conductivity at 600°C as compared with the simple tantalum-doped WSe_2. Thus, these complex solutions will only show an improved Figure of Merit if their electrical properties are better than that of tantalum-doped WSe_2.

Data have been collected covering a number of preparations of the composition $W_{0.99}Ta_{0.01}Se_2$ showing variations in the electrical properties of the resulting material and speculations are made as to the causes.

Hall coefficient measurements were carried out at room temperature on a number of Group VIB dichalcogenides. In addition, Hall coefficients versus temperatures have now been measured for several members of the family $W_{1-x}Ta_xSe_2$.

A number of Group VB chalcogenides have been synthesized and their electrical properties measured up to 600°C.

Experimental Procedures

The synthesis of the Group VB and VIB chalcogenides has been described in previous reports. One change was made in the apparatus for measuring Seebeck coefficient and resistivities at high temperatures. The wire chromel-alumel thermocouples used to read temperature gradient and voltage across the sample were replaced by sheathed megapak chromel-alumel thermocouples. This was necessitated because of the highly corrosive nature of the compounds containing tellurium; the lifetime of the sheathed thermocouples was approximately double that of the wire thermocouples. The D.C. Hall effect measuring apparatus and its high temperature furnace have been described in previous reports also.

Properties of Complex Group VIB Dichalcogenides

In the previous Quarterly Reports, electrical properties measured up to 600°C were summarized for the complex family of compositions $W_{(1-w)(1-x)}Mo_{w(1-x)}Ta_xSe_{2(1-y)}Te_{2y}$. As described there, a number of compositions were made up with a constant value of y = 1, a constant doping level of tantalum (x = 0.06) and varying values of w. Maximum S^2/ρ values of about 1×10^{-5} watts/deg^2-cm at 600° were found for the compositions w = 0, 0.5 and 0.8. It was also shown that for the composition w = 0.5 the electrical properties of samples having varying doping levels (values of x) conformed to the relation derived assuming a constant carrier mobility:

$$S = 200 \cdot 10^{-6} \log \rho + \text{Constant} \qquad (1)$$

where S is the Seebeck coefficient expressed in microvolts per degree and ρ is the resistivity in ohm-cm.[1]

Also in the last report, the preparation and properties of compositions with a constant value of w = 0.5 and with a constant level of tantalum (x = 0.06) and varying values of y were described. Here it was found that the optimum value of y was equal to 1 when w = 0.5. In this report, properties of compositions where w had the value of 0 and 1 with varying values of y are described. Compositions with w = 0.8 and varying values of y still remain to be synthesized and measured.

$\underline{W_{1-x}Ta_xSe_{2(1-y)}Te_{2y}}$

As in previous experiments, to reduce the number of compositions that had to be synthesized values of y were varied with a constant value of x = 0.06. The electrical properties measured at 600°C were extrapolated to optimum conditions where S = 172 µV/deg using equation (1). In Table B-1 are listed the thus extrapolated electrical properties for varying values of y. According to this table, the value y = 1 appears to be the best ratio of tellurium to selenium with $(S^2/\rho)_{opt} = 1.1 \times 10^{-5}$ watts/deg^2-cm. However, we know from previous experience that the series

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[1] See e.g., A. F. Ioffe, Semiconductor Thermoelements and Thermoelectric Cooling, Infosearch Ltd., London, 1957.

with y = 0 actually possesses an optimum S^2/ρ of 1.5×10^{-5} watts/deg^{2}cm at x = 0.01. As we shall see later in this report, this is due to an increase in the carrier mobility as the value of x is decreased from x = 0.06 for the series with y = 0. Thus, optimum electrical properties are obtained in this series with a Seebeck coefficient higher than the classical optimum Seebeck coefficient of 172 microvolts/deg. It was of interest then to try varying doping levels at the composition y = 1 to see if higher S^2/ρ values are obtained in this case when x is decreased from 0.06.

$\underline{W_{1-x}Ta_xSeTe}$

A number of samples were made in this system with values of x ranging from 0 to 0.20. It was found that this series deviates considerably from equation (1) when x is varied. This deviation may be due to a high degree of mixed conductivity. The actual electrical properties of these compositions are summarized by Figure B1 where S, ρ, and S^2/ρ are given at 600°C as a function of x. A first and second set of samples synthesized shows an improvement in the truncated Figure of Merit as the value of x is raised from 0.05 to 0.06. Subsequently a third series of compositions was made with values of x ranging from 0.06 to 0.20. It is shown by the plot that a further improvement in the Figure of Merit was shown in this set as x is increased from 0.06 to 0.08. However, the control sample in the second set of compositions (x = 0.06) had considerably inferior properties to that of the original set of compositions. Indeed, all of the other values of x in the second set of compositions are inferior to that of the first set. Further experiments are being carried out to find the source of such discrepancies. However, it appears that the family of compositions $W_{1-x}Ta_xSeTe$ is inferior at all doping levels to the family $W_{1-x}Ta_xSe_2$.

$Mo_{1-x}Ta_xSe_{2(1-y)}Te_{2y}$—

Table B-II shows electrical properties measured for this family at 600° with varying values of y. Again the electrical properties were extrapolated in this plot on a log S versus ρ plot to an optimum Seebeck coefficient of 172 microvolts/deg. It is seen that all of these S^2/ρ values are less than the best of those achieved for the previous family. Therefore, no further work will be done on this system.

Effect of Tungsten Sources on the Composition $W_{0.99}Ta_{0.01}Se_2$—

A problem has arisen in the reproducibility of the electrical properties of a number of samples of composition $W_{0.99}Ta_{0.01}Se_2$, all apparently made by the same experimental procedure. It is felt that since the reactions were carried out in sealed tubes, the compositions are close to those carefully weighed out into the capsules before the reaction. There may be some slight loss of selenium due to condensation during the reaction at 1150°C, but at least for the diselenides very little selenium remains on the tube when the contents are emptied. Table B-III lists electrical properties measured at 600° along with the measured density and metal-to-selenium ratio of the samples along with the source of tungsten used in each preparation. These sources are listed at the bottom of the table along with the manufacturer's analyses. In these preparations two lots of selenium, both of the same grade from the same manufacturer, American Smelting and Refining Co., were used but because of the high purity of this material (99.999%+) this is not considered an important variable. Little correlation is seen between electrical properties of the resulting compounds and the source of tungsten used in preparations made over a long period. However, in one set of compositions made at the same time, 603 to 606, there is some indication that the Seebeck value and, therefore, the Figure of Merit made from Fansteel tungsten was somewhat superior. Sample No. 382 was made with a slightly different procedure than the others in that the final reaction was carried out overnight at 1000°C instead of 1150°C. However, Sample No. 478 reacted finally at 1150°C shows almost equivalent properties to sample 382. The most apparent correlation which may be made from Table B-III in regard to samples made over a long period of time is the correlation between resistivity and the density of the pressed compacts. Specifically, the high resistivities of samples 603, 604 and 606 may be attributed to their low densities. This may result from these samples having a slight excess of metal over the stoichiometric composition (some of those compositions labelled stoichiometric may actually be slightly metal excess due to loss of selenium during the reaction). Improved results might be achieved then by reacting samples with a slight excess of selenium, e.g. 0.1%. Previous reports indicate that low density, high resistivity samples with low values of Seebeck coefficient were obtained when samples were made with a 1% or higher metal excess. Other process variables which might affect the electrical properties of the samples will be investigated. Hall measurements might indicate whether the change in varying electrical conductivity of the samples is due to the variation in the carrier concentration or the carrier mobility. A variation in the carrier mobility might indicate that the variations are due to a change in the physical structure of the samples as opposed to differences in the chemical composition.

Hall Effect Measurements

Hall Effect Measurements on $W_{1-x}Ta_xSe_2$ Versus Temperature

For the system $W_{1-x}Ta_xSe_2$, Hall effect measurements have now been made up to 600°C for the compositions $x = 0$, 0.01 and 0.03. These measurements are summarized in Figures B2, B3 and B4. In Figure B2, the logarithm of the electrical conductivity is plotted against the reciprocal of the absolute temperature for all three compositions. Here it may be seen that the conductivities of the doped compositions do not vary much with temperature while the conductivity of WSe_2 begins to increase at about 400°C. In Figure B3, the logarithm of the carrier concentration, calculated from the Hall effect measurements, is plotted versus the reciprocal of the absolute temperature. For the composition WSe_2, the carrier concentration remains virtually constant up to about 400°, then increases rapidly indicating the onset of the intrinsic region. The energy gap of WSe_2 may be calculated from this curve since the slope of the curve is equal to twice the energy gap divided by the Boltzmann constant. Thus, it is calculated that the energy gap is approximately 1.4 electron volts and this corresponds to an absorption edge at 0.9 microns. Dr. G. R. Anderson of the Central Research Department of this company has measured the reflectivity of a smooth surface of a pressed sample of WSe_2 as a function of wavelength and found an anomaly at 0.75 microns at room temperature which was intensified at liquid nitrogen temperature. However, the reflectivity increased with increasing wavelength, which is contrary to what one would expect for an absorption edge.

As shown by Figure B3 for the tantalum-doped compositions $x = 0.01$ and $x = 0.03$ no change in carrier concentration could be observed with changes in temperature. This indicates that these compositions are in an impurity exhaustion region, and the slight variation in electrical conductivity shown in Figure B2 for these compositions was due to small variations in the carrier mobility.

In Figure B4 is plotted the logarithm of the carrier mobility versus the logarithm of the absolute temperature for the same compositions. The carrier mobility was calculated by the formula $\mu = \sigma/nq$, where μ is the carrier mobility, σ is the electrical conductivity, n is the carrier concentration, and q is the electronic charge. For the compositions $x = 0.01$ and $x = 0.03$ a constant average value of the carrier concentration was used with the conductivity values given in Figure B2 to calculate the variation in mobility with temperature.

For the composition $x = 0$, the slope of the $\log \mu$ versus $\log T$ plot indicates that the carrier mobility varies as $T^{-1.7}$. This corresponds very closely to what one would expect for an atomic lattice[2] in which case μ should vary as $T^{-1.5}$. For this case also according to Ioffe's notation, the constant A in Pisarenko's formula should be equal to the integer 2. Using this constant with the formula, a Seebeck coefficient of 1025 microvolts/deg measured at room temperature for the composition $x = 0$, and the carrier concentration 2.1×10^{16} cm^{-3} shown in Figure B3, one may calculate an effective mass for holes in WSe_2 of 6.10 times the electron mass.

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[2] See e.g. A. F. Ioffe, <u>Semiconductor Thermoelements and Thermoelectric Cooling</u>, Infosearch Ltd., London, 1957.

For the composition x = 0.03 a line drawn through the points in Figure B4 shows that the mobility varies as $T^{-0.3}$. This is very close to what Ioffe calls ionic scattering where the mobility varies as $T^{-0.5}$ and in this case a constant of A = 3 should be used in Pisarenko's formula. Using the Seebeck coefficient of 96 microvolts/degree which was measured at room temperature for this composition, one may calculate an effective mass for holes of 1.46 times the electron mass for this composition.

For the composition x = 0.01, the mobility varies as $T^{+0.2}$. Thus, this composition may be placed between the "ionic" case where the mobility should vary as $T^{-0.5}$ and "scattering by impurity ions" where the mobility should vary as $T^{+1.5}$.

Ioffe (loc.cit.) shows that, if the carrier mobility remains constant as the carrier concentration is varied, optimum thermoelectric properties will occur in a material when the carrier concentration is achieved which yields a Seebeck coefficient of 172 microvolts/deg. It was shown previously that for the series $W_{1-x}Ta_xSe_2$, this is indeed the case for electrical properties measured at room temperature. However, the Figure of Merit of this material is small at room temperature and only becomes appreciable at 600°C due to the large increase in Seebeck coefficient with temperature. At this temperature, it was empirically shown previously that the optimum Figure of Merit in this series occurs at a composition x = 0.01, where the Seebeck coefficient (S = 370 microvolts/deg) is considerably above the classical optimum Seebeck coefficient value. Now it may be seen in Figure B4 that this is a direct result of the fact that the carrier mobilities of the two compositions x = 0.01 and x = 0.03 are all very close in value at room temperature but diverge considerably as the temperature of approximately 600°C (873°K) is reached. Thus, considerable care must be used in applying the constant carrier mobility rule as two cases have been seen in this report where this does not apply.

Comparison of Hall Effect Measurements on Group VIB Dichalcogenides

Table B-IV compiles the quantities derived from Hall effect measurements and resistivity measurements on a number of Group VIB dichalcogenides which have been doped with tantalum and one compound, $MoSe_2$, which has been doped with rhenium. In addition to the Hall effect parameters, the concentration of doping atoms (tantalum or rhenium) was calculated per unit volume of the pressed powder bars and this was divided into the carrier concentration as measured by Hall effect measurements to get the carrier contribution per doping atom. One might expect each tantalum atom since it has one less electron in its 5d shell than tungsten to show a constant contribution of one hole per tantalum atom. However, its actual contribution is somewhat less than this in the case of $W_{1-x}Ta_xSe_2$; it varies systematically from 0.4 at x = 0.01 to 0.7 at x = 0.05. An entrapment of a number of holes by impurities or lattice imperfections which remain constant as x is varied might explain this phenomenon. For the compounds $MoSe_2$ and $MoTe_2$, the contribution is about the same for a given value of x. Since in these latter two compounds for the same carrier concentrations the mobility is much lower than that for WSe_2, the lower Figures of Merit which were previously found for these compositions are not surprising.

Rhenium, possessing one more electron in the 5d shell than tungsten, might be expected to contribute one electron per rhenium atom to the conduction band. The actual contribution measured in $MoSe_2$ is only about 0.15 electrons per rhenium atom. It may be observed that the mobility for electrons in $MoSe_2$ is very close to that observed for holes in $MoSe_2$. Rhenium doping of WSe_2 as carried out by Dr. L. H. Brixner of this department was not successful in producing n-type materials of appreciable carrier concentrations. Since the carrier mobility in $MoSe_2$ is low it does not appear possible to make a good n-type thermoelectric material from the Group VIB dichalcogenides.

For the more complex series $W_{0.5(1-x)}Mo_{0.5(1-x)}Ta_xSeTe$ with values of x equal to 0.02 and 0.04, a similar carrier contantalum atom. However, its actual contribution is somewhat less than this in the case of $W_{1-x}Ta_xSe_2$; it varies systematically from 0.4 at $x = 0.01$ to 0.7 at $x = 0.05$. An entrapment of a number of holes by impurities or lattice imperfections which remain constant as x is varied might explain this phenomenon. For the compounds $MoSe_2$ and $MoTe_2$, the contribution is about the same for a given value of x. Since in these latter two compounds for the same carrier concentrations the mobility is much lower than that for WSe_2, the lower Figures of Merit which were previously found for these compositions are not surprising.

Rhenium, possessing one more electron in the 5d shell than tungsten, might be expected to contribute one electron per rhenium atom to conductivity. The actual contribution measured in $MoSe_2$ is only about 0.15 electrons per rhenium atom. It may be observed that the mobility for electrons in $MoSe_2$ is very close to that observed for holes in $MoSe_2$. Rhenium doping of WSe_2 as carried out by Dr. L. H. Brixner of this department was not successful in producing n-type materials of appreciable carrier concentrations. Since the carrier mobility in $MoSe_2$ is low it does appear possible to make a good n-type thermoelectric material from the Group VIB dichalcogenides.

For the more complex series $W_{0.5(1-x)}Mo_{0.5(1-x)}Ta_xSeTe$ with values of x equal to 0.02 and 0.04, a similar carrier concentration was found as for WSe_2. The carrier mobility is lower, however, by a factor of 2 or 3, thus explaining the poorer electrical properties of these more complex compositions. However, for the compositions x = 0.01 and x = 0.06 anomalously low carrier concentrations and high carrier mobilities have been measured and these values are difficult to explain. Room temperature Seebeck coefficients on the samples were not very accurate and thus cannot be used to confirm these anomalies. The composition x = 0.06 was prepared at a different time than the other compositions and this could partially explain the high mobility. At 600°C a log S versus ρ plot for these compositions is linear and conforms to equation (1) indicating a constant carrier mobility. However, since these materials undergo an apparent phase transformation between 400 and 500°C this is not directly related to the room temperature anomalies.

Properties of Group VB Chalcogenides

All the compositions of type AB, A_2B_3 and AB_2 were prepared where A is either Nb or Ta and B is either Se or Te. X-ray diffraction patterns of the compositions AB and AB_2 gave distinct complex patterns with no sign of metallic elements. All of the compositions A_2B_3 appear to be two-phase consisting of the phases AB plus AB_2 with the exception of Ta_2Se_3 where there may be a solid solution region between the compositions TaSe and

$TaSe_2$. All the compositions having less than two chalcogenide atoms per metal atom showed signs of reaction with moisture in the atmosphere when stored at room temperature in unsealed containers. Thus bars of these compositions crumbled to powder on storage unless they were stored in desiccators.

These observations are somewhat in conflict with those made by Brixner in an earlier preparation of these compounds. He indicated solid solution behavior from the compositions AB to AB_2 for most of these systems and found that many times the powders exhibited pyrophoric behavior. Such differences in observations might be due to different conditions of humidity and methods of handling these reactive compounds.

Because of the reactive nature of these materials, the reactive compositions were stored as much as possible in a desiccator except for the operations of crushing the materials after reaction in evacuated sealed quartz tubes at 1150°C and the molding of the powder bars. The high temperature measurements are made in a protective argon atmosphere as standard procedure for all materials.

The electrical properties of these materials are summarized in Table B-V. Most of these compositions showed an increasing truncated Figure of Merit as temperature was increased to 600°C. However, the best Figure of Merit shown by these compositions was that for $TaTe_2$, approximately 1 x 10^{-7} watts/deg^2-cm. This is considerably inferior to the best shown by tantalum-doped WSe_2 (1.5 x 10^{-5} watts/deg^2-cm). Therefore, no further work is contemplated for these compositions other than completing the measurements on the compositions NbSe and $NbTe_2$ which samples were broken before the high temperature measurements could be made. Because of their instability even at room temperature, Hall measurements were not attempted on compositions having less than two chalcogenide atoms per metal atom. Room temperature measurements on $NbSe_2$ indicate a carrier concentration in excess of 2 x 10^{21} cm^{-3} and a carrier mobility of less than or equal to 8 cm^2/volt-sec. For the composition $TaTe_2$, a carrier composition limit of greater than 2 x 10^{21} cm^{-3} was also found with a carrier mobility less than or equal to 3 cm^2/volt-sec. These measurements also help to eliminate these compounds from consideration as thermoelectric materials.

ACKNOWLEDGMENT

Several helpful discussions were had with Dr. L. H. Brixner. Sample preparation and electrical measurements were made by Mr. A. R. Sohodski.

TABLE B-I

EXTRAPOLATED OPTIMUM ELECTRICAL PROPERTIES AT 600°C FOR $W_{1-x}Ta_xSe_{2(1-y)}Te_{2y}$

y	ρ opt (mΩ-cm)	(S^2/ρ)opt(w/deg^2-cm)$\cdot 10^5$
0	5.2	0.57
0.5	4.8	0.62
1.0	2.8	1.06
2.0	4.7	0.63

TABLE B-II

EXTRAPOLATED OPTIMUM ELECTRICAL PROPERTIES AT 600°C FOR $Mo_{1-x}Ta_xSe_{2(1-y)}Te_{2y}$

y	ρ opt (mΩ-cm)	(S^2/ρ)opt(w/deg^2-cm)$\cdot 10^5$
0	11.5	0.26
0.5	12.0	.25
1.0	5.5	.54
1.5	5.5	.54
2.0	8.0	.37

TABLE B-III

PROPERTIES OF $W_{0.99}Ta_{0.01}Se_2$ MADE FROM DIFFERENT TUNGSTEN SOURCES

Sample	W Source	Metal Atoms / 2 Se Atoms	% of Theor. X-ray Dens.	$S_{600°C}$ (μV/deg)	ρ (mΩ-cm)	S^2/ρ (w/deg^2-cm)$\cdot 10^5$
382	1	0.9995	92.44	372	9.3	1.48
478	2	1.0000	92.35	353	8.0	1.52
483	2	1.0002	91.93	305	8.3	1.12
549	3	1.0000	92.89	300	9.8	0.92
603	3	1.0000	91.18	298	14.3	.62
604	3	1.0001	90.94	300	19.6	.46
606	1	1.0002	91.02	370	16	.85
630	1	1.0002	91.98	320	10.6	.96

W Sources:

1. Fansteel Metallurgical Corporation, Lot A5103-F, 200 mesh powder; Their analysis: O, 300; Mo, 100; Cu, 50; Ni, 10; Si, 10; Ca, 10; Mg, 10; Ti, 10; and Al, 10 ppm.

2. M & R Refractory Metals, Inc., -60/+100 mesh powder, Low oxygen grade, analysis not available, but should be similar to (3) below.

3. M & R Refractory Metals, Inc., Lot #5822, -60/+100 mesh powder; Their analysis: O, 180; H, 7; N, 3; Mo, 80; Ni, 60; Si, 30; Al, <10; C, 20; Co, <10; Fe, 50; Mn, <10; P, <10; Pb, <10; S, <10; and Sn, <10 ppm.

TABLE B-IV

ROOM TEMPERATURE HALL EFFECT DATA FOR GROUP VIB DICHALCOGENIDES

Composition	ρ(mΩ-cm)	n(cm^{-3})·10^{-20}	Carriers/ doping atom	μ(cm^2/v-sec)
$W_{1-x}Ta_xSe_2$				
x = 0.01	11.94	0.63	0.41	8.3
0.02	3.92	1.8	.59	8.9
0.03	3.26	2.6	.58	7.4
0.04	4.36	3.5	.62	4.1
0.05	3.89	5.2	.72	3.1
$Mo_{0.99}Ta_{0.01}Se_2$	22.83	0.6	.4	5
$Mo_{0.97}Ta_{0.03}Te_2$	37.8	2.6	.7	0.6
$Mo_{0.98}Re_{0.02}Se_2$	43.1	.45	.15	4
$W_{0.5(1-x)}Mo_{0.5(1-x)}Ta_xSeTe$				
x = 0.01	24.8	0.28	0.20	7.7
0.02	12.2	1.5	.56	3.5
0.04	7.15	2.7	.50	3.3
0.06	4.69	1.5	.19	9

TABLE B-V

ELECTRICAL PROPERTIES OF GROUP VB CHALCOGENIDES

Composition	100°C		600°C		
	S* (µv/deg)	ρ (mΩ-cm)	S* (µv/deg)	ρ (mΩ-cm)	S^2/ρ (µ/deg^2-cm)
NbSe	+2.7	5	-0.2	0.58	$6.9 \cdot 10^{-11}$
**$NbSe_2$	-1.4	0.50			
TaSe	+5.6	3.0	+13.6	3.2	$5.8 \cdot 10^{-8}$
$TaSe_2$	-6.9	8.5	- 9.6	9	$1.0 \cdot 10^{-8}$
NbTe	+4.7	4.8	+14.2	2.6	$7.8 \cdot 10^{-8}$
TaTe	-7.5	5.1	+14	2.7	$7.5 \cdot 10^{-8}$
$TaTe_2$	+17.5	5	+26	7	$9.7 \cdot 10^{-8}$

* Measured with chromel wire and corrected to absolute values. Positive values indicate p-type; negative, n-type.

** Reached maximum S^2/ρ at 150°C; $S = -6.9$ µv/deg; $\rho = 0.44$ mΩ-cm; $S^2/\rho = 1.08 \cdot 10^{-7}$ w/deg^2-cm.

Electrical Properties
of $W_{1-x}Ta_x$ Se Te at 600°C

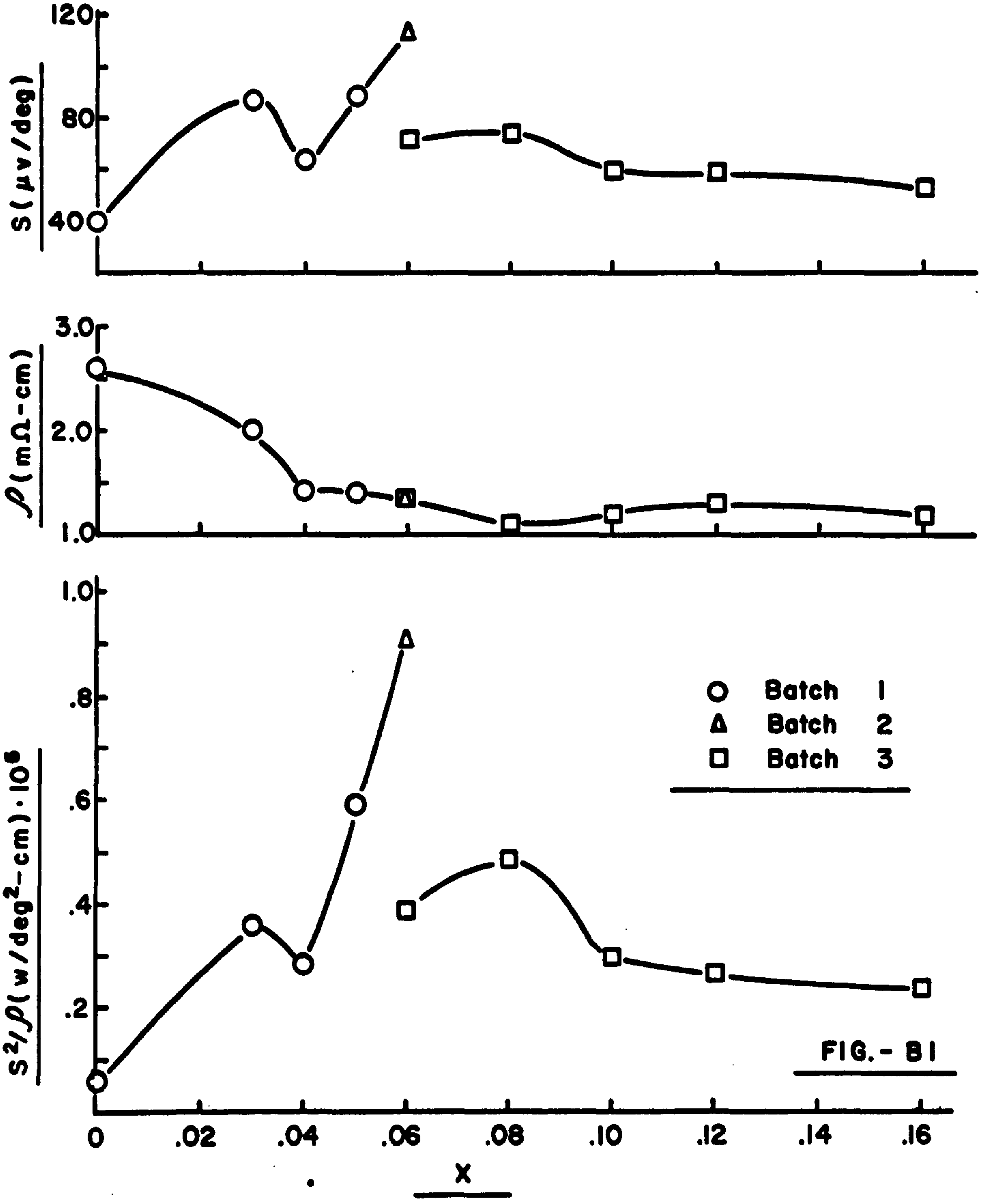
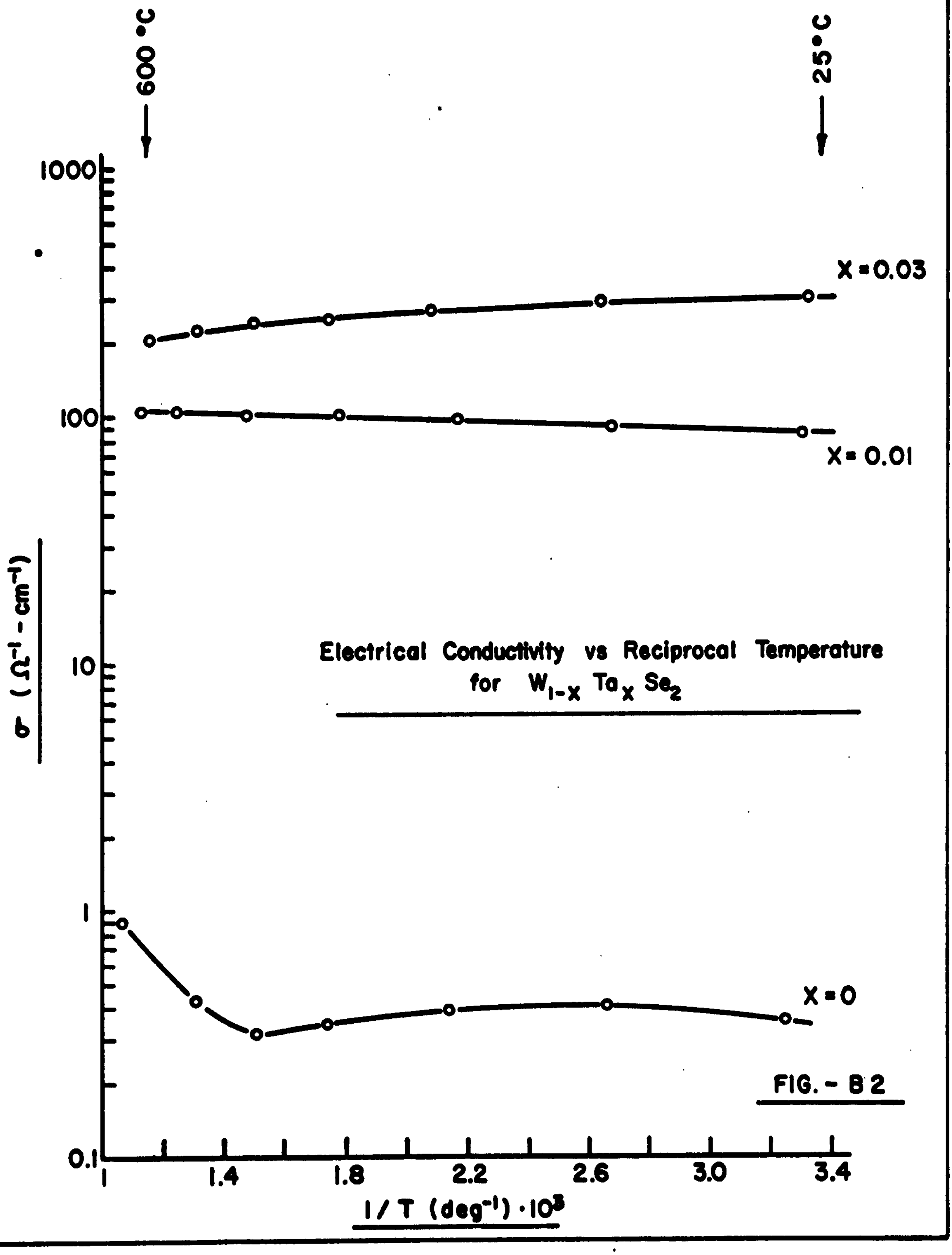
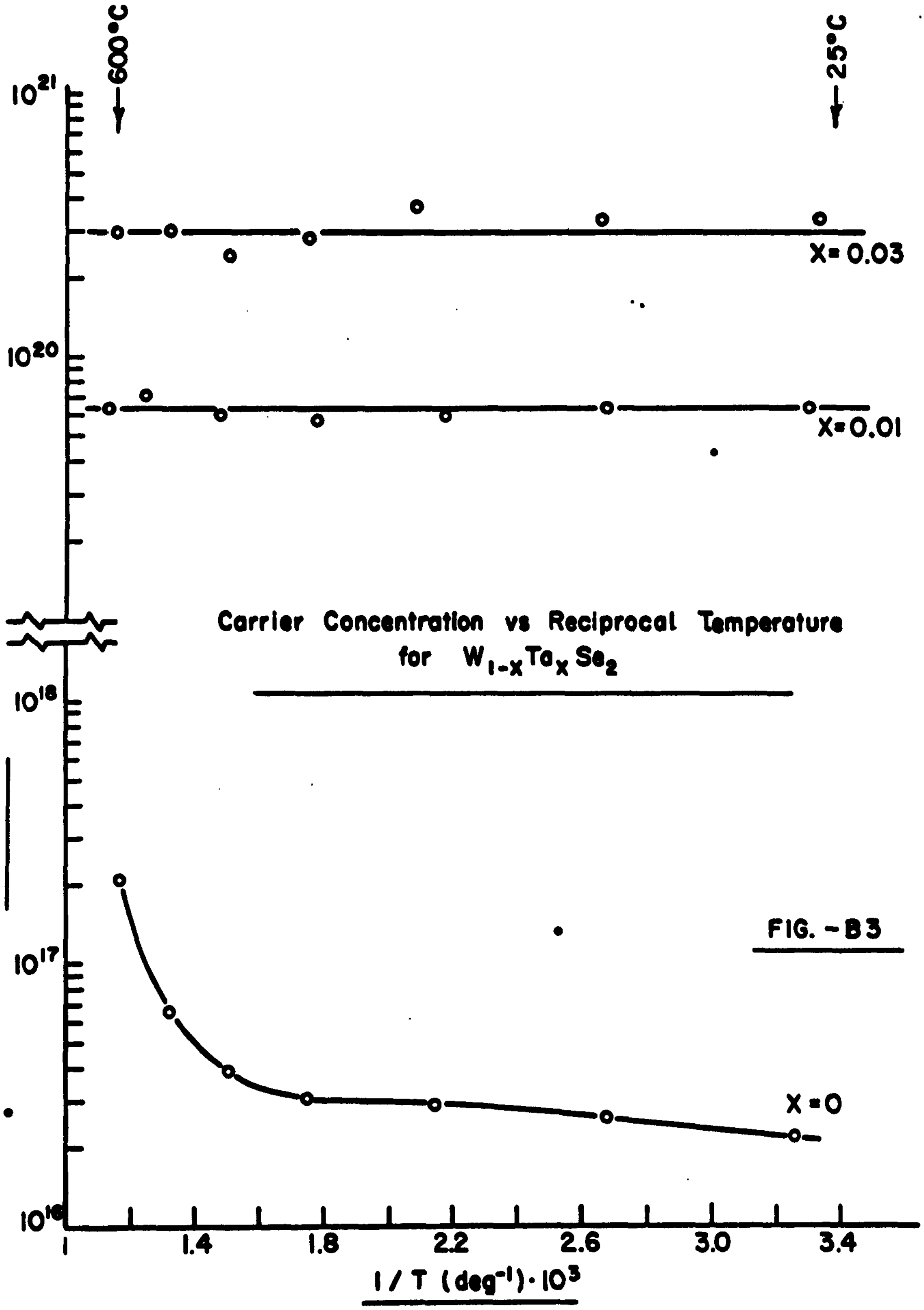


FIG. - B1



Electrical Conductivity vs Reciprocal Temperature
for $W_{1-x}Ta_xSe_2$

FIG. - B2



Carrier Concentration vs Reciprocal Temperature for $W_{1-x}Ta_xSe_2$

FIG. – B3

Carrier Mobility vs Absolute Temperature for $W_{1-x}Ta_xSe_2$

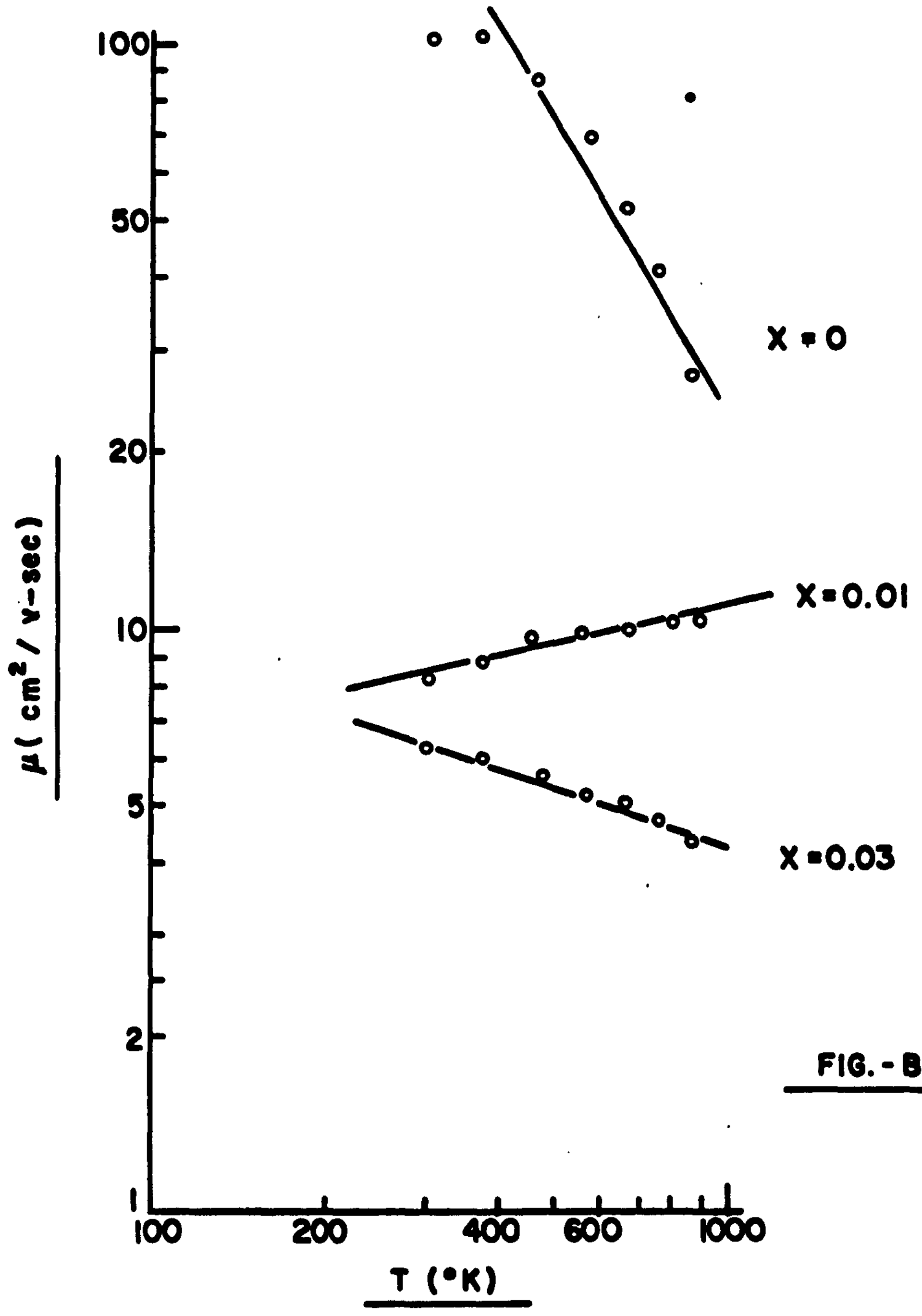


FIG. - B4

C. THERMOELECTRIC DEVICES - Herbert Valdsaar

Our primary effort of recent months has been devoted to testing components for a practical thermocouple design utilizing tantalum-doped tungsten diselenide. For high-temperature contacts, iron seems to be satisfactory. In the preliminary design, the negative half of the thermocouple will be composed of constantan (Advance) alloy.

General studies are directed toward fuller characterization of tungsten diselenide's behavior at high temperatures. A specific objective is to determine the physical conditions for melting the compound.

Standard Test Modules

The basic type of test module remained the alumina capsule with a nickel cap (6.4 mm I.D., 23 mm long) as described in the previous report. This small capsule was used for comparing different preparations of tungsten selenide at varied doping levels. It was found in separate tests that nickel severely corrodes when in contact with tungsten selenide at 1000°C. Therefore, a circular piece of 10 mil iron sheet was usually fitted into the capsule between the nickel cap and the tungsten selenide bar. A little iron powder was sprinkled around the edges at the bottom. The cold end of the capsule was sealed with lead-tin solder. See Figure C4.

The second type of test module incorporated constantan wire as the negative half of the thermocouple. An iron plug (solid bar or sintered powder) was placed between the tungsten selenide and the constantan wire. The arrangement was seated in a straight ceramic tube which was heated in the center. Practical problems arose with producing a reliable bond between iron and WSe_2 without the use of spring loading. It was found that a thin-walled iron tube adheres to the WSe_2 bar when heated to 900°C. The remaining section of the soft iron tube envelopes an iron plug, to which constantan wire is attached. The technique can further be improved by fitting together slanted end-surfaces and by addition of iron powder for sintered, large-area contacts. These refinements were not yet applied for Module #8, described in the following section.

Test Results

1. Composition Comparisons

The standard physical shape of the material was a 1/4" square bar pressed from tungsten selenide powder under 40 tsi at room temperature. The edges of the rectangular bar were shaved off so that a 2 cm long section could be fitted into the cylindrical cavity of the alumina capsule. As installed, the pressing direction of the bar was normal to the direction of the heat flow during testing.

The compositional range of practical interest lies between 1 and 2 atom percent tantalum in tungsten selenide. Two new preparations with 2.0 and 1.5% Ta were compared. One of these, the composition $W_{.985}Ta_{.015}Se_2$ rendered the highest power yield achieved so far. (See Table I and Figure 1 and 2.) Low contact resistance for the particular module certainly contributed much to the highest amperage reading.

2. Straight Tube Thermocouples

The purpose of the arrangement is to assess the potentialities WSe_2 in combination with other thermoelectric materials under actual operating conditions.

Particular attention is presently directed to the combination WSe_2-iron-constantan. The components are joined in a tube furnace under argon atmosphere. For testing, the device is inserted in a ceramic tube or a quartz envelope. The parts can also be assembled inside the ceramic tube and the hot junctions formed as the center of the tube is heated.

The latter technique was used for the construction of a thermocouple which consisted of a 5 cm long WSe_2 bar (cold-pressed under 40 tsi), and a 2.5 cm long iron screw to which was attached a double section of constantan wire (1 mm in diameter). Some iron powder was placed around the contacts in the center. The alumina tube, 5" long, 1/4" I.D., was closed at one end with a nickel cap; the other end was sealed with lead solder and a copper plate. The free space around the wire was filled with zirconia powder.

The material was $W_{.99}Ta_{.01}Se_2$, with a resistivity of 8.3 milliohm-cm. The calculated resistance for the full length of the bar was 140 milliohms, and for the constantan wire, 15 milliohms. Total measured resistance of the assembly fluctuated between 186-200 milliohms during testing. Thus, the contact resistances, including the iron center section, amounted to about 20% of the total.

With increasing temperature, the open voltage measured across the two cold ends increased almost linearly. See Figure C3.

After a 5-hour heating period, the thermocouple was cooled, then reheated the next day. The resistance had remained the same, but the voltage readings were lower. As the temperature interval increased, the voltage climbed to a maximum of 318 mV for ΔT = 1076°C, at a temperature reading of 1130°C in the hot zone. The thermocouple was located outside the alumina tube; the actual temperature inside the tube may have been considerably lower.

Upon cooling after the second heating period, the components evidently separated, because the resistance rose to a high value. The thermocouple section which housed the WSe_2

bar was cut from the rest and tested by itself (Module #9). This time the end with the nickel became the hot end. The module behaved in a regular manner, although it gave a somewhat lower voltage than it had contributed in the full thermocouple.

It is yet undetermined whether the decrease in the open circuit voltage upon repetition of the heating cycles was partly due to changes in the thermoelectric material, or resulted solely from mechanical changes in the assembly.

Stability of Tungsten Selenide at High Temperatures

Upon heating under atmospheric pressure tungsten selenide gradually decomposes by releasing selenium vapor. Some selenium evaporation becomes noticeable above 700°C, but even at 1000°C the selenium transfer is slow and compressed WSe_2 bars could be held at this temperature for hours under purified argon without appreciable degradation. Presence of oxygen effects a rapid oxidation of the compound below 500°C. Therefore, the main purpose of the material encapsulation is to exclude oxygen from the hot selenide.

Tungsten selenide powder sealed in a narrow quartz capillary was heated to 1400°C without external pressure. There was no change in the physical appearance of the powder.

A similar sample was subjected to 1000 atmospheres external pressure at approximately 1600°C (at which temperature quartz softens). A growth of the crystal surfaces evidently had taken place. Compare Figures 5, 6, 7.

Larger samples will be tested with the purpose of establishing the conditions for melting WSe_2 if it can be done in a practical manner. There is incentive to produce tungsten selenide from a molten phase, because at maximum density and with improved homogeneity the thermoelectric properties of the material might be enhanced.

TABLE C-I

Peak Performance of Materials with Varied Doping Levels*

Composition	$W_{.980}Ta_{.020}Se_2$	$W_{.985}Ta_{.015}Se_2$
Module No.	#10	#13
Resistivity, milliohm-cm	3.2	5.5
Temperature, °C		
Hot End	985	1025
Cold End	105	125
Difference	880	900
Open Circuit Voltage, mV	108	137
Closed Circuit Voltage, mV	52	72
Current, amperes	1.58	2.41
Power, milliwatts	82	173
Seebeck coefficient (average) microvolts/°C	121	152
Inner Resistance, milliohms	35**	30

* The materials were pressed under 40 tsi.

** The contact resistance for Module #10 was relatively high (about 30% of the total resistance). Therefore, the recorded amperage is lower than expected.

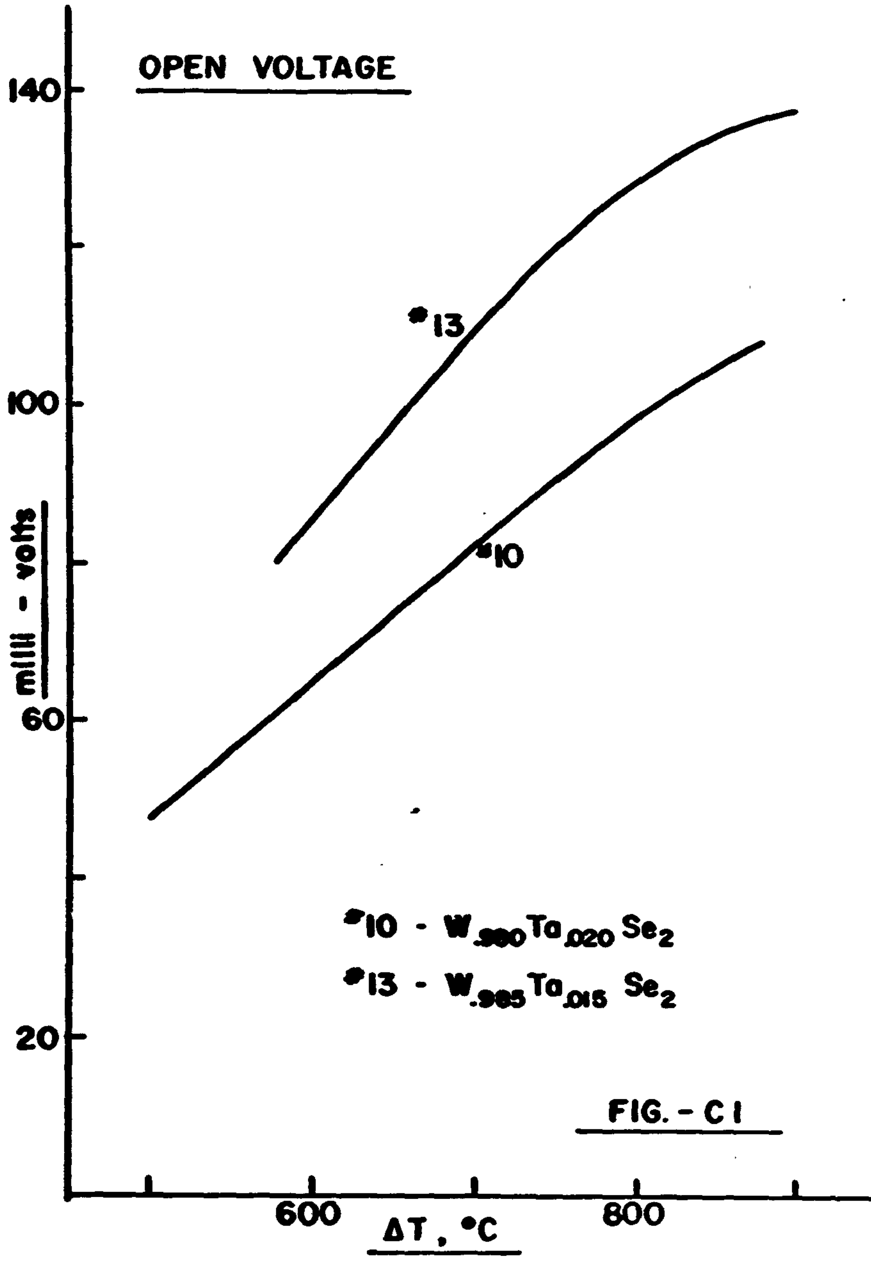

OPEN VOLTAGE
milli - volts
140
100
60
20
#13
#10
$\#10 - W_{.980}Ta_{.020}Se_2$
$\#13 - W_{.985}Ta_{.015}Se_2$
600
800
ΔT, °C

FIG. - C1

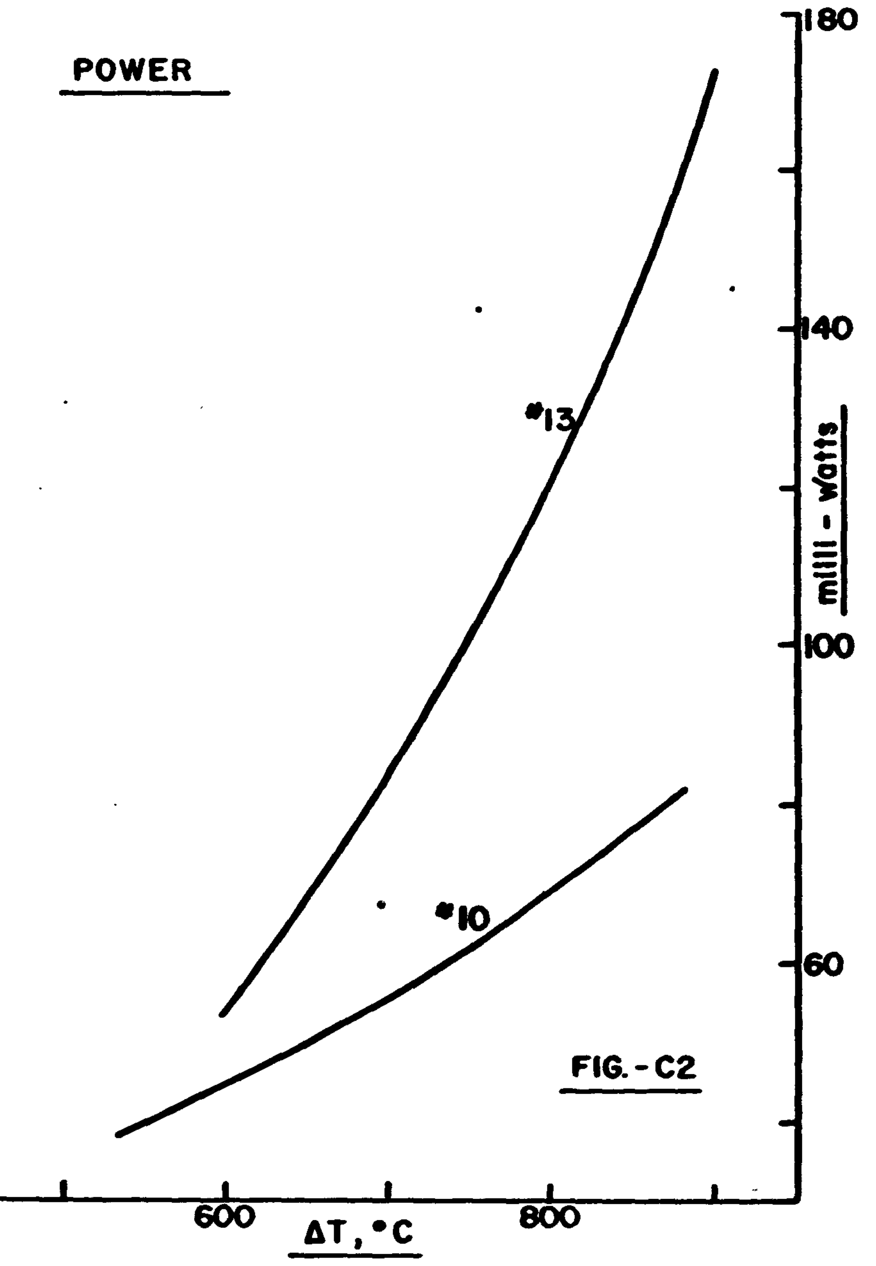

POWER
milli - watts
180
140
100
60
#13
#10
600
800
ΔT, °C

FIG. - C2

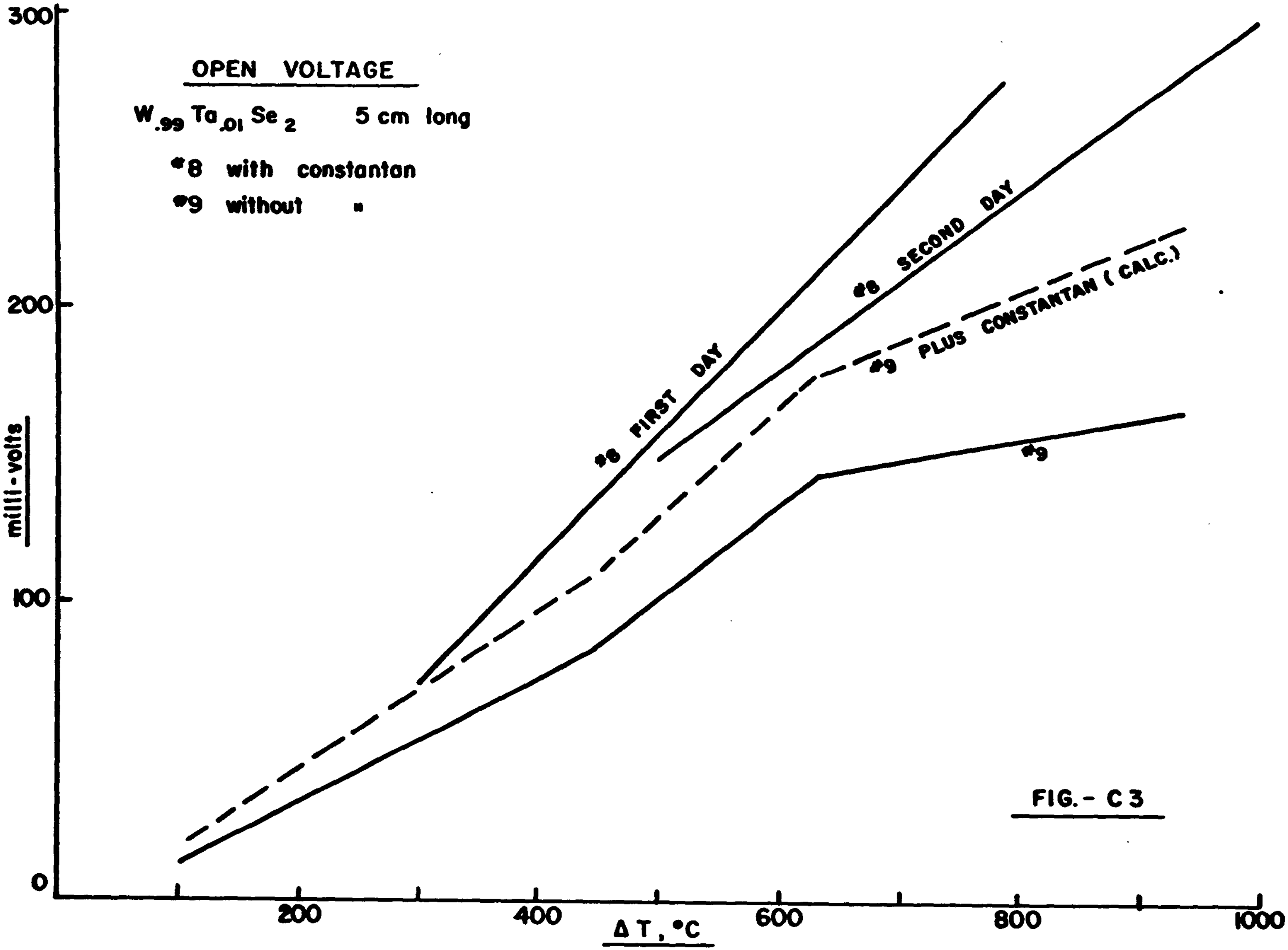

OPEN VOLTAGE
$W_{.99}Ta_{.01}Se_2$ 5 cm long
#8 with constantan
#9 without "
#8 FIRST DAY
#8 SECOND DAY
#9 PLUS CONSTANTAN (CALC.)
#9
milli-volts
0
100
200
300
200
400
600
800
1000
ΔT, °C

FIG.- C3

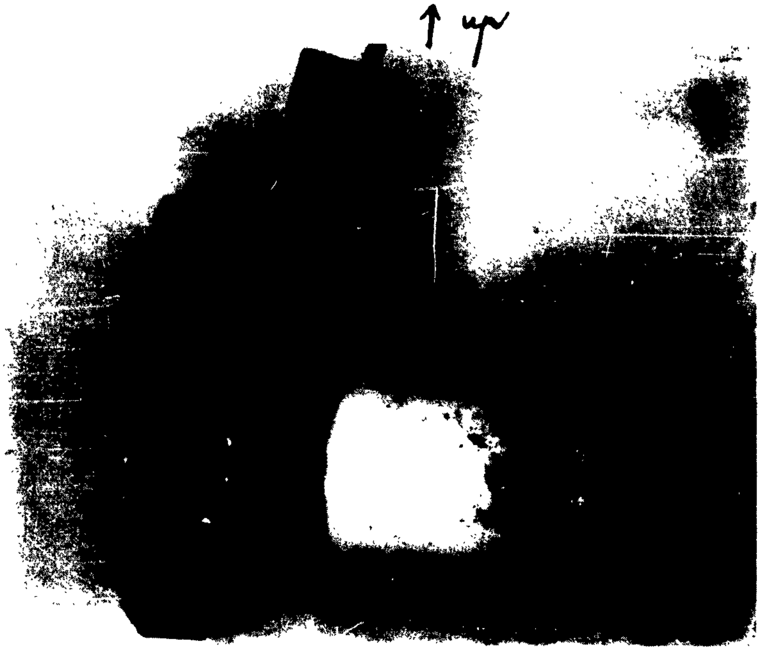


Figure - C4 - 3 X Magnification. Standard small alumina test capsule. Hot end (at left) with a heavy nickel plate, and cold end with solder in a copper collar.

Figure - C5 - 150 X Magnification. A group of WSe_2 flakes (bright areas) imbedded at random in Bakelite for a polished cross-section.

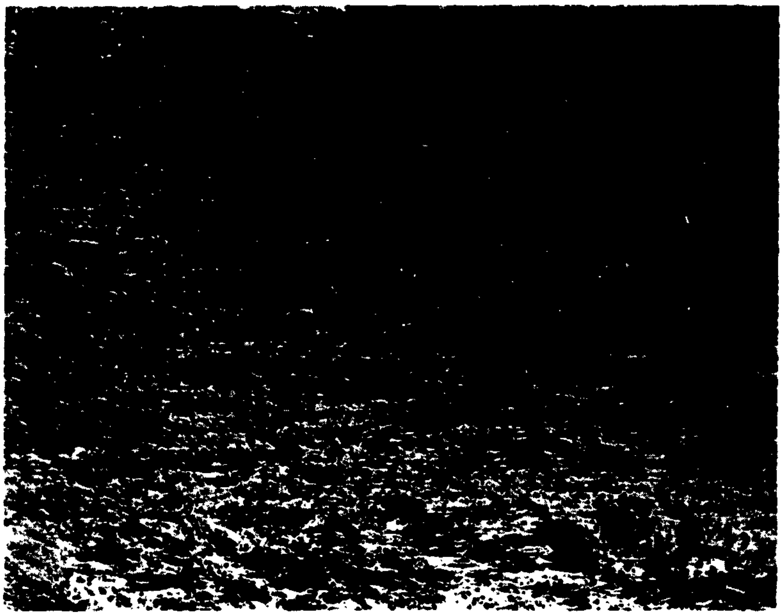


Figure - C6 - 150 X Magnification. Polished cross-section of a pressed WSe_2 bar (40 tsi), normal to the pressing direction.

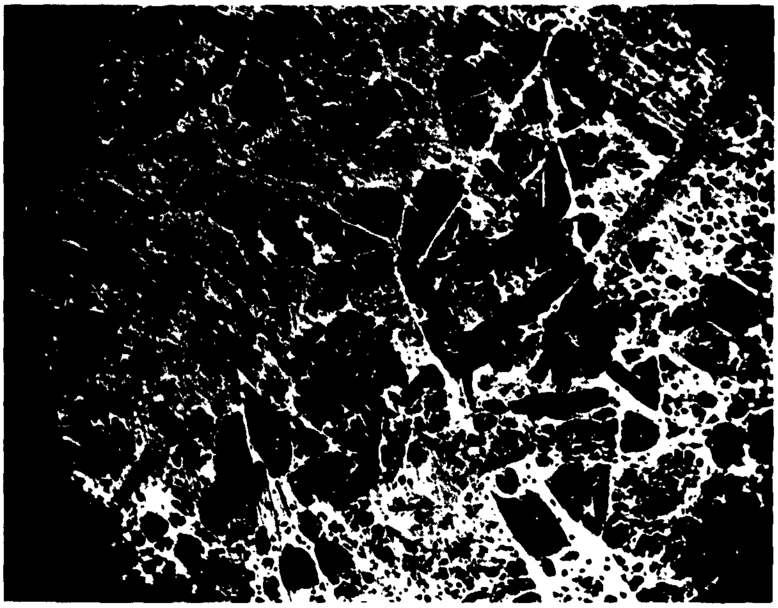


Figure - C7 - 150 X Magnification. Polished cross-section of WSe_2 powder in a quartz capillary, after heating to ∿1500°C under 1000°C.