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ISOTEC FINAL REPORT

by

**N. B. ELSNER, J. CHIN, G. H. REYNOLDS,
J. H. NORMAN, J. C. BASS, and H. G. STALEY**

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ABSTRACT

General Atomic (GA) developed processes to prepare $\text{NdSe}_{1.5-x}$. The partial pressure of Se_2 above the $\text{NdSe}_{1.5-x}$ was found to be a function of x . The thermoelectric properties and the friability of the hot pressed element were also a function of x . Process modification changed the value of x , providing a method to control the properties of N-type $\text{NdSe}_{1.5-x}$ elements. A method of joining $\text{NdSe}_{1.5-x}$ to a nickel hot cap was developed using a gold foil intermediate. $\text{NdSe}_{1.5-x}$ was diffusion-bonded to PbTe by the same process developed for Gd_2Se_3 . Couples were fabricated from $(\text{Cu,Ag})_2\text{Se}/\text{Fe}/(\text{Bi,Sb})_2\text{Te}_3$ and $\text{NdSe}_{1.5-x}\text{PbTe}$ elements. Limited couple test data were obtained.

General Atomic examined methods to develop high-efficiency couples made from segmented elements containing $(\text{Cu,Ag})_2\text{Se}$ P-type material and $\text{NdSe}_{1.5-x}$ N-type material. Techniques were developed to reproducibly prepare and hot press $(\text{Cu,Ag})_2\text{Se}$ segments and elements with a metallurgically joined MoRe hot cap. This hot cap and a W-26/Re wire mesh used to make the hot cap junction were found to be stable in contact with $(\text{Cu,Ag})_2\text{Se}$ at 750°C . Stability of $(\text{Cu,Ag})_2\text{Se}$ to current flow in a thermal gradient was examined. This report describes specifications for vapor suppression to improve the stability of P-type $(\text{Cu,Ag})_2\text{Se}$ in thermal gradient life tests and presents life test information on match-loaded $(\text{Cu,Ag})_2\text{Se}$ and $(\text{Cu,Ag})_2\text{Se}/\text{Fe}/(\text{Bi,Sb})_2\text{Te}_3$ elements.

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1. INTRODUCTION

General Atomic (GA) conducted a program to develop selenide thermoelectric materials to improve the performance and useful life of P-type $(\text{Cu,Ag})_2\text{Se}$ and N-type rare earth selenide thermoelectric materials for the Department of Energy (DOE).

The studies on $(\text{Cu,Ag})_2\text{Se}$ and rare earth selenide materials are generally intended to develop a high-temperature radioisotope thermoelectric generator (RTG) achieving efficiencies of $\geq 10\%$. These efficiencies could presumably be obtained with the GA design (radiation-coupled, many-parallel-circuit, 3.4-W/lb) or with designs pursued by other contractors.

The emphasis of the Isotec Technology Program shifted from the development of a Galileo generator to the study of a segmented selenide element and of couple technology. Originally, the program was to determine the feasibility of fabricating segmented selenide P and N elements which exploit the high thermoelectric efficiency of $(\text{Cu,Ag})_2\text{Se}$ and Gd_2Se_3 materials. A preliminary evaluation of segmented element efficiencies, material compatibilities, and fabrication abilities was used to select $(\text{Cu,Ag})_2\text{Se}/\text{Fe}/(\text{Bi,Sb})_2\text{Te}_3$ for the P element and $\text{Gd}_2\text{Se}_3/\text{PbTe}$ for the N element. An iron barrier between the $(\text{Cu,Ag})_2\text{Se}$ and $(\text{Bi,Sb})_2\text{Te}_3$ prevented thermoelectric properties from degrading due to copper contamination of the $(\text{Bi,Sb})_2\text{Te}_3$.

Processes for fabricating both elements were developed, but the $(\text{Cu,Ag})_2\text{Se}$ hot cap design needed improvement. Also, Gd_2Se_3 was friable and difficult to fabricate crack free. It exhibited a phase transition from cubic to orthorhombic at processing temperatures. The phase transition increased its susceptibility to microcracking and reduced its thermoelectric efficiency.

Life testing of an all-bonded couple with unsegmented $(\text{Cu,Ag})_2\text{Se}$ P-type and Gd_2Se_3 N-type elements was performed for 3300 h in a nominal $830^\circ/390^\circ\text{C}$ thermal gradient. The Gd_2Se_3 leg did not show any significant degradation during the test. Examination of the hot end of the P element showed the need for a less reactive hot cap material and an improved vapor suppression system. Thus, the general class of materials, the rare earth selenide N leg and $(\text{Cu,Ag})_2\text{Se}$ P-type leg, appears correct for a thermoelectric stability.

The phase transition which occurs in Gd_2Se_3 near its processing and operating temperature is not easily circumvented. The choices are either to process and operate at a lower temperature or to change the material. Since lowering the operating temperature would defeat the reason for selecting Gd_2Se_3 , other N-type selenide materials were investigated. One choice would be a mixed rare earth selenide which includes gadolinium. Another would be a rare earth selenide which has thermoelectric properties approaching that of Gd_2Se_3 but which is single phase at the processing and operating temperature.

Nd_2Se_3 meets these criteria. The goal of the FY 80-81 program was thus to continue evaluating $(\text{Cu,Ag})_2\text{Se}$ as the high-temperature segment of a P-type thermoelectric element and Nd_2Se_3 as the high-temperature segment of an N-type thermoelectric element. Together, these form a high-efficiency thermoelectric couple.

2. SEGMENTED P-TYPE ELEMENT STUDIES

In this reporting period, the study on the segmented P-type element was primarily directed toward $(\text{Cu,Ag})_2\text{Se}/\text{Fe}/(\text{Bi,Sb})_2\text{Te}_3$ in the configuration shown in Fig. 2-1. A fabrication sequence was developed in FY 79 which made mechanically strong segmented elements with a barrier of iron across the element to prevent copper from contaminating the $(\text{Bi,Sb})_2\text{Te}_3$ segment. These elements still had inconsistent thermoelectric properties. One goal of this effort was to find and correct the cause of these inconsistencies. Another was to examine methods to prevent elements from the hot cap from diffusing into the $(\text{Cu,Ag})_2\text{Se}$ segment. These efforts were part of a general evaluation of techniques to optimize the useful operating temperature and life of the segmented P-type element.

2.1. FABRICATION DEVELOPMENT OF SEGMENTED P-TYPE ELEMENTS

2.1.1. Hot Pressing Modification

Examination of segmented P-type elements prepared by processes developed in FY 79 showed copper contamination of the outer surface of $(\text{Bi,Sb})_2\text{Te}_3$ segments and the iron barrier. This contamination resulted primarily from worn dies containing copper inclusions. Thus, hot pressed segments of $(\text{Bi,Sb})_2\text{Te}_3$ had low Seebeck values when processed in these dies. Contamination occurred in both one- and two-step hot pressing of the segmented P element.

The following measures to overcome this copper were successful:

1. Worn die inserts were replaced with newly purchased tungsten-carbide (WC) inserts.
2. Dies used for hot pressing $(\text{Cu,Ag})_2\text{Se}$ were not used to hot press $(\text{Bi,Sb})_2\text{Te}_3$.
3. $(\text{Cu,Ag})_2\text{Se}$ segments placed in dies during the $(\text{Bi,Sb})_2\text{Te}_3$ hot pressing were given a thorough precleaning to remove residual surface copper.

Thus, the key change in the fabrication sequence shown in Fig. 2-2 is that a different die is used to hot press the $(\text{Bi,Sb})_2\text{Te}_3$ segment than is used to hot press the $(\text{Cu,Ag})_2\text{Se}$ segment. This eliminated contamination of the $(\text{Bi,Sb})_2\text{Te}_3$ segment during fabrication of the element. Section 2.2.2 gives the results of test evaluations of this concept.

Fig. 2-1. Segmented P element $(\text{Cu, Ag})_2\text{Se}/(\text{Bi, Sb})_2\text{Te}_3$

Fig. 2-2. Fabrication sequence for the preparation of $(\text{Cu,Ag})_2\text{Se}/(\text{Bi,Sb})_2\text{Te}_3$ segmented elements

2.1.2. Mo-Re Hot Caps

All gradient life tests of stainless-steel hot caps showed a corrosive reaction between the stainless steel and $(\text{Cu,Ag})_2\text{Se}$. This generally resulted in the transport of iron, chromium, and nickel down the thermal gradient. Molybdenum, tungsten, and rhenium coatings were used to coat the stainless steel to prevent these elements from diffusing. Even when the coating appeared impermeable, as the magnified view seen in Fig. 2-3 shows, the diffusion of iron, chromium, and nickel was slowed but not prevented. Table 2-1 summarizes the experimental findings on the thin film barrier coatings. Thin foil metal inserts were tried, as shown in Fig. 2-4, between the $(\text{Cu,Ag})_2\text{Se}$ and the stainless-steel cap. The foil barriers were difficult to fabricate, and stainless-steel-to- $(\text{Cu,Ag})_2\text{Se}$ contact around the element edges could not be prevented. The investigators then decided to use a refractory metal hot cap. Tungsten and molybdenum caps were avoided because of joining difficulties to collectors and interelement current straps. Molybdenum-rhenium alloys were chosen as the hot cap materials. The first Mo-47/Re hot caps for P-type selenide elements were made from Teledyne-supplied 254- μm (10-mil) thick Mo-47/Re sheet stock dimpled to accommodate the GA mesh-bonded cap concept. The wire mesh used for this joint was made from W-26/Re 0.76-cm (0.003-in.) wire. Tack welding the W-26/Re wire to the Mo-47/Re cap was more difficult than tack welding it to stainless steel, but the joints were adequate. Figure 2-5 shows the Mo-47/Re foil hot cap on a doubly segmented $(\text{Cu,Ag})_2\text{Se}/\text{Fe}/(\text{Bi,Sb})_2\text{Te}_3$ element.

2.1.3. Hot Cap to $(\text{Cu,Ag})_2\text{Se}_3$ Joint

Hot-cap-to-element joints in both the P and N elements have been revised. This effort was intended to minimize wires external to the hot cap which form channels for vaporization. The wires on the bottom side of the hot cap were originally intended to help hold the bonded vapor suppression glass sleeve. In the newer vapor suppression concept, a locking metal washer holds the vapor suppression sleeve; thus, the external wires are no longer needed.

The W-26 wires were diffusion-bonded to the Mo-50/Re hot cap, as shown in Fig. 2-6. Overhang wires were folded inward to increase the wire-element contact area. Diffusion bonding of the wires was successfully accomplished (Fig. 2-7). An as-fabricated element made with the diffusion-bonded wire mesh was mounted and polished. The mount showed the wires to be encapsulated in the $(\text{Cu,Ag})_2\text{Se}$ material where the wires were not touching the hot cap surface. The diffusion and hot pressing steps collapsed most of the space between the wire mesh and hot cap surface. Figure 2-8 schematically shows several other configurations examined of the joint between the wire mesh and the hot cap.

Configuration 1A was used in the first segmented couples. Resistivity values of the first P element of the first couple became cyclic then erratic after 190 test hours. Element examination after 400 test hours showed joint loss between the mesh and $(\text{Cu,Ag})_2\text{Se}$. This loss was attributed to a loss of copper in $(\text{Cu,Ag})_2\text{Se}$ due to current flow, Se_2 loss, and differential expansion between the N and P legs of the couple. Configurations 1B and

Fig. 2-3. Scanning electron photomicrograph of the ion-plated rhenium coating, run 8029-65, on 316 stainless steel

TABLE 2-1
EFFECTIVENESS OF THIN FILM COATINGS ON STAINLESS
STEEL TO PREVENT CORROSIVE REACTION BETWEEN
STAINLESS STEEL HOT CAPS AND (Cu,Ag)₂Se

Coating	Effect
Molybdenum	Will not react with (Cu,Ag) ₂ Se directly but showed a strong reaction in the presence of chromium
Tungsten	Nonreactive with (Cu,Ag) ₂ Se, but microcracks allow coatings to be breached and eventually lost
Rhenium	No reaction with (Cu,Ag) ₂ Se evident, more ductile than tungsten and less likely to form microcracks, but did not prevent the reaction between the stainless steel cap and (Cu,Ag) ₂ Se

Fig. 2-4. Nickel hot cap/tungsten foil/(Cu, Ag)₂Se (sample 6875-110-24) after 172 h at 750°C

Fig. 2-5. Macro view of a $(\text{Cu,Ag})_2\text{Se}/(\text{Bi,Sb})_2\text{Te}_3$ segmented element with a Mo-47/Re hot cap

Fig. 2-6. Diffusion-bonded W-26/Re mesh in a Mo-50/Re cap as fabricated (7958-83-1)

Fig. 2-7. Diffusion-bonded W-26/Re mesh in a Mo-50/Re cap with wire ends folded inward ready for element hot pressing (7958-83-1)

Fig. 2-8. Hot cap to $(\text{Cu,Ag})_2\text{Se}$ joint configurations

1C accommodate the differential thermal expansion of hot cap and element materials better than configuration 1A. Configuration 1B is the joint used in element test 8236-3-13 which had 6356 h at 755°C at an iL/A of 7.4 through the $(\text{Cu,Ag})_2\text{Se}$ segment before it was removed from testing. This element was made by hot pressing the element with the wire embedded in it, then tack welding the wire to the 2.54-cm (0.010-in.) thick Mo-47/Re hot cap.

A modification of configuration 1C is recommended for future $(\text{Cu,Ag})_2\text{Se}$ metallurgical joints for thermoelectric P-type elements. The wire mesh is encapsulated in the element first during hot pressing, as shown in Fig. 2-9. It is then removed from the hot press (Fig. 2-10) and tack-welded to the machined hot cap.

2.1.4. Vapor Suppression

The GA concept for vapor suppression has evolved into a multibarrier system schematically shown in Fig. 2-11 and summarized in Table 2-2. The baffling factors quoted for the Nd_2O_3 and Pyrex coating were experimentally determined. Baffling factors for the vapor suppression sleeve are theoretical estimates made earlier in this program. Baffling factors for the molybdenum-opacified quartz insulation came from experimental examination of the same materials and designs used in other programs to develop thermoelectric materials.

Figures 2-12 through 2-14 show three P-type segmented element designs evaluated for the hot cap joint and locking vapor suppression sleeve inclusion. Electrical contact was lost in the configuration in Fig. 2-12 in less than 200 h at temperature in a thermal gradient with current flowing. Metallographic examinations showed gaps between the $(\text{Cu,Ag})_2\text{Se}$ and the wire mesh. The gap is caused by the rigid configuration of the compressed and diffusion-bonded wire mesh. The rigidity of the configuration could not accommodate differential thermal expansions between the hot cap and $(\text{Cu,Ag})_2\text{Se}$ materials.

The wire mesh configurations shown in Figs. 2-13 and 2-14 accommodate differential thermal expansions between the hot cap and $(\text{Cu,Ag})_2\text{Se}$ materials, as life tests have shown. Since the configuration in Fig. 2-13 was much more difficult to fabricate, it was abandoned in favor of that shown in Fig. 2-14. Figure 2-14 also shows the element in its normal configuration in a test thermoelectric couple.

Quartz was chosen as the vapor suppression sleeve material for these elements. Design optimization studies are needed to determine the sleeve dimensions for each material selected for this application. This optimization is necessary to maximize the vapor suppression but to minimize heat transfer and element efficiency loss. Since these analyses were not within the scope of this program, the sleeve dimensions were arbitrarily selected.

Fig. 2-9. Pushing the bottom die off the element

Fig. 2-10. Pressing element out of upper die

Fig. 2-11. Schematic diagram of a segmented $(\text{Cu,Ag})_2\text{Se}/(\text{Bi,Sb})_2\text{Te}_3$ element showing the vapor suppression sleeve, coating, and insulation with their effective baffling factors

TABLE 2-2
VAPOR SUPPRESSION SUMMARY

Coatings on (Cu,Ag)₂Se

Glass plus Pr₂O₃ or Nd₂O₃, ion plated, baffling factor > 10

Cr_xO_y, baffling factor > 20 promising coating

Vapor suppression sleeve

Glass bonded to hot cap through mesh interface, baffling factor > 50

SiO₂ sleeve held in place with a welded metal collar, baffling factor > 50

Element insulation

Molybdenum-opacified quartz paper washers, baffling factor of 50, presently used on all elements

Fig. 2-12. Schematic diagram of a segmented P element with the W-26/Re wire mesh tack-welded to the center of a one-piece Mo-Re hot cap

Fig. 2-13. Schematic diagram of a segmented P element with the W-26/Re wire mesh tack-welded to the edge of a one-piece Mo-Re hot cap

Fig. 2-14. Schematic diagram of a segmented P element with W-26/Re wire mesh tack-welded to the edge of a two-piece rhenium hot cap

2.2. EVALUATION OF SEGMENTED P-TYPE ELEMENTS

2.2.1. Isothermal Testing

Table 2-3 summarizes the results of measurements of Seebeck coefficients before and after isothermal compatibility tests of different doubly segmented elements. Microprobe examination of specimen 6875-102-1, Fig. 2-15, and other probe examinations show the following:

1. The sharp boundary between $(\text{Cu,Ag})_2\text{Se}$ and PbSnMnTe-3P no longer exists. In its place are two new phases between these segments.
2. A PbSnMnSe phase has formed in the selenide segment boundary.
3. A $(\text{Cu,Ag})_2\text{Te}$ phase has formed in the telluride segment boundary.

In spite of the phase formations, the Seebeck coefficients for the total element show a slight increase after 400 h at 470°C . The slight decrease in Seebeck coefficients after 1470 h clearly indicates that more testing is needed before definitive answers can be obtained about the stability of the $(\text{Cu,Ag})_2\text{Se}/\text{PbSnMnTe}$ segment combination.

The 275°C , 748-h, isothermal tests of the $(\text{Cu,Ag})_2\text{Se}/(\text{Bi,Sb})_2\text{Te}_3$ segmented element show no time-dependent degradation mechanism for the $(\text{Bi,Sb})_2\text{Te}_3$ segment. The overall Seebeck coefficients for these early specimens were so low to begin with that the $(\text{Bi,Sb})_2\text{Te}_3$ segment was probably saturated with copper during element fabrication.

2.2.2. Zero-Current Thermal Gradient Testing

The objectives of zero-current thermal gradient tests were to (1) compare bonded segmented elements with unbonded but stacked segments, (2) compare segmented elements hot pressed sequentially in two different dies with those hot pressed in the same die, and (3) identify chemical potential influences on element stability.

2.2.2.1. $(\text{Cu,Ag})_2\text{Se}$ and $(\text{Bi,Sb})_2\text{Te}_3$ Segments Hot Pressed in the Same Die. Two elements, 6875-132-12 and 6875-132-35, with $(\text{Cu,Ag})_2\text{Se}$ and $(\text{Bi,Sb})_2\text{Te}_3$ segments fabricated in the same die were tested in a thermal gradient. Sample 6875-132-35 had an ion-plated molybdenum coating on the bottom of the stainless-steel cap to inhibit elements from the cap from diffusing through the $(\text{Cu,Ag})_2\text{Se}$ and accumulating at the iron barrier. Sample 6875-132-12 contained no molybdenum barrier coating. These elements were sequentially hot pressed as follows:

1. The $(\text{Cu,Ag})_2\text{Se}$ plus iron segment was hot pressed at 600°C and 138 MPa (20,000 psi), then postannealed at 800°C for 1 h. Stainless-steel hot caps with molybdenum wire mesh were used.
2. The hot pressed $(\text{Cu,Ag})_2\text{Se}/\text{Fe}$ segment was removed from the die, and the end was squared off to make a sharp, uniform $\text{Fe}/(\text{Bi,Sb})_2\text{Te}_3$ interface.
3. The $(\text{Cu,Ag})_2\text{Se}/\text{Fe}$ segment was reinstalled in the die, $(\text{Bi,Sb})_2\text{Te}_3$ powder was added, and the second hot pressing was made at 450°C and 138 MPa (20,000 psi) in vacuo.

TABLE 2-3
SEGMENTED P-ELEMENT ISOTHERMAL COMPATIBILITY
TEST SUMMARY, STABILITY OF SEEBECK COEFFICIENTS

Specimen No.	Upper Segment	Barrier	Lower Segment	Test Temperature (°C)	Total Test (h)	Seebeck Coefficient, α ($\mu\text{V}/^\circ\text{C}$)	
						Start	End of Test
6875-85-2	(Cu,Ag) ₂ Se	Iron	PbSnMnTe-3P	470	330	162	153
6875-85-4	(Cu,Ag) ₂ Se	Iron	PbSnMnTe-3P	470	145	159	146
6875-85-1	(Cu,Ag) ₂ Se	Iron	PbSnMnTe-3P	470	628	166	154
6875-85-3	(Cu,Ag) ₂ Se	Iron	PbSnMnTe-3P	470	318	155	154
6875-102-1	(Cu,Ag) ₂ Se	None	PbSnMnTe-3P	470	400	118	142
6875-102-2	(Cu,Ag) ₂ Se	None	PbSnMnTe-3P	470	662	110	132
6875-102-3	(Cu,Ag) ₂ Se	Iron	PbSnMnTe-3P	470	304	167	155
6875-102-4	(Cu,Ag) ₂ Se	Iron	PbSnMnTe-3P	470	304	171	161
6875-102-2	(Cu,Ag) ₂ Se	None	PbSnMnTe-3P	465	1407	110	90
6875-110-11	(Cu,Ag) ₂ Se	Hot-side graded zone/Iron	PbSnMnTe-3P	465	745	213	201
6875-110-16	(Cu,Ag) ₂ Se	Hot-side graded zone/Iron/ Cold-side graded zone	PbSnMnTe-3P	465	745	210	202
6875-112-31	(Cu,Ag) ₂ Se + 5% Nd ₂ O ₃	None	PbSnMnTe-3P	465	745	73	57
6875-112-36	(Cu,Ag) ₂ Se + 5% Pr ₂ O ₃	None	PbSnMnTe-3P	465	745	92	56
6875-112-11	(Cu,Ag) ₂ Se + 5% Mo	None	PbSnMnTe-3P	465	745	58	55
6875-110-36	(Cu,Ag) ₂ Se	None	(Bi,Sb) ₂ Te ₃	275	748	61	61
6875-118-8	(Cu,Ag) ₂ Se	None	(Bi,Sb) ₂ Te ₃	275	748	57	58
6875-118-11	(Cu,Ag) ₂ Se	None	(Bi,Sb) ₂ Te ₃	275	748	63	61
6875-118-12	(Cu,Ag) ₂ Se	Hot-side graded zone/Iron/ Cold-side graded zone	(Bi,Sb) ₂ Te ₃	275	748	198	198

Fig. 2-15. Microprobe scan of double segmented P element specimen 6875-102-1 after a 400-h, 475°C isothermal heat treatment

Cold caps were added to the elements, and thermocouples were attached for thermal gradient testing. Figure 2-16 shows sample 6875-132-12, removed from testing after 64 h at temperature. With no barrier between the stainless-steel cap and $(\text{Cu,Ag})_2\text{Se}$, the cap elements transported and accumulated above the iron barrier (note the metal collar around the middle of the sample). Figures 2-17 and 2-18 show the data for the first 350 test hours of sample 6875-132-35. The $(\text{Bi,Sb})_2\text{Te}_3$ segment was evidently contaminated with copper during hot pressing, and its thermoelectric properties did not change significantly after that. Thermocouples were tack-welded to the iron barrier between the $(\text{Cu,Ag})_2\text{Se}$ and $(\text{Bi,Sb})_2\text{Te}_3$ segments of sample 6875-132-35. This allowed each segment and the overall element performance to be monitored. The middle thermocouple was lost as were the data on the lower segment. Figures 2-19 and 2-20 show the overall stability of the Seebeck coefficient and resistivity of segmented element 6875-132-35. The result shows only small changes in the thermoelectric properties during the hot-cap temperature (T_H) = $754^\circ\text{C} \pm 5^\circ\text{C}$ and cold-cap temperature (T_C) = $107^\circ\text{C} \pm 8^\circ\text{C}$, 2490-h test. These early test samples were originally intended to evaluate the fabrication process and thus had no vapor suppression coating or sleeves. They were, therefore, expected to show copper movement and accelerated degradation. This was not the case. Without current flow, the segmented $(\text{Cu,Ag})_2\text{Se}/\text{Fe}/(\text{Bi,Sb})_2\text{Te}_3$ element was reasonably stable. The overall stability of the thermoelectric properties of the element keeps it on test longer than was originally intended. Post-test examinations showed significantly fewer changes in the appearance of the $(\text{Cu,Ag})_2\text{Se}$ segment than those described in the similarly tested unbonded P element without a barrier coating on the hot cap. The molybdenum cap barrier, however, was breached, and corrosion at this interface had begun.

The movement of copper was stopped at the iron barrier. The $(\text{Cu,Ag})_2\text{Se}/\text{Fe}$ joint did not degrade, and copper did not tend to transport through or around the iron barrier. The rather modest changes in Seebeck coefficient and resistivity did not reflect the appearance changes in the molybdenum mesh or the $(\text{Cu,Ag})_2\text{Se}$ segment. Microprobe examinations, schematically summarized in Fig. 2-21, show a $\text{Mo}_x\text{Cu}_y\text{Se}$ compound formed around the molybdenum wire. This reactivity of the $(\text{Cu,Ag})_2\text{Se}$ with molybdenum is thought to be catalyzed by nickel or chromium coming from the hot cap. In previous compatibility tests between slabs of $(\text{Cu,Ag})_2\text{Se}$ and molybdenum without stainless steel, microprobes did not observe that any reaction occurred between these materials even when held in contact at 900°C . The occurrence of the nickel, chromium, and iron in islands above the segment interface shows that the molybdenum-coated 316 stainless steel did not prevent nickel, chromium, and iron from diffusing in this test.

2.2.2.2. $(\text{Cu,Ag})_2\text{Se}$ and $(\text{Bi,Sb})_2\text{Te}_3$ Segments Hot Pressed in Different Dies. A third doubly segmented P element, 6875-141-1, was thermal gradient tested with zero-current flow. The element composition was identical to 6875-132-35; the elements differed in the processing sequence. Element 6875-141-1 was hot pressed with two different dies, one for each segment, to avoid copper contamination of the $(\text{Bi,Sb})_2\text{Te}_3$ segment.

Figures 2-22 and 2-23 show zero-current, life-test, Seebeck coefficient and resistivity values for this element. The thermal gradient across the $(\text{Cu,Ag})_2\text{Se}$ segment was $T_H = 752^\circ\text{C} \pm 10^\circ\text{C}$ and $T_C = 190^\circ\text{C} \pm 5^\circ\text{C}$. The thermal gradient across the $(\text{Bi,Sb})_2\text{Te}_3$ segment was $T_H = 190^\circ\text{C} \pm 5^\circ\text{C}$ and $T_C = 47^\circ\text{C} \pm 5^\circ\text{C}$. After 1100 test hours, Seebeck coefficient and resistivity values began to change radically. The element was removed

Fig. 2-16. Macrophoto of doubly segmented P-type element 6875-132-12 after 64 h in a $T_{11} = 755^{\circ}\text{C}$, $T_c = 133^{\circ}\text{C}$ zero-current thermal gradient test

Fig. 2-17. Seebeck coefficients of segmented P-type element 6875-132-35 during zero-current thermal gradient compatibility testing

Fig. 2-18. Resistivity values of segmented P-type element 6875-132-35 during zero-current thermal gradient compatibility testing

Fig. 2-19. Seebeck coefficients of P-type element 6875-132-35 containing $(\text{Cu}, \text{Ag})_2\text{Se}/\text{Fe}/(\text{Bi}, \text{Sb})_2\text{Te}_3$ segments sequentially hot-pressed zero-current, $754^\circ\text{C}/107^\circ\text{C}$, thermal gradient testing

Fig. 2-20. Resistivity values of P-type element 6875-132-35 containing $(\text{Cu}, \text{Ag})_2\text{Se}/\text{Fe}/(\text{Bi}, \text{Sb})_2\text{Te}_3$ segments sequentially hot-pressed zero-current, $754^\circ\text{C}/107^\circ\text{C}$, thermal gradient testing

Fig. 2-21. Microprobe examination of doubly segmented P element 6875-132-35 after 2490 h in a $754^\circ\text{C}/107^\circ\text{C}$ thermal gradient

Fig. 2-22. Seebeck coefficients of P-type element 6875-141 containing $(\text{Cu, Ag})_2\text{Se}/\text{Fe}/(\text{Bi, Sb})_2\text{Te}_3$ segments sequentially hot pressed in separate dies during zero-current, $752^\circ\text{C}/190^\circ\text{C}/47^\circ\text{C}$, thermal gradient testing

Fig. 2-23. Resistivity values of P-type element 6875-141 containing $(Cu, Ag)_2Se/Fe/(Bi, Sb)_2Te_3$ segments sequentially hot pressed in separate dies during zero-current, $752^\circ C/190^\circ C/47^\circ C$, thermal gradient testing

from test and examined. A vapor-deposited copper coating could be seen over most of the element (Fig. 2-24). A bulge was also noted above the iron barrier. The copper coating was due to vaporization of a copper shim placed between the hot cap and specimen heater to maximize heat transfer to the hot cap. The copper coating was grit-blast-removed, electrodes and thermocouples were reattached to the element, and the element was re-mounted in the test stand. Seebeck coefficient and resistivity values after reheating show that the apparent element degradation was an artifact due to the vapor-deposited copper coating. Encouragingly, the $(\text{Bi,Sb})_2\text{Te}_3$ segment did not degrade when in direct contact with copper on its surface. The operating temperatures of the $(\text{Bi,Sb})_2\text{Te}_3$ segment were apparently low enough to make the reaction between $(\text{Bi,Sb})_2\text{Te}_3$ and copper very sluggish. Seebeck coefficient and resistivity values of this element were stable after the 1100-h test interruption. No degradation of the $(\text{Bi,Sb})_2\text{Te}_3$ segment from copper contamination is evident.

The sample was removed from the thermal gradient test after 2717 h. Metallographic examination of this sample was essentially the same as 6875-132-35. The sample interacted corrosively with the hot cap. The molybdenum wire mesh was still encapsulated in the $(\text{Cu,Ag})_2\text{Se}$ with the same formation of a MoCrCu compound in an intermediate layer between the wire and P-type element. Chromium, copper, nickel, and iron diffused as on all the stainless-steel hot cap samples tested. No copper bypassed the barrier. This was verified by the stable Seebeck coefficient of the $(\text{Bi,Sb})_2\text{Te}_3$ layer. This test showed that the $(\text{Bi,Sb})_2\text{Te}_3$ layer in sample 6875-132-35 was degraded because the same die was used to hot press both segments. As long as separate dies are used, contamination of the $(\text{Bi,Sb})_2\text{Te}_3$ with copper can be prevented.

2.2.2.3. $(\text{Cu,Ag})_2\text{Se}$ and $(\text{Bi,Sb})_2\text{Te}_3$ Segments Behavior in Contact but Unbonded. A fourth zero-current thermal gradient test (6875-139-3) was conducted containing $(\text{Cu,Ag})_2\text{Se}/\text{Fe}$ and $(\text{Bi,Sb})_2\text{Te}_3/\text{Fe}$ segments. The $(\text{Cu,Ag})_2\text{Se}/\text{Fe}$ segment was bonded to a hot cap through a mesh bond. The $(\text{Bi,Sb})_2\text{Te}_3/\text{Fe}$ was soldered to a cold cap on the iron side of the segment. Thermocouples were attached to the hot cap, the cold cap, and the iron of the $(\text{Cu,Ag})_2\text{Se}$ segment. The thermal gradient across the $(\text{Cu,Ag})_2\text{Se}$ segment was $T_H = 752^\circ\text{C} \pm 4^\circ\text{C}$ and $T_C = 300^\circ\text{C} \pm 22^\circ\text{C}$. The thermal gradient across the $(\text{Bi,Sb})_2\text{Te}_3$ segment was $T_H = 300^\circ\text{C} \pm 22^\circ\text{C}$ and $T_C = 118^\circ\text{C} \pm 12^\circ\text{C}$. Figures 2-25 and 2-26 show Seebeck coefficients and resistivities as a function of test time for these segments. The sample was held in place by a weighted heater block which put a 2.5 MPa (363 psi) load on the element.

The upper and lower segments of the element were still unbonded at the end of the 1492-h test. Two gross features were noticed from the sample after removal from the test: A prominent bulge developed in the $(\text{Cu,Ag})_2\text{Se}$ segment above the iron layer, and the $(\text{Cu,Ag})_2\text{Se}$ corrosively reacted with the stainless-steel hot cap. Metallographic examination of a cross section of this element (Fig. 2-27) shows a necked down zone above the bulge from microprobe examinations (Fig. 2-28). This was thought to result from metal transport down the thermal gradient in the $(\text{Cu,Ag})_2\text{Se}$ segment. The stainless-steel cap was not protected against reaction with the $(\text{Cu,Ag})_2\text{Se}$. The weighted hot cap continued to react with the $(\text{Cu,Ag})_2\text{Se}$ segment. Material was continually transported down this segment to the iron barrier. This created the bulge and cut a hole through the hot cap.

Fig. 2-24. Segmented P-type element 6875-141-1 removed from test after 1100 test hours for visual examination

Fig. 2-25. Seebeck coefficients of P-type $(\text{Cu, Ag})_2\text{Se}$ and $(\text{Bi, Sb})_2\text{Te}_3$ segments stacked unbonded and heated with $T_{11} = 750^\circ\text{C}$, $T_c = 300^\circ\text{C}$, and $T_{11} = 300^\circ\text{C}$, $T_c = 107^\circ\text{C}$, respectively, in vacuo in zero-current test 6875-139-3

Fig. 2-26. Resistivity values of P-type $(Cu, Ag)_2Se/Fe$ and $(Bi, Sb)_2Te_3$ segments stacked unbonded and heated with $T_{11} = 750^\circ C$, $T_c = 300^\circ C$, and $T_{11} = 300^\circ C$, $T_c = 107^\circ C$, respectively, in vacuo in zero-current test 6875-139-3

Fig. 2-27. Metallographic examination of a 1492-h, 300°C interface temperature, vacuo compatibility test of unbonded $(\text{Cu,Ag})_2\text{Se}$ and $(\text{Bi,Sb})_2\text{Te}_3$ segments separated from each other by an iron barrier in a thermal gradient of 754°C/300°C/118°C. The molybdenum mesh in the $(\text{Cu,Ag})_2\text{Se}$ shows attack apparently because of the presence of iron, nickel, or chromium from the 316 stainless steel cap. Under normal conditions, molybdenum exhibits no attack.

Fig. 2-28. Results of microprobe examinations of stacked unbonded segments of $(\text{Cu, Ag})_2\text{Se}/\text{Fe}$ and $(\text{Bi, Sb})_2\text{Te}_3$ after 1492 h in a zero-current $754^\circ\text{C}/300^\circ\text{C}/118^\circ\text{C}$ thermal gradient

Important results of this test were

1. Copper and other elements from the stainless-steel cap transported down the thermal gradient and formed a bulge at the iron barrier interface. The bulge, however, did not bridge the iron barrier between the $(\text{Cu,Ag})_2\text{Se}$ and $(\text{Bi,Sb})_2\text{Te}_3$ segments.
2. The $(\text{Bi,Sb})_2\text{Te}_3$ segment was unaffected by metal transport in $(\text{Cu,Ag})_2\text{Se}$ when separated from it by a 0.05-cm iron barrier in a 1492-h, 300°C interface test.
3. The thermoelectric properties of $(\text{Cu,Ag})_2\text{Se}$ show surprisingly little sensitivity to dissolved nickel, chromium, and iron.
4. Unbonded segments of $(\text{Cu,Ag})_2\text{Se/Fe}$ and $(\text{Bi,Sb})_2\text{Te}_3$, when stacked, behaved similarly to segmented-but-bonded elements in thermal gradient tests. Thus, sequentially hot pressed elements are satisfactory if hot pressed in separate dies.

2.2.3. Life Testing of P Element with Current

When an electrical potential is connected across a segmented P-type element and load, the stability of the segmented $(\text{Cu,Ag})_2\text{Se}$ can change dramatically. One objective of the thermal gradient tests with current flow was to determine if $(\text{Cu,Ag})_2\text{Se}$ would function stably with current flow. Another objective was to examine the behavior of $(\text{Cu,Ag})_2\text{Se}$ in an operational mode to understand the degradation mechanisms operating.

2.2.3.1. Current Flow and $(\text{Cu,Ag})_2\text{Se}$ Resistivity. A segmented $(\text{Cu,Ag})_2\text{Se/Fe/}(\text{Bi,Sb})_2\text{Te}_3$ P element (6875-144-4) was operated with $T_H = 757^\circ\text{C}$ and $T_C = 55^\circ\text{C}$ for 307 h. A current of 1.52 A was passed through the element; this corresponds to an iL/A of 8. This element had no vapor suppression system or barrier coating between the 316 stainless-steel hot cap and $(\text{Cu,Ag})_2\text{Se}$. These deletions were intended to directly compare zero-current operations of a segmented element in a thermal gradient test. The test conditions caused the copper and the hot cap materials to move down the element. A gap developed at the $(\text{Cu,Ag})_2\text{Se}$ -mesh/hot cap interface and caused the test to be terminated.

A replacement test (6875-146-2) was substituted with a tungsten barrier coating on the hot cap. Resistivity changes in this element were monitored as a function of iL/A for six thermal gradients. Figure 2-29 shows the results of these examinations for the $(\text{Cu,Ag})_2\text{Se}$ segment. Resistivity values for the $(\text{Bi,Sb})_2\text{Te}_3$ segment were relatively uniform and were thus not plotted.

For each of the thermal gradients examined, the higher the iL/A , the lower the resistivity of the $(\text{Cu,Ag})_2\text{Se}$ segment. One reason speculated for this is that a larger fractional current is carried by ions at larger iL/A values. Enhanced vaporization of $(\text{Cu,Ag})_2\text{Se}$ as iL/A is increased (i.e., more copper ions) gives credence to this argument. The resistivity of this segment decreases as the average temperature of the material increases. Above a T_H of 400°C, the resistivity of the segment appears to be controlled by the higher resistance of the cold end of the segment.

Fig. 2-29. Resistivity values for the $(\text{Cu}, \text{Ag})_2\text{Se}$ segment of a doubly segmented $(\text{Cu}, \text{Ag})_2\text{Se}/\text{Fe}/(\text{Bi}, \text{Sb})_2\text{Te}_3$ element 6875-146-2 as a function of iL/A and thermal gradient

2.2.3.2. Ratcheting. General Atomic investigated ratcheting of V_2 and, thus, calculated resistance, assuming that V_o is constant, in P-type $(Cu,Ag)_2Se$. Ratcheting is an irregular phenomena that requires many test hours to establish (Fig. 2-30) (that is, it is cyclic, but the cycle frequency is somewhat irregular). The ratchet pattern is dependent on current in the general manner shown in Fig. 2-31. In spite of short-term irregularity, if the average cycle frequencies are plotted versus iL/A for a large number of ratchet cycles, a curve typical of the one shown in Fig. 2-32 results. At iL/A values above the maximum cycle frequency, open circuit measurements temporarily threw the element into its low resistivity mode. Figure 2-33 shows that the iL/A also affected the time spent by each cycle in the low resistivity mode.

Geometry and temperature also influence ratcheting. Figure 2-34 shows ratcheting to be sensitive to either or both geometry and temperature. Two segmented and one unsegmented sample with differing geometries and T_C had peak ratcheting frequencies at different values of iL/A . Similarly, the ratchet behavior of one element is different even if T_C is the only variable (Fig. 2-35).

Ratcheting occurred with molybdenum-, tungsten-, and rhenium-coated hot caps. Metallographic examination (Fig. 2-36) showed that the $(Cu,Ag)_2Se$ of ratchet sample 6875-146-2 still had intimate contact with the wire mesh. Thus, neither cap material nor hot cap contact appeared to cause ratcheting. No change in T_H or current occurred which could account for the change in the calculated resistivity observed.

The magnitudes of calculated resistance changes during ratcheting of $(Cu,Ag)_2Se$ were estimated for segmented and unsegmented elements. Figures 2-37 and 2-38 show the results. The amplitudes of the voltage changes for each element are nearly the same for all values of iL/A except for very low current flows. When translated to resistance, the fractional change in resistance is minimum at the highest iL/A values where ratcheting occurs. The resistance change during ratcheting, like the ratchet cycle frequency, appears to be related to the geometry and temperature profile of the $(Cu,Ag)_2Se$ segment. Data on ratcheting were insufficient to quantify or verify these assumed relationships.

Specimen geometry is also speculated to affect voltage-time behavior of the tested element. Examples of this occurred in two test elements in which the mesh joint was connected on the element circumference to the hot cap. One segmented $(Cu,Ag)_2Se/Fe(Bi,Sb)_2Te_3$ element, 8236-3-1B, and one nonsegmented $(Cu,Ag)_2Se$ element, 8236-4-1A, show this configuration-induced behavior. Both elements had Mo-47/Re hot caps. The $(Cu,Ag)_2Se$ segments of both elements experienced resistivity ratcheting.

In addition to resistivity ratcheting, the elements showed instantaneous open-circuit voltage ramping. As seen in Fig. 2-39, large swings were observed in the load voltages. Figures 2-40 and 2-41 show portions of the recorder tracings near the beginning of life of the load voltages across the $(Cu,Ag)_2Se$ segments for these elements. Ramping had no readily detectable effect on resistivity ratcheting in the segmented element (Fig. 2-42) but occurred with measurable resistivity changes in the unsegmented element. The principal thermoelectric property change during ramping is a change in the apparent Seebeck coefficient, as shown in Figs. 2-43 and 2-44. The accompanying change in nonsegmented element resistivity (Fig. 2-45) began as not much more than the normal scatter in resistivity observed in the data. As noted earlier, P elements underwent ramping only when the wire mesh was attached to the rim of the hot cap.

Fig. 2-30. Typical time load voltage plot showing the onset of ratcheting in $(\text{Cu, Ag})_2\text{Se}$ elements

Fig. 2-31. Typical $(\text{Cu, Ag})_2\text{Se}$ resistivity ratcheting patterns $T_{11} = 750^\circ\text{C}$, $T_c = 200^\circ\text{C}$

Fig. 2-32. Effect of iL/A on the ratchet frequency of the $(\text{Cu, Ag})_2\text{Se}$ segment of element 6875-146-2

Fig. 2-33. Dwell time for $(Cu, Ag)_2Se$ segment of P element 6875-146-2 as a function of iL/A

Fig. 2-34. Ratchet cycles as a function of iL/A for two segmented and one unsegmented P-type elements

Fig. 2-35. Effect of T_C on the resistivity ratchet cycle time for $(\text{Cu}, \text{Ag})_2\text{Se}$ element 6875-151-1B

Fig. 2-36. Photomicrograph of the wire mesh/(Cu,Ag)₂Se joint region of sample 6875-146-2 after resistivity ratcheting experiments

Fig. 2-37. Resistance change during ratcheting of $(\text{Cu}, \text{Ag})_2\text{Se}$ in segmented and unsegmented elements

Fig. 2-38. Resistance change during ratcheting of the $(\text{Cu, Ag})_2\text{Se}$ segment of sample 6875-146-2

Fig. 2-39. Typical voltage ramping profile showing time, temperature, and load voltage behavior of edge tack-welded mesh $(\text{Cu,Ag})_2\text{Se}$ elements operating in a thermal gradient with current

Fig.. 2-40. Load voltage of unsegmented $(\text{Cu,Ag})_2\text{Se}$ of element 8236-4-1A

Fig. 2-41. Load voltage for $(\text{Cu,Ag})_2\text{Se}$ segment of element 8326-3-1B

Fig. 2-42. Resistivity values of segmented P-type element 8236-3-1B tested in a thermal gradient of 755°C/237°C/160°C at an iL/A value of 7.4 across the $(Cu, Ag)_2Se$ segment

Fig. 2-43. Seebeck coefficients of segmented P-type element 8236-3-1B tested in a thermal gradient of $755^\circ\text{C}/237^\circ\text{C}/160^\circ\text{C}$ at an iL/A value of 7.4 across the $(\text{Cu,Ag})_2\text{Se}$ segment

Fig. 2-44. Seebeck coefficients of unsegmented P-type element 8236-4-1A tested in a thermal gradient of $755^\circ\text{C}/124^\circ\text{C}$ at an iL/A value of 7

Fig. 2-45. Resistivity values of unsegmented P-type element 8236-4-1A tested in a thermal gradient of 755°C/124°C at an iL/A value of 7

Ramping may be an artifact created by the hot-cap-to-element-joint configuration. The wire mesh of this element was tack-welded to the rim of the hot cap. The element had no bonded contact with the center of the hot cap. This ramping is speculated to be caused by cyclic changes in the actual T_H of the element. The T_H was monitored at the hot cap and did not account for the ΔT caused by a changing gap between the hot cap and the $(\text{Cu,Ag})_2\text{Se}$ segment.

Initially, the hot cap and the element are in contact, as shown in Fig. 2-46. The measured and actual T_H temperatures are therefore nearly the same at the beginning of the test. Current flow causes the $(\text{Cu,Ag})_2\text{Se}$ segment to cool. The $(\text{Cu,Ag})_2\text{Se}$ then shrinks away from contact with the hot cap, as shown in Fig. 2-47. A step drop in Seebeck coefficient then occurs. The difference between the assumed T_H and the actual T_H becomes large, and the calculated Seebeck coefficient becomes much lower as the ΔT across the element is lowered. As the current is decreased and the element is thus warmed, it again expands until it touches the hot cap. This contact causes a sharp increase in the T_H of the $(\text{Cu,Ag})_2\text{Se}$ and a corresponding step increase in the Seebeck coefficient.

The difference in the Seebeck coefficient and resistivity for the unsegmented and segmented elements is probably more artificial than actual. Copper transported down the thermal gradient precipitates at a temperature warmer than the cold cap, and thus before it reaches the cold cap, precipitation has been seen in all the elements tested in a thermal gradient where the cold end is less than 200°C . This precipitation shortens the effective length of the element which is contributing to the thermoelectric potential and thus makes Seebeck coefficient and resistivity appear lower than they truly are. Speculating that ratcheting indicates copper movement in $(\text{Cu,Ag})_2\text{Se}$, Fig. 2-48 presents one possible scenario for ratcheting.

2.2.3.3. *Cu,Ag₂Se Thermodynamics and Transport Phenomena.* The experimental observation of copper movement prompted a theoretical examination of transport phenomena in Cu_2Se . Appendix A gives an abbreviated overview of copper movement in Cu_2Se .

2.2.3.4. *Thermal Gradient Testing of P-Type Elements.* Test sample 6875-132-36 was a segmented $(\text{Cu,Ag})_2\text{Se}/\text{Fe}/(\text{Bi,Sb})_2\text{Te}_3$ element with a molybdenum-coated stainless-steel hot cap and a molybdenum wire mesh. Test sample 6875-151-18 was an unsegmented $(\text{Cu,Ag})_2\text{Se}$ element with a rhenium-coated stainless-steel cap and a W/3% Re wire mesh. These test elements were used in resistivity ratcheting tests which were kept on test at iL/A values of 8 and 9.58, respectively. These tests were intended to determine if the characteristics of resistivity ratcheting changes with time. Another goal of these tests was to qualitatively evaluate life behavior of these elements in a thermal gradient with high current operation. Sample 6875-132-36 had accumulated 506 h in thermal gradient resistivity ratcheting tests before the high-current life tests began. The iL/A values for these ratcheting tests varied from 0.2 to 4. Sample 6875-151-1B operated for 475 h in thermal gradient resistivity ratcheting experiments before its high current life testing. The iL/A values for the resistivity ratcheting tests of sample 6875-151-1B varied from 6 to 9.58.

Fig. 2-46. As-fabricated mesh-in-cap design where wire mesh only is tack-welded to the hot cap

Fig. 2-47. Mesh-in-cap design where wire mesh only is tack-welded to the hot cap at operating temperatures

NO CURRENT IN A
THERMAL GRADIENT

Cu/Se RATIO ESTABLISHED BY THE TEMPERATURE PROFILE
IN Cu_{2-x}Se MATERIAL.

BEGINNING OF LOW
CURRENT IN A THERMAL
GRADIENT

Cu^+ DRIFT TO COLD END. THIS CAUSES HIGHER Cu/Se RATIOS
AT THE COLD END THAN TEMPERATURE ABOVE DICTATES. THE
OVERALL ELEMENT RESISTANCE INCREASES WITH TIME.

AFTER MANY HOURS
OF CURRENT
OPERATION IN A
THERMAL GRADIENT

PRECIPITATION OF Cu FROM THE SUPER SATURATED Cu_2Se REDUCES
THE TOTAL Cu_2Se AT THE COLD END AND HAS THE EFFECT OF MAKING
A SHARP DROP IN THE OVERALL ELEMENT RESISTANCE. PRECIPITATION
CREATES MORE SITES FOR FURTHER Cu^+ MIGRATION.

CONTINUED OPERATION
OF CURRENT AND
THERMAL GRADIENT

CYCLIC INCREASES IN Cu^+ CONCENTRATION AT THE COLD END OF
THE Cu_{2-x}Se MATERIAL FOLLOWED BY SUDDEN PRECIPITATION OF
EXCESS Cu. THIS CAUSES

- CYCLIC CHANGES IN THE RESISTANCE.
- GRADUAL LAYER BUILDUP OF Cu AT THE COLD END
- AN EFFECTIVE SHORTENING OF THE ELEMENT (I.E., LOWERING
OF THE OUTPUT VOLTAGE).
- INCREASED POROSITY AT THE HOT END FROM Cu MIGRATION AND
 Se_2 VAPORIZATION.

AS Cu LAYERS INCREASE (I.E., WITH TEST TIME, THE TEMPERATURE AT
WHICH PRECIPITATION OF THE Cu INCREASES WHICH AFFECTS THE
FREQUENCY AND AMPLITUDE OF THE RESISTIVITY RATCHETING).

Fig. 2-48. A macro view of the Cu_2Se resistivity ratcheting process

Figures 2-49 and 2-50 show the Seebeck coefficient and resistivity histories of these two elements after the resistivity ratcheting experiments. Large perturbations in the Seebeck coefficient and resistivity measurements occurred when unexpected power outages occurred. The ratcheting experiments showed that these perturbations could be expected. The recovery time for the unsegmented element was more rapid than the segmented element.

A ring bulge above the iron interface of the segmented element, developed during the first few hours of current operation, did not enlarge since its first appearance. A swelling in the lower 25% of the unsegmented element also appeared in the first few hours of high-current testing. This swelling also did not increase in the last 600 test hours. These swollen zones are due to transport of copper and stainless-steel hot cap materials through the $(\text{Cu,Ag})_2\text{Se}$.

Ratcheting observed at lower iL/A values in segmented sample 6875-132-36 did not occur during the life test of this element. Ratcheting was observed in the unsegmented element at an iL/A value of 9.58 at the beginning of testing. It was still observed 600 test hours later. The ratchet cycle frequency of element 6875-151-1B was irregular and increased during the life tests.

8236-4-1A. Element 8236-4-1A was shut down when the test stand developed an air leak. The test was terminated after visual examination of the element showed that the element had been damaged by the air exposure. Seebeck coefficient and resistivity remained reasonably stable for the ≥ 1400 test hours, as shown in Figs. 2-44 and 2-45. The shape and frequency of ramping of the output voltage changed during the test, but the amplitude of this ramping remained approximately the same. The shape and frequency of the open circuit voltage ramping of the $(\text{Cu,Ag})_2\text{Se}$ changed with time. The dwell time in the high ramping mode decreased with time. The amplitude of the ramping apparently decreased with time.

8236-3-1B. The components of this segmented P-type element are $(\text{Cu,Ag})_2\text{Se}$ upper segment with a W-26/Re wire-mesh-to-hot-cap joint. The hot cap was made from a 0.058-cm-thick Mo-Re sheet. The element was sequentially hot pressed with iron powder and a lower segment of $(\text{Bi,Sb})_2\text{Te}_3$. The iron formed a 0.075-cm barrier between the two segments to prevent copper diffusion into the $(\text{Bi,Sb})_2\text{Te}_3$. The cold side was also covered with 0.048-cm iron to ensure cold-side thermal heat transfer and electrical contact integrity. Electrodes were attached to the hot and cold caps and the iron barrier between the upper and lower thermoelectric segments. The hot side of the element was heated to 750°C without thermal barriers for 101 h with 0 to 0.694 A current flows for initial diagnostics on the element. The current was increased to 1.288 A, which corresponds to an iL/A value of 7.4 through the $(\text{Cu,Ag})_2\text{Se}$ segment of the element. The element was then life tested for 6356 h in a nominal $755^\circ\text{C}/230^\circ\text{C}/160^\circ\text{C}$ thermal gradient in vacuo. The external appearance of the element remained essentially the same for the last 6000 test hours. During the first 300 test hours, a small collar developed just above the iron barrier. This collar did not enlarge during the remainder of the test.

Plant power loss caused three test interruptions at 1437, 2876, and 5899 test hours. The test element went to room temperature each time. Figures 2-51 through 2-53 show that the major effect on the Seebeck coefficient and resistivity occurred during the first cooldown at 1437 test hours. The thermoelectric behavior of this element was reasonably stable for the last 4900 test hours; this was in spite of not providing a vapor suppression system.

Fig. 2-49. Seebeck coefficients of P-type elements 6875-132-36 and 6825-151B

Fig. 2-50. Resistivity values of P-type elements 6875-132-36 and 6875-151B

Fig. 2-51. Seebeck coefficients of the $(\text{Cu,Ag})_2\text{Se}$ segment of P-type element 8236-3-1B tested in a thermal gradient of $755^\circ\text{C}/220^\circ\text{C}$

Fig. 2-52. Seebeck coefficients of the $(\text{Bi,Sb})_2\text{Te}_3$ segment of P-type element 8236-3-1B tested in a thermal gradient of $220^\circ\text{C}/160^\circ\text{C}$

Fig. 2-53. Resistivity values of segmented P-type element 8236-3-1B tested in a thermal gradient of 755°C/220°C/160°C

8236-10. To eliminate the possibility that the weighted hot cap is the reason that contact is being maintained with the element, a new segmented P-type element test, 8236-10, was begun. This element had no contact with the heater; instead, it was radiation-coupled to the heat source. It also had a quartz vapor suppression sleeve which was held in place by a welded Mo-50/Re collar. Molybdenum-specified paper washers were placed around the element for additional insulation, making the element very much like those for couples and modules. The element was fabricated with a W-26/Re wire mesh diffusion-bonded to the inside surface of the Mo-50/Re hot cap to form the element hot-cap joint. Figures 2-54 and 2-55 show Seebeck coefficient and resistivity measurements during the test. The values reported are for the overall element and only indirectly reflect performances of individual $(\text{Cu,Ag})_2\text{Se}$ and $(\text{Bi,Sb})_2\text{Te}$ segments. The test element was cooled to room temperature for 30 h following a power shutdown. Resistivity and Seebeck coefficient measurements before and after the power loss were approximately the same.

Fig. 2-54. Resistivity values of segmented P-type element 8236-10 tested in a thermal gradient of 695°C/45°C

Fig. 2-55. Seebeck coefficients for segmented P-type element 8236-10 tested in a thermal gradient of 695°C/45°C

3. SEGMENTED N-ELEMENT DEVELOPMENT

Early segmented N-element studies emphasize the development of Gd_2Se_3 as the high-temperature component of the segmented N-type element. Phase instability at proposed operating temperatures was found to be a more difficult problem than originally thought. Alternative materials were sought as possible solutions to the phase instability problem. Nd_2Se_3 was reported to have approximately the same thermoelectric properties as Gd_2Se_3 and only one crystal structure at target fabricating and operating temperatures. $\text{NdSe}_{1.5-x}$ was thus the primary material examined in this recent effort to develop segmented N-type thermoelectric materials. This portion of the program was in three parts:

1. Evaluate processes to prepare $\text{NdSe}_{1.5-x}$ and control the Nd/Se ratio.
2. Examine element fabrication processes, including investigate additives to aid in reducing the friability of $\text{NdSe}_{1.5-x}$ elements.
3. Evaluate techniques to join the hot cap to NdSe_x .

3.1. PREPARATION OF $\text{NdSe}_{1.5-x}$

Both GA and Ames Laboratory prepared $\text{NdSe}_{1.5-x}$ samples. The results from examinations of materials from both organizations are reported below.

3.1.1. Processes Evaluated

3.1.1.1. Method 1: Control of Nd/Se Ratio by Controlling the Starting Alloy Composition. Tables 3-1 and 3-2 show the critical features of the processes of GA and Ames Laboratory to prepare $\text{NdSe}_{1.5-x}$ by controlling the starting alloy composition and physical form. Table 3-3 shows the results from three of the GA Method 1 Nd_2Se_3 alloys. The heat treatment schedules involved heating the elemental ingredients to 1050°C followed by an extended exposure at 1050°C and melting in a sealed graphite crucible. As shown in Table 3-3, melting resulted in significant losses of selenium, although a homogeneous cubic product was obtained. This cubic product is believed to be Nd_3Se_4 . Homogenization of the alloy at 1600°C in a sealed graphite crucible rather than melting (row 3, Table 3-3) resulted in much lower selenium losses, although the product was a mixture of two cubic phases.

The process was modified to try to inhibit selenium loss. This involved heating of the elemental ingredients in evacuated quartz vials to approximately 1000°C and holding them at temperature long enough for complete reaction (approximately 100 h). During heating, the vials were held at intermediate temperatures (approximately 450° and 750°C) overnight to avoid excessive pressure buildup in the vials. Although the processing schedule is cumbersome, material suitable for hot pressing was obtained. The reaction product was not homogeneous, but was completely reacted (i.e., no elemental neodymium was present). The reaction product was mechanically homogenized by grinding and mixing to provide powder for hot pressing.

TABLE 3-1
GA METHOD 1: NdSe_{1.5} ALLOY DEVELOPMENT THROUGH
CONTROL OF STARTING ALLOY COMPOSITION

Reaction of neodymium pellets and selenium powder
 T = 1045°C at rate <150°C/h (melting point of neodymium is 1019°C)
 Hold 100 h minimum
 Use finely divided neodymium
 Homogenization to ≈1600°C/15 min (optional)
 Crush and grind product to ≈-60 mesh
 Add 1% nickel ≈-270 mesh and blend
 Vacuum hot press

TABLE 3-2
NdSe_{1.5} ALLOY DEVELOPMENT, AMES LABORATORY
TECHNIQUES FOR NdSe_{1.5} PRODUCTION

Method 1

React neodymium thin sheets with selenium powder (processing sequence similar to GA)

Process starts with desired composition

Method 2 Diselenide Process

Same as Method 1 but produces NdSe₂ as an intermediate compound

Thermal decomposition of NdSe₂ (selenium distillation) to produce desired NdSe_x alloy

TABLE 3-3
GA METHOD 1 Nd₂Se₃ ALLOY DEVELOPMENT

Original Chemistry	Heating Schedule ^(a)	Final Chemistry	Crystal Structure	Comments
NdSe _{1.50}	A B D	NdSe _{1.36}	Cubic	Measured lattice parameter 8.864 Å versus 8.659 Å literature value for Nd ₃ Se ₄
NdSe _{1.49}	A D	NdSe _{1.39}	Cubic	—
NdSe _{1.48}	A C E	NdSe _{1.46}	Cubic (two phase)	Mixture sequence versus second monoselenides

^(a)A = Room temperature to 1050°C at 15°C/h.

B = 168 h at 1050°C.

C = 96 h at 1050°C.

D = Melted at 1700°C.

E = 1 h at 1500°C.

Vacuum hot pressing trials were conducted on three $\text{NdSe}_{1.5-x}$ alloys produced by GA and Ames Laboratory. Hot pressing was performed in graphite dies at 1575°C and 34.5 MPa (5000 psi) for 10 min. In each case, the hot pressed pellets were dense but quite friable. Table 3-4 shows the results of these trials.

3.1.1.2. Method 2: $\text{NdSe}_{1.5-x}$ by NdSe_2 Diselenization. Batches of $\text{NdSe}_{1.5-x}$ prepared by Ames Laboratory by their diselenide method (Table 3-2) were examined. The material had a more homogeneous appearance than batches prepared by other processes. Thermal gravimetric analysis showed the composition of one batch to be $\text{NdSe}_{1.495 \pm 0.005}$. X-ray examination of this sample showed only the presence of cubic Nd_2Se_3 . This material was melted for further homogenization. Three gram batches of melted $\text{NdSe}_{1.5-x}$ were prepared. Table 3-5 summarizes these and other melting trials. Very little Se_2 was lost after these melt runs. Cubic Nd_2Se_3 remained the only detectable phase, and the Se/Nd ratio did not drop below 1.45. Although the quantitative, laboratory measured distinctions between these melted samples were small, the samples had qualitative, visual differences. The unmelted starting Nd_2Se_3 from Ames Laboratory was reddish with small black and yellow specks. The melted samples were black with brown zones. Some samples melted at lower power settings had a small number of translucent red crystals.

Figure 3-1 shows the GA process steps which are now being designated as standard. Process steps used by 3M Company are shown for comparison. The two processes differ in the steps to produce $\text{NdSe}_{1.5-x}$. In the 3M Company process, the Se/Nd formula weight ratio of the starting material is 1.5. Selenium losses from each of the four major process steps determines the final Se/Nd ratio. Controlling the loss in selenium requires very careful weighing and geometry control of the starting materials and a certainty that all conversion processes are complete. Any variation in the reproducibility of the steps in the preparation results in a variation in the final $\text{NdSe}_{1.5-x}$ composition.

The GA process is a slight modification of the Ames Laboratory diselenide process. Excess selenium is mixed with neodymium in the initial conversion to make NdSe_2 . The NdSe_2 is then decomposed into Nd_2Se_3 and selenium at 1050°C. NdSe_2 is again formed by heating Nd_2Se_3 with selenium at 650°C. Once formed, the final $\text{NdSe}_{1.5-x}$ composition is controlled by holding Nd_2Se_3 at its melting point. In this way, the final melting step is critical to the Se/Nd ratio. The Nd_2Se_3 vapor pressure measurements evidence this.

3.1.2. $\text{NdSe}_{1.5-x}$ Process Controls

Table 3-6 gives the process controls used in preparing $\text{NdSe}_{1.5-x}$. The appearance uniformity, composition, and thermoelectric property measurements determine the final acceptance or rejection of an $\text{NdSe}_{1.5-x}$ batch. The melting trial results (Table 3-5) show that the processes of Ames Laboratory and GA produce materials with no significant difference in Se/Nd ratios or Seebeck coefficients. It also shows that melting $\text{NdSe}_{1.5-x}$ with or without a crucible lid had no apparent effect on the final product. Red phases were observed in melted samples briefly held at the melting points. These phases disappeared when the melt was held for 10 min or more at melting temperature.

TABLE 3-4
METHOD 1 Nd₂Se₃ ALLOY DEVELOPMENT EVALUATION

Alloy	Producer	Structure of Starting Material	Room Temperature Seebeck Coefficient, α, After Hot Pressing ($\mu\text{V}/^\circ\text{C}$)
NdSe _{1.46}	GA	Cubic (two phase)	-40.1
NdSe _{1.49}	Ames Laboratory	Cubic	-142.0
NdSe _{1.50}	Ames Laboratory	Cubic	-136.1

TABLE 3-5
Nd₂Se₃ MELTING TRIALS

Batch No.	Additives	Melt Gas	Observed Temp (°C)	Melt Time at Temp (min)	Se/Nd	T = 80°C Seebeck Coefficient, α ($\mu\text{V}/^\circ\text{C}$)	Notes
7958-56	0	0	—	—	1.495 $\pm$ 0.005	ND ^(a)	Ames Laboratory Nd ₂ Se ₃
7958-57	0	He	~1770	4 at 1600, 2 at 1850	1.45	-70	Reduce pressure melt (2 tries)
7958-58-1	0	Ar	1725	1.0	1.50	-127	
7958-58-2	0	Ar	1740	1.0	1.49	-124	
7958-58-3	0	Ar	1750	1.5	1.50	-120	
7958-65-1	Se 1%	Ar	1745	2.0	1.49	-125	
7958-65-2	Se 1%, C 0.1%	Ar	1750	2.0	1.48	-124	
7958-63-2	0	Ar	1750	1.5	1.498	-133	GA Nd ₂ Se ₃
7958-71-1	0	Ar	1850	Ames Laboratory material melted at Ames	1.487	-94.8	Ames Laboratory Nd ₂ Se ₃
7958-78-1	0	Ar	1750	1.5	1.488	-114	GA Nd ₂ Se ₃
7958-90-1	0	Ar	~1800	3.0	1.494		
7958-105C	0	Ar	~1800	10.0	1.482	-101	
7958-105D	0	He	~1800	30.0	1.471	-88.4	

^(a)Not determined.

Fig. 3-1. Flowchart for preparation of Nd_2Se_3

TABLE 3-6
NdSe_{1.5} PROCESS CONTROLS

Process	Control
Neodymium and selenium starting materials	99.999% pure neodymium and selenium. Selenium is purified at GA to reduce O ₂ . (99.999% pure material is not sold with respect to O ₂ .)
Heating of sealed off quartz vials	Performed in inert atmosphere to minimize O ₂ diffusion through the quartz vials
Reaction of neodymium and selenium after 1050°C treatment	Material is ground and visually inspected for unreacted neodymium via color differences and uniformity of grinding
NdSe _{1.5} melting and cooling	Setup controlled to ensure repeatability
NdSe _{1.5} stoichiometry measurement and structure	Seebeck coefficient on melted ingot chemical analyses via the several techniques discussed. Neutron activation analysis for O ₂ will be performed. X-ray diffraction. Se ₂ vapor pressure measurements.
Grinding	Performed by hand to observe any inhomogeneities. All grinding performed in glove box.
Hot pressing	Seebeck coefficient and resistivity of pressed element. Chemical analyses similar to above mechanical properties.

3.1.3. NdSe_{1.5-x} Property Measurements

Table 3-7 summarizes the methods of determining the Se/Nd ratios. Neodymium content was determined from thermogravimetric apparatus (TGA) measurements. A wet chemistry ethylenedraminetetracetic acid (EDTA) titration of Nd⁺³ is being used by Ames Laboratory for their Se/Nd ratio measurements. General Atomic did not evaluate the EDTA and Na₂S₂O₃ titration techniques because of the accuracy limitations of these measurements.

The most sensitive measure of the Se/Nd ratio appears to be vapor pressure measurements. Figure 3-2 shows partial pressures of Se₂ over several batches of melted and hot pressed NdSe_{1.5-x} samples. Knudsen cells were used for these measurements in a mass spectrometer. The cell holes were calibrated by measuring silver signals from each, at the same temperature. The Se₂ signals were corrected for the different hole sizes, using this information. The cells were tantalum tubes, closed at one end and lined with graphite foil. The temperatures were measured using a platinum versus Pt/10% Rh thermocouple attached to one of the tubes. The Se₂ mass 160+, was monitored as the cells were heated from room temperature. A very small amount of Se₂ was observed from one sample between 240° and 360°C for ~10 min. Se₂ was again observed above 950°C. The signal would go up as the temperature was raised, then go down very quickly. At ~1250°C, Se₂ was observed from samples. The Se₂ from the cells reached a steady state at 1350°C after about 2 h of heating. Signal versus temperature data were then taken. The results show that the partial pressure of Se₂ is strongly dependent on the total time that the NdSe_{1.5-x} is held above 1700°C. Whether this is during melting or post-hot-press annealing apparently does not matter. A comparison of Se₂ partial pressures over samples which were examined as chunks and after powdering showed that powdering caused almost two orders of magnitude change in the measured vapor pressures. The surface of Nd₂Se₃ is sensitive to oxygen pickup. The surface-to-volume ratio of the chunks is small enough to make oxygen pickup insignificant. This is not true in powdered samples.

Figure 3-3 shows that the log of the Se₂ partial pressure over NdSe_{1.5-x} is related to 130°C/30°C Seebeck coefficient measurements. These are, in turn, related to the log of the resistivity of the NdSe_{1.5-x} elements, as shown in Fig. 3-4. The partial pressures of Se₂ over NdSe_{1.5-x} solid solution were expected to undergo logarithmic changes with composition. This is what the Seebeck coefficient measurements suggest, but verification of this has not been made from chemical analyses. The figures show that control of the NdSe_{1.5-x} thermoelectric properties of Seebeck coefficient and resistivity can be achieved by selective time-temperature annealing above 1700°C. An effort was made to relate Se/Nd ratios and Seebeck coefficients of NdSe_{1.5-x} to process time at the melting temperature.

Figure 3-5 shows that both the Se/Nd ratios and the Seebeck coefficients are related to the process time at temperature. Vaporization loss of Se₂ reduces the Se/Nd ratio in the NdSe_{1.5-x} solid solution. This, in turn, increases the doping and lowers the Seebeck coefficient. The results of experimental measurements (shown in Fig. 3-6), Seebeck coefficient, and the Se/Nd ratios are linearly related.

TABLE 3-7
Nd/Se MEASUREMENTS

Neodymium by TGA

Nd/Se ratio calculated from NdSe_x and Nd_2O_3 weight measurements

Limitations = $\pm 0.3\%$ accuracy

Original material is assumed to be unoxidized

Neodymium by wet chemistry

EDTA titration of Nd^{+3} in a solution buffered to a PH of 5

Limitation = $\pm 0.5\%$ accuracy

Selenium by wet chemistry

$\text{Na}_2\text{S}_2\text{O}_3$ titration in a KI starch solution

Limitation = $\pm 0.5\%$ accuracy

Fig. 3-2. Se_2 vapor pressure over various NdSe_x chunks

Fig. 3-3. Low-temperature Seebeck coefficient versus 1200°C Se_2 vapor pressure for Nd_2Se_3 .

Fig. 3-4. As-fabricated low-temperature Seebeck coefficient versus resistivity for Nd_2Se_3 elements

Fig. 3-5. Control of $NdSe_{1.5-x}$ composition and Seebeck coefficient

Fig. 3-6. Seebeck coefficient versus Se/Nd ratios for melted $\text{NdSe}_{1.5-x}$ samples

The significance of these experiments is that the Se/Nd ratio, Seebeck coefficient, and resistivity of $\text{NdSe}_{1.5-x}$ can be controlled by the total time held at the melting temperature. A relationship should also exist between thermal conductivity and Se/Nd ratio, but this was not determined. Optimizing these thermoelectric properties plus factoring in practical considerations of element strength, a Se/Nd ratio can be selected which will maximize the efficiency of the $\text{NdSe}_{1.5-x}$ used for N-element fabrication.

3.2. $\text{NdSe}_{1.5-x}$ Element Fabrication Studies

Trial hot pressing of $\text{NdSe}_{1.5-x}$ elements was evaluated. This effort was intended to optimize the mechanical strength and thermoelectric properties of the N element.

3.2.1. Hot pressing $\text{NdSe}_{1.5-x}$ Made by Method 1 GA or Ames Laboratory Processes from Controlled Ratios of Neodymium and Selenium Starting Materials

3.2.1.1. $\text{NdSe}_{1.5-x}$ and $\text{NdSe}_{1.5-x}$ Plus Additives. Several experiments have been conducted on vacuum hot pressing of Method 1 $\text{NdSe}_{1.49}$ powder produced by Ames Laboratory. For all hot pressing temperatures, a dense compact was produced. The compacts were very friable as produced, even when nickel powder (-270 mesh) was used as a hot pressing additive. Compacts with 1% nickel added showed much higher room temperature Seebeck coefficients after hot pressing than did those without nickel, and densification could be accomplished at lower temperatures when nickel was added. At a hot pressing temperature of 1400°C, increasing the nickel content from 1% to 2% resulted in a much lower Seebeck value. Table 3-8 gives the results of these hot pressing experiments. Sound compacts were fabricated for both the $\text{NdSe}_{1.49}$ and $\text{NdSe}_{1.50}$ Method 1 compositions produced by Ames Laboratory. Both alloys contained 1 wt % nickel powder as a pressing aid. Hot pressing was performed at 1400°C and 34.5 MPa (5000 psi) for 15 min in 0.5-cm (0.200-in.) diameter graphite dies. The die was slow cooled from the hot pressing temperature to minimize thermal stressing of the compact. The compacts were crack free and ejected from the die without difficulty. Density for compacts of both alloys was 6.1 g/cm³. The Seebeck coefficients of the $\text{NdSe}_{1.49}$ plus 1% nickel and $\text{NdSe}_{1.50}$ plus 1% nickel alloys were -303 and -311 $\mu\text{V}/^\circ\text{C}$, respectively, which are somewhat higher than previously obtained.

One compact of the $\text{NdSe}_{1.50}$ plus 1% nickel alloy was tested in the thermal gradient station at zero current to determine the Seebeck coefficient at elevated temperatures. Table 3-9 shows the results.

Scanning electron microscopy (SEM) examinations of hot pressed alloys were performed both with and without nickel additions. Figures 3-7 and 3-8 show typical microstructures observed on fracture surfaces. Very little surface-connected porosity was observed on the material hot pressed without nickel, while numerous cleavage facets were seen. The material hot pressed with nickel additions showed very few cleavage facets, considerable surface-connected porosity, and uniformly dispersed nickel particles.

Additional experiments were performed to develop a satisfactory vacuum hot pressing schedule for $\text{NdSe}_{1.5-x}$. These experiments used selenide compositions supplied by the Ames Laboratory Method 1 process. Table 3-10 shows the results of Seebeck coefficient determinations at room temperature after hot pressing. Alloys with nickel additions

TABLE 3-8
THERMAL EMF OF HOT PRESSED NdSe_{1.49}

Hot-Pressing Temperature (°C) ^(a)	Additive	Room Temperature Seebeck Coefficient, α , After Hot Pressing ($\mu\text{V}/^\circ\text{C}$)
1575	—	—142.0
1675	—	—118.6
1300	1% Ni	—260.8
1400	1% Ni	—210.0
1400	2% Ni	—60.0

^(a)34.5 MPa (5000 psi) pressure, 10 min under load.

TABLE 3-9
NdSe_{1.50} + 1% NICKEL SEEBECK COEFFICIENT

Temperature (°C)			Seebeck Coefficient, α ($\mu\text{V}/^\circ\text{C}$)
T _H	T _C	$\bar{T}$	
100	16	58	—365.00
200	17	108	—334.43
300	18	159	—333.33
400	20	210	—339.47
500	23	262	—335.43
600	29	315	—331.09
700	35	368	—337.11
748	41	395	—339.82
749	90	420	—355.08
749	119	434	—365.40

50 μm

20 μm

Fig. 3-7. Fracture surface of hot-pressed $\text{NdSe}_{1.5}$ with no nickel powder additions

Fig. 3-8. Fracture surface of hot-pressed NdSe_{1.5} plus 1% nickel

TABLE 3-10
SEEBECK COEFFICIENT OF NdSe_{1.5}
AND NdSe_{1.5} + 1% NICKEL ALLOYS

Alloy	Hot-Pressed Temperature (°C)	Hot-Pressed Pressure [MPa (psi)]	Seebeck Coefficient, α ($\mu\text{V}/^\circ\text{C}$)
NdSe _{1.495}	1400	98 (14,250)	-193.3
NdSe _{1.495} + 1% Ni	1100	98 (14,250)	-1.1
NdSe _{1.498}	1400	98 (14,250)	-237.4
NdSe _{1.498} + 1% Ni	1100	112 (16,280)	-3.3
NdSe _{1.504}	1400	112 (16,280)	-188.0
NdSe _{1.504} + 1% Ni	1150	112 (16,280)	-4.3
NdSe _{1.49} + 1% Ni	1300	55 (8,000)	-259.0
NdSe _{1.495}	1300	96.5 (14,000)	-240.1
NdSe _{1.495}	1300	82.7 (12,000)	-267.4
NdSe _{1.495} + 1% Ni	1300	96.5 (14,000)	-65.0
NdSe _{1.495} + 1% Ni	1200	96.5 (14,000)	-61.0
NdSe _{1.495} + 1.5% Ni	1100	96.5 (14,000)	-86.0
NdSe _{1.5} + 1% Ni	1300	96.5 (14,000)	-175.0

consistently show greatly reduced Seebeck coefficients in the as-hot-pressed condition. Several compacts were aged for 17 and 64 h at 1000°C, and the Seebeck coefficient was remeasured. Table 3-11 shows these results. The alloy prepared without nickel additions showed a slight increase in Seebeck coefficient, while some alloys containing nickel additions showed P-type behavior after aging for 17 h and the expected N-type behavior after 64 h.

Elements hot pressed from $\text{NdSe}_{1.5}$ powder without nickel additions show much improved Seebeck coefficients but are extremely friable and could not be handled for further processing. The original intent of nickel additions to the $\text{NdSe}_{1.5}$ alloys was to improve as-fabricated strength of the selenide elements. Figure 3-9 shows a compilation of recent data on the as-fabricated Seebeck coefficient of three $\text{NdSe}_{1.5}$ alloys with 1% nickel added as a hot pressing aid. The Seebeck coefficient clearly increases with hot pressing temperatures, although the alloys pressed at lower temperatures are felt to attain the same level of thermal electromotive force (emf) after aging.

Table 3-12 summarizes the results of hot pressing. In $\text{NdSe}_{1.5-x}$, which was prepared by controlled composition starting materials, the addition of nickel helped to reduce the friability of the hot pressed elements but degraded the thermoelectric properties. A variety of other dispersed phases was examined as hot-pressing aids because of the transient chemical instability of nickel additions in the $\text{NdSe}_{1.5}$ alloys. These include iron, chromium, rhenium, molybdenum, tungsten, graphite, and Cr_{23}C_6 . Table 3-13 shows the results of hot pressing trials using these additives. Chromium, tungsten, and graphite appear to warrant further investigation. Chromium was especially attractive because high Seebeck coefficients were obtained after hot pressing at fairly low temperatures. (Note in Fig. 3-9, described previously, that nickel additions result in much lower Seebeck coefficients than observed for chromium when hot pressing is performed at 1200°C). The ends of the $\text{NdSe}_{1.495}$ plus 1% chromium compact were ion plated with rhenium for resistivity and Seebeck coefficient measurements at T_H up to 750°C. These results (Table 3-14) show that Seebeck coefficients and resistances increased continuously with temperature. The 392.3 milliohm resistance at $T = 66^\circ\text{C}$ corresponds to a resistivity 30 milliohm-cm, while the 548.0 milliohm resistance at 428°C corresponds to a resistivity of 42.03 milliohm-cm.

The Method 1 $\text{NdSe}_{1.495}$ alloy elements with several different hot pressing additives were aged at 965°C for 94 h. The Seebeck coefficient, after aging, was measured for comparison with the as-hot-pressed value. This test was performed to assess the relative stability of the dispersed metal phases in the $\text{NdSe}_{1.5-x}$ matrix. Table 3-15 shows the results. Those compacts showing positive Seebeck coefficients as-hot pressed showed relatively little change in Seebeck coefficient. Compacts showing negative Seebeck coefficients as-hot pressed become more negative after aging. None of the additives shown appear adequate for hot pressing with $\text{NdSe}_{1.5-x}$.

Additional elements have been prepared from the $\text{NdSe}_{1.495}$ composition using 1% chromium or the combination of 0.5% tungsten and 0.5% chromium as hot-pressing aids. Table 3-16 shows as-fabricated properties of these elements. Metallographic examination of the alloys containing chromium additions showed cracking in the vicinity of large chromium particles. Areas of the element containing fine chromium powder particles were generally crack free.

TABLE 3-11
NdSe_{1.5-x} PROPERTIES AFTER AGING AT 1000°C

Alloy	Aging Time (h)	Seebeck Coefficient, α ($\mu\text{V}/^\circ\text{C}$)
NdSe _{1.495}	0	-267.4
NdSe _{1.495}	17	-293.0
NdSe _{1.495}	64	-294.0
NdSe _{1.495} + 1% Ni	0	-65.0
NdSe _{1.495} + 1% Ni	17	+6.3
NdSe _{1.495} + 1% Ni	64	-100.0
NdSe _{1.495} + 1.5% Ni	0	-86.0
NdSe _{1.495} + 1.5% Ni	17	+5.3
NdSe _{1.495} + 1.5% Ni	64	-142.0
NdSe _{1.5} + 1% Ni	0	-175.0
NdSe _{1.5} + 1% Ni	17	+6.8
NdSe _{1.5} + 1% Ni	64	-157.0

TABLE 3-12
TYPICAL HOT-PRESSED NdSe_x PROPERTIES

x	Hot-Pressed Schedule ($^\circ\text{C}/\text{psi}/\text{min}$)	Seebeck Coefficient, α ($\mu\text{V}/^\circ\text{C}$)	Comments
1.46 (GA)	1575/5000/10	-40.1	Two-phase produce
1.49 (Ames)	1575/5000/10	-142.0	Single phase
1.49	1675/5000/10	-118.6	Single phase
1.49 + 1% Ni	1300/5000/10	-260.8	Single phase
1.49 + 1% Ni	1400/5000/10	-210.0	Single phase
1.49 + 1% Ni	1400/5000/15 ^(a)	-303.0	Sound element
1.5 (Ames)	1575/5000/10	-136.1	Inhomogeneous single phase
1.5 + 1% Ni	1400/5000/15 ^(a)	-311.0	Sound element

^(a)Small diameter die and slow cooling rate.

Fig. 3-9. Seebeck coefficient of $\text{NdSe}_{1.5}$ plus 1% nickel alloys

TABLE 3-13
HOT PRESSING ADDITIVES FOR NdSe_{1.495}

Additive (1%)	Pressing Temperature (°C)	Seebeck Coefficient, α ($\mu\text{V}/^\circ\text{C}$)	Comments
Iron	1150	+11.6	Numerous cracks in element
Chromium	1200	-187.0	Sound element
Rhenium	1400	+8.5	Sound element
Molybdenum	1400	+8.8	Sound element
Tungsten	1400	-308.4	Slight cracking
Graphite	1475	-260.0	Sound element, low density
Chromium carbide	1500	-250.6	Slight cracking

TABLE 3-14
IN-GRADIENT TESTING OF Nd₂Se₃ + 1% Cr

Temperature (°C)			Output Voltage, V_o (mV)	Seebeck Coefficient, α ($\mu\text{V}/^\circ\text{C}$)	Resistance (m Ω)
T_H	T_C	$\bar{T}$			
19	31	—	—	—	378.4
100	32	66	12.10	177.94	392.3
133	33	83	17.40	174.00	392.7
150	35	93	20.80	180.87	409.0
200	36	118	31.00	189.02	414.0
200	39	120	35.60	221.11	410.4
250	44	147	48.20	233.98	420.6
300	46	173	61.70	242.91	428.5
350	50	200	75.00	250.00	434.4
400	56	228	89.30	259.59	448.5
450	60	255	103.10	264.36	459.7
500	65	283	119.00	273.56	479.0
550	70	310	134.40	280.00	510.9
600	78	339	150.50	288.31	548.5
650	84	367	167.30	295.58	574.2
700	93	397	183.40	302.14	555.6
750	105	428	200.00	310.08	548.0

TABLE 3-15
AGING EFFECTS ON NdSe_{1.495} MATRIX ALLOYS

Additive	Seebeck Coefficient, α ($\mu\text{V}/^\circ\text{C}$)	
	As-Pressed	Post-Age ^(a)
Iron	+11.6	+6.4
Rhenium	+8.5	+7.3
Molybdenum	8.8	+7.4
Tungsten	-308.4	-445.3
Graphite	-260.0	-90.0
Chromium carbide	-250.6	-535.4

^(a)94 h/965°C.

TABLE 3-16
PROPERTIES OF NdSe_{1.495} ALLOYS

Additive	Hot Pressing Temperature ($^\circ\text{C}$)	$\bar{T} = 80^\circ\text{C}$ Seebeck Coefficient, α ($\mu\text{V}/^\circ\text{C}$)	Room Temperature Resistivity, ρ ($\Omega\text{-cm}$)	Density (g/cm^3)
1% Cr	1275	-192.0	ND ^(a)	6.52
1% Cr	1275	-220.0	0.054 ^(b)	6.53
0.5% W + 0.5% Cr	1500	-174.0	ND	6.60

^(a)Not determined.

^(b)After ion plating rhenium end caps.

The compact containing 0.5% tungsten and 0.5% chromium additions was mounted in the test station for elevated temperature Seebeck coefficient measurements. Table 3-17 shows the results of this test. After 39 h exposure at $T_H = 734^\circ\text{C}$, $T_C = 78^\circ\text{C}$, and $T = 406^\circ\text{C}$, the mV output was 185.0 and the Seebeck coefficient was $282.20 \mu\text{V}/^\circ\text{C}$, which is somewhat lower than the value obtained during heatup. The test was terminated after 69 h total exposure.

3.2.1.2. (Nd,Gd)Se_{1.5-x} Alloys. Gadolinium was added to accelerate the reaction kinetics. The neodymium was present to stabilize cubic rare earth selenide. A series of (Nd,Gd)Se_{1.5} alloys was prepared by reacting elemental ingredients to 1010°C in evacuated quartz vials. The alloys were held at temperature for 100 h. The compositions prepared correspond to Nd_{0.898}, Gd_{0.102}Se_{1.493}, Nd_{0.76}Gd_{0.24}Se_{1.479}, Nd_{0.495}Gd_{0.505}Se_{1.479}, and Nd_{0.253}Gd_{0.747}Se_{1.478}. After reaction, X-ray diffraction examination of the products indicated that each was two phase, consisting of one cubic phase (presumably NdSe_{1.5}) and one orthorhombic phase (presumably GdSe_{1.5}). The reaction product was ground and hot pressed at temperatures sufficient to produce cubic materials and reexamined by X-ray diffraction.

In no case was a structurally sound 0.95-cm (0.375-in.) diameter compact obtained. This is probably to be expected in light of the recent results on NdSe_{1.5} plus 1% nickel which indicate that small compact diameters and slow cooling rates are required. Each composition still consisted of two cubic phases with very similar lattice parameters. The amount of second (cubic) phase increased with increasing Gd/Nd ratio to approximately 50% at the Nd_{0.25}Gd_{0.75}Se_{1.50} composition. Table 3-18 summarizes observations on the (Nd,Gd)Se_{1.5} alloys.

3.2.2. Hot Pressing NdSe_{1.5-x} Made by Method 2 from the Diselenide Process

An evaluation was made of elements prepared by hot pressing Nd₂Se₃ from the deselenide NdSe₂ process from NdSe_{1.5-x} prepared and melted by both GA and Ames Laboratory. Table 3-19 shows the reproducibility of the results of near-ambient-temperature measurements of density, Seebeck coefficient, and resistivity of some Ames Laboratory-supplied NdSe_{1.489}. Density and Seebeck coefficient were quite repeatable. Resistivity measurements were made with a four-point probe, but without coated contacts on the ends of the elements. Data scatter in this measurement was partly because the ends were not metallized.

The Seebeck coefficients and resistivities were compared for NdSe_{1.5-x} by the following methods:

1. Prepared and melted at GA.
2. Prepared at Ames Laboratory and melted at GA.
3. Prepared and melted at Ames Laboratory.

TABLE 3-17
SEEBECK COEFFICIENT OF NdSe_{1.45}
+ 0.5% W + 0.5% Cr (7958-48-3)

Temperature (°C)				Output Voltage, V _o (mV)	Seebeck Coefficient, α ($\mu\text{V}/^\circ\text{C}$)	Comments
T _H	T _C	ΔT	$\bar{T}$			
23	20	—	—	0.5	—	
50	21	29	36	7.7	265.52	
150	24	126	87	26.0	206.35	
175	25	150	100	31.3	208.67	
200	25	175	113	40.8	233.14	
250	26	224	138	53.7	239.73	
300	27	273	164	67.4	246.89	
350	29	321	190	81.5	253.89	
400	31	369	216	95.5	258.81	
450	32	418	241	110.8	265.07	
500	34	466	267	125.8	269.96	
550	36	514	293	142.0	276.26	
600	38	562	319	158.8	282.56	
650	41	609	346	176.4	289.66	
700	43	657	372	193.3	294.22	
750	46	704	398	211.9	300.99	
752	46	706	399	217.4	307.93	
752	46	706	399	218.8	309.92	
751	46	705	399	218.2	309.50	
751	45	706	398	214.7	304.11	Hold 14 h
748	45	703	397	204.3	290.62	
751	70	681	411	200.7	294.71	
751	80	671	416	199.0	296.57	
752	90	662	421	197.2	297.89	
751	100	651	426	195.3	300.00	
751	110	641	431	193.5	301.87	
751	120	631	436	191.8	303.96	
749	129	620	439	189.9	306.29	
748	138	610	443	187.8	307.87	
747	141	606	444	187.2	308.91	Decrease cold side temp at 30 h
734	78	656	406	185.0	282.20	69 h

TABLE 3-18
RESULTS ON HOT-PRESSED (Nd,Gd)Se_{1.5} ALLOYS

Composition	Hot-Pressed Schedule (°C/psi/min)	Seebeck Coefficient, α ($\mu\text{V}/^\circ\text{C}$)	Comments
Nd _{0.899} Gd _{0.102} Se _{1.493}	1500/5000/10	-139.7	Very small amount of second (cubic) phase
Nd _{0.898} Gd _{0.102} Se _{1.493} + 1% Ni	1400/5000/10	-223.6	Very small amount of second (cubic) phase
Nd _{0.898} Gd _{0.102} Se _{1.493} + 1% Ni	1200/7000/10	-177.0	Very small amount of second (cubic) phase
Nd _{0.760} Gd _{0.240} Se _{1.479}	1500/5000/10	-269.0	Very small amount of second (cubic) phase
Nd _{0.253} Gd _{0.747} Se _{1.478}	1500/5000/10	-135.0	Increasing amounts of second (cubic) phase

TABLE 3-19
HOT-PRESSING REPRODUCIBILITY TRIALS

Sample 7958-97-	Density (g/cm ³)	130°C/30°C Seebeck Coefficient, α ($\mu\text{V}/^\circ\text{C}$)	23°C Resistivity, ρ (m Ω -cm)
1	6.62	-93.0	5.50
2	6.64	-101.0	4.57
3	6.68	-105.0	3.01
4	6.63	-105.8	3.39
5	6.67	-107.4	4.72
6	6.62	-107.0	5.37
7	6.65	-108.0	5.49
8	6.64	-105.0	5.48
9	6.64	-105.0	5.94
$\bar{X}$	6.64	-104.1	4.83
σ	0.021	4.64	1.02

The examinations suggested a high degree of pre-hot-pressed material variability that was not detectable by chemical compositions or X-ray crystal structure examinations. Vapor pressure measurements appeared to be sensitive enough to detect sufficient mobile selenium in melted $\text{NdSe}_{1.5-x}$ to cause differences in measured thermoelectric properties. The vapor pressure of selenium over $\text{NdSe}_{1.5-x}$ at elevated temperatures appears to be related to the time at temperature and the $\text{NdSe}_{1.5-x}$ rate of cooling after melting. These data are in agreement with the work of Vickery and Muir (Ref. 3-1) on Gd_2Se_3 , which suggests the formation of a monophase of 90% Gd_2Se_3 and that GdSe is responsible for the high thermoelectric figure-of-merit of this material.

Figure 3-10 compares GA and 3M Company $\text{NdSe}_{1.5-x}$ element fabrication for fabricating $\text{NdSe}_{1.5-x}$ elements. The 3M Company uses a cold press and sintering process, while GA uses a hot press process. Thermoelectric property measurements show that these differing processes produce elements whose thermoelectric properties are indistinguishable. Photomicrographs of GA material (Figs. 3-11 and 3-12) and the 3M Company material (Figs. 3-13 and 3-14) show the two microstructures to be comparable. The dark spots in the 3M Company material are pores. This can be expected in cold pressed and sintered material. Scanning electron microscopy photomicrographs of the two materials (Figs. 3-15 and 3-16) show that both materials are dense.

Table 3-20 lists and Table 3-21 summarizes the recent hot pressing trials of $\text{NdSe}_{1.5-x}$. Elements which were hot pressed from melted Method 2 $\text{NdSe}_{1.5-x}$ were stronger than those which were hot pressed from unmelted material. Resistivities of N elements hot pressed at 1400°C and post-annealed at 1700°C were one to two orders of magnitude lower than elements which were not post-hot-press annealed. Thermoelectric properties of elements hot pressed from $\text{NdSe}_{1.5-x}$ material prepared by Ames Laboratory or GA Method 2 were indistinguishable. The lowest resistivities of the hot pressed elements were from $\text{NdSe}_{1.5-x}$ which had been held at its melting temperature for 30 min.

Additional hot pressing trials were made to determine if metal additives to diselenide $\text{NdSe}_{1.5-x}$ material during hot pressing would reduce its friability. Table 3-22 summarizes the results of these experiments. The results show that 1% additions of nickel and platinum increase the resistivity and lower the Seebeck coefficient of $\text{NdSe}_{1.5-x}$ prepared by Method 2 which is hot pressed at 1400°C . Additions of molybdenum, rhenium, chromium, La_2Se_3 , Gd_2Se_3 , carbon, and graphite had no significant influence on the thermoelectric properties of the hot-pressed $\text{NdSe}_{1.5-x}$ elements. The effect of these additions on the mechanical properties of the element were qualitatively mixed. Some elements were stronger and less friable, some were less friable but weaker, and some showed no apparent change in mechanical properties.

3.2.3. $\text{NdSe}_{1.5-x}$ Hot Pressing Summary

Results of hot pressing trials for $\text{NdSe}_{1.5-x}$ prepared from both stoichiometric and diselenide starting materials can be summarized as follows:

1. The most consistent $\text{NdSe}_{1.5-x}$ with thermoelectric properties producing the best figure of merit came from melted material which was prepared by some variation of the Ames Laboratory diselenide process.

Fig. 3-10. Flowchart for element fabrication

100 μm

Fig. 3-11. Photomicrograph of Nd_2Se_3 , hot pressed at 1400°C and post-heat treated at 1700°C

100 μm

Fig. 3-12. Second photomicrograph of Nd_2Se_3 , hot pressed at 1400°C and post-heat treated at 1700°C

100 μm

Fig. 3-13. Photomicrograph of 3M Company Nd_2Se_3 as received from Purdue University (black holes are pores)

Fig. 3-14. Photomicrograph of etched 3M Company Nd_2Se_3 , as received from Purdue University. Grain size is approximately comparable to GA material.

Fig. 3-15. Scanning electron microscopy photomicrograph of GA hot-pressed and annealed Nd_2Se_3 showing very dense structure

Fig. 3-16. Scanning electron microscopy photomicrograph of 3M Company cold-pressed and sintered Nd_2Se_3 as received from Purdue University

TABLE 3-20
HOT PRESSING OF NdSe_{1.5-x}

Specimen No.	Nd ₂ Se ₃ Source	Hot Press			Post-Heat Treatment			130°C/30°C Seebeck Coefficient, α ($\mu\text{V}/^\circ\text{C}$)	23°C Resistivity, ρ ($\text{m}\Omega\text{-cm}$)
		Temp ($^\circ\text{C}$)	Pressure [MPa (psi)]	Time (min)	Temp ($^\circ\text{C}$)	Gas	Time (min)		
7958-59-1	7958-56 ^(a)	1400	100.6 (14,600)	10	—	—	—	-261	157.1
7958-59-2	7958-56 ^(a)	1400	100.6 (14,600)	10	1700	vac	30	-109	—
7958-61-1	7958-56 ^(a)	1400	100.6 (14,600)	10	1700	He	30	-129	5.85
7958-61-2	7958-58-1 ^(b)	1400	100.6 (14,600)	10	—	—	—	-229	418.8
7958-67-1	7958-58-2 ^(b)	1400	100.6 (14,600)	10	1700	vac	30	-133	—
7958-67-2	7958-58-2 ^(b)	1400	100.6 (14,600)	10	1700	He	30	-127	8.59
7958-69-1	7958-58-3 ^(b)	1400	100.6 (14,600)	10	1800	He	30	-103	4.65
7958-73-2	7958-63-2 ^(c)	1350	100.6 (14,600)	10	—	—	—	-319	141.0
7958-74-1	7958-63-2 ^(c)	1400	100.6 (14,600)	10	1700	He	30	-117	—
7958-72-2	7958-63-2 ^(c)	1375	100.6 (14,600)	10	1800	He	120	-104	—
7958-78-2	7958-78-1 ^(c)	1400	100.6 (14,600)	10	1700	He	30	-96	9.27
7958-88	7958-78-1 ^(c)	1350	50.3 (7,300)	15	1700	He	30	-138	—
7958-84-1	7958-84-1 ^(c)	1400	100.6 (14,600)	10	1700	He	30	-140	—
7958-92-3	7958-90 ^(d)	1350	100.6 (14,600)	10	1700	He	30	-114	—
7958-94-2	7958-90 ^(d)	1400	100.6 (14,600)	10	1700	He	30	-106	—
7958-94-1	7958-90 ^(d)	1400	100.6 (14,600)	10	1700	He	30	-97	7.88
7958-97(1-9)	7958-71-2 ^(e)	1400	100.6 (14,600)	10	1700	He	30	-104 ^(f)	4.83 ^(f)
7958-105E	7958-105D ^(g)	1400	100.6 (14,600)	10	1700	He	30	-75	1.95
7958-106-2	7958-105D ^(g)	1400	100.6 (14,600)	10	1700	He	30	-78	2.50
7958-106-3	7958-105C ^(h)	1400	100.6 (14,600)	10	1700	He	30	-93	4.59

^(a)Unmelted Nd₂Se₃ prepared by Ames Laboratory.

^(b)Ames Laboratory Nd₂Se₃ melted 1 min at GA in argon.

^(c)General Atomic Nd₂Se₃ melted 1.5 min at GA in argon.

^(d)General Atomic Nd₂Se₃ melted in 3 min at GA in argon.

^(e)Ames Laboratory Nd₂Se₃ melted at Ames Laboratory (see reproducibility runs).

^(f)Average of nine samples.

^(g)General Atomic Nd₂Se₃ melted 30 min in helium at GA.

^(h)General Atomic Nd₂Se₃ melted 10 min in argon.

TABLE 3-21
SUMMARY
HOT PRESS Nd₂Se₃ RESULTS^(a)

	130°C/30°C Seebeck Coefficient, α ($\mu\text{V}/^\circ\text{C}$)	23°C Resistivity, ρ ($\text{m}\Omega\text{-cm}$)
Unmelted Ames Laboratory Nd ₂ Se ₃ , hot pressed with no-post-heat treatment	-261	157.1
1 min melted Ames Laboratory Nd ₂ Se ₃ , hot pressed with no post-heat treatment	-229	418.8
1.5 min melted GA Nd ₂ Se ₃ , hot pressed with no post-heat treatment	-319	141.0
Unmelted Ames Laboratory Nd ₂ Se ₃ , hot pressed with 1700°C, 30-min helium post-heat treatment	-129	5.85
1 min melted Ames Laboratory Nd ₂ Se ₃ , hot pressed with 1700°C, 30 min helium post-heat treatment	-115	6.62
1.5 to 3 min melted GA Nd ₂ Se ₃ , hot pressed with 1700°C, 30 min helium post-heat treatment	-115	8.57
Ames Laboratory Nd ₂ Se ₃ melted at Ames Laboratory, hot pressed with 1700°C, 30 min helium post-heat treatment	-104	4.83
10 min melted GA Nd ₂ Se ₃ , hot pressed with 1700°C, 30 min helium post-heat treatment	-93	4.59
30 min melted GA Nd ₂ Se ₃ hot pressed with 1700°C, 30 min helium post-heat treatment	-77	2.23

^(a)Results may be averages of two or more samples.

TABLE 3-22
EFFECT OF HOT PRESSING ADDITIVES ON
THE THERMAL ELECTRIC PROPERTIES OF NdSe_{1.5-x}

Specimen No.	Nd ₂ Se ₃ Source	Additive/ wt %	Hot Pressing 10 min at		Post-Heat Treatment			130°C/30°C Seebeck Coefficient, α ($\mu\text{V}/^\circ\text{C}$)	23°C Resistivity, ρ (m Ω -cm)
			Temp (°C)	Pressure [MPa(psi)]	Temp (°C)	Gas	Time (min)		
7958-59-1	7958-56 ^(a)	None	1400	100.6 (14,600)	—	—	—	-261	157
7958-60-1	7958-50 ^(a)	Ni/1	1400	100.6 (14,600)	—	—	—	-10	>1000
7958-60-2	7958-56 ^(a)	Ni/1	1400	100.6 (14,600)	—	—	—	+115	>1000
7958-61-3	7958-58-1 ^(b)	Ni/1	1400	100.6 (14,600)	—	—	—	-261	755
7958-72-2	7958-63-2 ^(c)	Ni/1	1400	100.6 (14,600)	—	—	—	-31	—
7958-78-2	7958-78-1 ^(c)	None	1400	100.6 (14,600)	1700	He	30	-96	9.27
7958-79-2	7958-78-1 ^(c)	Mo/2	1400	100.6 (14,600)	1700	He	30	-118	13.07
7958-74-2	7958-63-2 ^(c)	Mo/25	1400	100.6 (14,600)	1700	He	30	-114	5.54
7958-79-1	7958-78-1 ^(c)	Graphite/0.1	1400	100.6 (14,600)	1700	He	30	-103	5.52
7958-82-1	7958-78-1 ^(c)	Carbon/1	1400	100.6 (14,600)	1700	He	30	-106	—
7958-81-1	7958-78-1 ^(c)	Re/1	1400	100.6 (14,600)	1700	He	30	-101	—
7958-81-2	7958-78-1 ^(c)	Pt/1	1400	100.6 (14,600)	1700	He	30	-87.6	>600
7958-93-1	7958-90 ^(d)	Cr/5	1400	100.6 (14,600)	1700	He	30	-116	—
7958-93-2	7958-90 ^(d)	La ₂ S ₃ /5	1400	100.6 (14,600)	1700	He	30	-123	—
7958-93-3	7958-90 ^(d)	Gd ₂ Se ₃ /5	1400	100.6 (14,600)	1700	He	30	-98.6	—

^(a)Ames Laboratory Nd₂Se₃ unmelted.

^(b)Ames Laboratory Nd₂Se₃ melted 1 min in argon.

^(c)General Atomic Nd₂Se₃ melted 1.5 min in argon.

^(d)General Atomic Nd₂Se₃ melted 3 min in argon.

2. Post-hot-press annealing at 1700°C for 30 min reduces the electrical resistivity of hot pressed $\text{NdSe}_{1.5-x}$.
3. The use of additives to improve the mechanical properties of the hot pressed element will, in the case of nickel or platinum, ruin the thermoelectric properties of the N-type $\text{NdSe}_{1.5-x}$. Additives which do not adversely affect the thermoelectric properties of the hot pressed element still may not improve its mechanical properties.

3.3. N-ELEMENT HOT CAP JOINING STUDIES

Nd_2Se_3 was found to have a high coefficient of thermal expansion (as shown in Table 3-23) and a high modulus of elasticity. It also has a low thermal conductivity. These properties make this material thermal shock sensitive and account for the friability experienced when it is hot pressed. It is also a major problem which must be overcome when selecting a method of metallurgically joining an electrical conductor to this material.

First attempts to make a hot-cap-to- $\text{NdSe}_{1.5-x}$ joint used a molybdenum or W-Re wire mesh that was hot pressed in place during $\text{NdSe}_{1.5-x}$ element formation, as shown in Fig. 3-17. The thermal shock sensitivity of the $\text{NdSe}_{1.5-x}$, combined with the significant differences in thermal expansion between the two materials, resulted in cracks in the element, as shown in Fig. 3-17. Efforts were made to overcome this weakness by making a graded $\text{Mo}/\text{Nd}_2\text{Se}_3$ zone. The graded zone permitted the fabrication of an element with a wire-mesh-bonded hot cap. Photomicrographic examination of the graded zone and mesh (Fig. 3-18) showed the generation of multiple cracks but no crack which totally traversed the graded zone. Strengthening the joint by adding molybdenum and making a graded joint improved the crack resistance of the graded zone but shifted element failure to below the graded zone, as shown in Fig. 3-19. Clearly, satisfactory element-to-hot-cap joints can only be made if the materials are chemically compatible at their temperature of use, accommodation for thermal expansion differences are built into the joint, and diffusion problems, such as Kirkendall separation, do not occur with time.

Compatibility tests of $\text{NdSe}_{1.5-x}$ in contact with nickel, tantalum, niobium, and gold from 800° to 1070°C were conducted to select potential hot-cap materials. The results of these trials, as shown in Table 3-24, show MoRe and tantalum to have no apparent reaction with Nd_2Se_3 either as a braze alloy or in diffusion bonding. These materials have no obvious corrosive interaction. Direct contact of nickel against $\text{NdSe}_{1.5-x}$ continues to be questionable.

Differential thermal expansion between materials always exists but should be minimized in any brittle-to-ductile material joint. Measurements of the thermal expansion of a hot-pressed $\text{NdSe}_{1.5-x}$ element (Table 3-23) show that the coefficient of thermal expansion of Nd_2Se_3 is approximately $17.5 \times 10^6/^\circ\text{C}$ and is linear. Being chemically compatible and close in thermal expansion, gold was a prime candidate for use in joining $\text{NdSe}_{1.5-x}$ to potential hot-cap materials.

Several hot-cap-to- $\text{NdSe}_{1.5-x}$ joints were considered in addition to the wire mesh plus a metal- $\text{NdSe}_{1.5}$ graded zone already discussed. Figures 3-20 through 3-22 show these schematically. Some satisfactory joints were made by diffusion-bonding thin foil gold to $\text{NdSe}_{1.5-x}$. This was, in turn, tack-welded to nickel hot and cold caps. This joint was destructively examined and found satisfactory. This was the joint selected to prepare elements and couples. All recent N-type element cap joints were made by metallizing

TABLE 3-23
Nd₂Se₃ THERMAL EXPANSION

Sample No.	Sample Source	CTE^(a) at Room Temperature to 500°C (10⁻⁶ °C)	CTE^(a) at Room Temperature to 900°C (10⁻⁶ °C)
7958-97-1-1	GA	17.60	17.94
7958-97-1-2	GA	16.58	17.14
5192-73-1-1	3M Company	16.20	17.12
5192-73-1-2	3M Company	15.80	16.75
316 stainless steel	Commercial	19.28	20.06
		19.16	19.52
Ref. data		18.51	19.95
ASM handbook		(to 649°C)	(to 816°C)

^(a)Coefficient of thermal expansion.

Fig. 3-17. Nd_2Se_3 hot pressed with W-26/Re wire mesh

Fig. 3-18. Photomicrograph of the graded $\text{Mo/Nd}_2\text{Se}$ and W-26/Re mesh joint of N-type element 7958-84-1

Fig. 3-19. Nd_2Se_3 hot pressed with a Mo-Re cap

**TABLE 3-24
COMPATIBILITY TESTS**

Test No.	Nd ₂ Se ₃ Sample No.	Material 1	Results	Material 2	Results	Temp/Time/Gas (°C/h/)
7958-76-1	7958-62-1	270 Ni	Ni embrittled	205 Ni	Reaction noted	820/22/0.5 atmosphere He
7958-76-2	7958-70-2	270 Ni	Ni embrittled	50/50 Mo/Re	No reaction	800 to 850/23/0.5 atmosphere Ar
7958-77-3	7958-72-2	Ta foil	No reaction	Nb foil	Cap bluish overall, no reaction	820/62/Ar
7958-77-4	7958-73-1	Ta foil	No reaction	Nb foil	Cap bluish overall, no reaction	820/21/Ar
7958-80-5	7958-70-1	MoRe	No reaction	Nb foil	System black neobium brittle	820/66/Ar
7958-80-6	5192-73-2	270 Ni	Reaction not certain	MoRe	No reaction	845/25/Ar
(Samples wrapped in tantalum to remove O ₂ in the specimens that follow)						
7958-87-7	5192-73-2	270 Ni	No reaction	MoRe	No reaction	850/112/Ar
7958-87-8	7958-70-1	270 Ni	No reaction	MoRe	No reaction	845 to 850/92/Ar
7958-89-1	7958-61-2	Au/316 SS	Bonded, no corrosion	Au/Mo	Bonded, no corrosion	1070/5 to 7 min/vacuum

- CONCEPT INITIALLY DEVELOPED WITH SiGe AND Mo
- COMPONENTS CAN BE JOINED WITH A DIFFERENCE IN ΔT
- JOINT CAN ALSO BE BRAZED
- $\text{NdSe}_{1.5}$ IS HELD IN COMPRESSION

Fig. 3-20. Compression hot-cap-to-element joint

- FOIL OR MESH IS SPRING LOADED AGAINST NdSe_{1.5} CYLINDER
- FOIL OR MESH IS BRAZED TO THE NdSe_{1.5}
- Mo OR Ni ION PLATING FACILITATES CURRENT DISTRIBUTION

Fig. 3-21. Compression flexible metal-to-element joint

- MESH IS MORE FLEXIBLE THAN FOIL
- Au GRAZE IS VERY DUCTILE
- FOIL OR MESH CAN BE JOINED TO THE COLLECTOR BY SPOT WELDING

Fig. 3-22. Flexible metal-to-N-element joint

NdSe_{1.5-x} with ion plated nickel, then diffusion-bonding gold to the metallized surface. The gold was tack-welded to a nickel hot cap to complete the hot-cap-to-element joint. Gold-brazed, sweat-fitted iron caps were also evaluated. The Nd₂Se₃ cracked slightly. Program limitations prevented this concept from being examined further. The compression flexible metal-to-element joint was difficult to fabricate. Several samples were prepared, but none had a satisfactory braze joint. No further work on this concept was done.

3.2.4. Preparation of Segmented N Elements

The process for preparing the segmented NdSe_{1.5-x}/PbTe elements as partially developed for Gd₂Se₃/PbTe was as follows:

1. Prepare NdSe_{1.5-x} by the diselenide process.
2. Vacuum hot press NdSe_{1.5-x} with 1700°C, 30-min post-annealing to control the Nd/Se ratio.
3. Ion plate the NdSe_{1.5-x} with PbTe.
4. Hot press PbTe on the PbTe-ion-plated end of the NdSe_{1.5} element.

No difficulties were experienced in preparing the NdSe_{1.5-x}/PbTe-bonded segments. Reproducibility of the hot cap joint still needs to be improved.

REFERENCE

- 3.1. Vickery, R. C., and H. M. Muir, "Anomalous Thermoelectric Properties of Gadolinium Selenide," Nature 190, 336-337 (1961).

4. SELENIDE COUPLE DEVELOPMENT

4.1. TEST COUPLE 7958-109

4.1.1. Fabrication

Figure 4-1 shows the components of the selenide test couple 7958-109. The P element consists of $(\text{Cu,Ag})_2\text{Se}$ and $(\text{Bi,Sb})_2\text{Te}_3$ segments separated by an iron barrier. MoRe is used as the P-element hot cap with a W-26/Re wire mesh in the cap joint. The N element was $\text{NdSe}_{1.471}$, which was diffusion-bonded at the hot cap and cold caps to 0.005-cm (0.002-in.) thick gold foil. The gold foil was, in turn, spot-welded to nickel caps at the outer rim of the gold foil. The cold caps of both elements were laser-welded to nickel radiator buttons, which were soldered to silver cold straps and a BeO insulator disk. The hot caps were laser-welded to nickel collectors, which were diffusion-bonded to nickel collectors. Molybdenum-opacified quartz washers were cut and wrapped around both P and N elements. Alternate layers of quartz paper and nickel foil made up the final insulation around the couple. Thermocouples were attached to the hot cap and cold caps and placed in the gap between the cold cap and the nickel radiator button. The couple was mounted in a ion-pumped vacuum system with the heater elements radiation coupled to the thermoelectric couple. This setup was quite different than previous tests in which the heaters rested on top of the P-element hot cap.

4.1.2. Couple 7958-109 Thermal Gradient Testing

Figures 4-2 and 4-3 show the change in Seebeck coefficient and resistivity measurements for the N elements of couple 7958-109 during heatup, respectively. The results show that above a T of 175°C these thermoelectric properties increase linearly with temperature.

The couple suffered two unplanned shutdowns to ambient temperature during the first 100 test hours. The couple was operated at matched load for 400 h. The P element developed load voltage excursions after 152 test hours which became quite unstable at 190 h, increasing in amplitude and frequency. These load voltage excursions were similar to those reported by 3M Company and had not been observed in previous $(\text{Cu,Ag})_2\text{Se}$ thermal gradient tests.

The resistivity of the P element increased from an average of approximately 9.8 milliohm-cm to 11 milliohm-cm between 300 and 400 test hours. Figure 4-4 shows the resistivities and Seebeck coefficients for the P leg. Resistivities reported for the $(\text{Cu,Ag})_2\text{Se}$ segment are estimates based on an assumed fixed value for the $(\text{Bi,Sb})_2\text{Te}_3$ segment. After 400 test hours, the couple was operated for nearly 200 h open circuit. The resistivity of the P element increased by a factor of five just after the open circuit testing began. The electrical measurements behaved as if there were a loose electrical contact.

Fig. 4-1. Couple 7958-109

Fig. 4-2. Seebeck coefficient as a function of average temperature for N leg of couple 7958-109

Fig. 4-3. Resistivity as a function of average temperature for N leg of couple 7958-109

Fig. 4-4. P leg of couple test 7958-109

The current was briefly reversed to determine if voids had developed at the hot-cap interface which would be filled by copper from the reversed current. After 2 days with reversed current, the couple was again operated with matched load. The reversed current did not lower the resistivity of the P element. The couple was then operated primarily to test the N element. A constant current supply was used to maintain an iL/A value of 1.22 through the N element. The load voltage of the couple was still unstable. The decision was made after 782 test hours to isolate the N leg, which had a very stable operation (as shown in Fig. 4-5), and continue as an element rather than a couple test. After the isolation, the current was increased to maintain an iL/A of 7 through the N element. The N element operated very stably until it was shut down after 918 test hours to make room for another couple test. Examination of this element after test showed that damage was done to the cold cap joint, apparently during gold transport from the cold cap joint into the thermoelectric element. Thus, materials which contain atoms or ions which are readily transported through $NdSe_{1.5-x}$ in an electropotential gradient should not be used on the cold cap end of $NdSe_{1.5-x}$ elements.

Microprobe examination of the P element from couple test 7958-109 showed traces of iron throughout the element resulting from the current reversal or contamination during element fabrication. What appeared to be a swollen portion of the $(Cu,Ag)_2Se$ segment turned out to be an $FeSe_x$ scale. No molybdenum, rhenium, bismuth, antimony, or tellurium were detected in the $(Cu,Ag)_2Se$ segment.

4.2. TEST COUPLE 7958-125

4.2.1. Fabrication

The P leg of couple 7958-125 was fabricated the same as 7958-109. The N leg was segmented with a 0.457-cm-long $NdSe_{1.498}$ segment and a 0.203-cm-long PbTe segment, both 0.318 cm in diameter. Gold foil diffusion-bonded to the $NdSe_{1.498}$ and a nickel cold cap formed the hot cap joint. Iron powder hot pressed to the PbTe segment and tack-welded to the iron cold cap formed the cold cap joint. A 0.025-cm nickel current strap joined the two elements together.

4.2.2. Couple 7958-125 Testing

The segmented element of couple 7958-125 failed when heated to a T_H of 455°C. Examinations of the couple after cooldown show that tensile failure of the $NdSe_{1.498}$ segment had occurred. The strain from the differential expansion between the N and P elements was apparently translated between them through the too stiff collector, as shown in Fig. 4-6. The moment of force from this strain may have also caused some partial damage of the P-element-to-hot-cap joint. The joint between the hot cap and element did not fail.

The P element from couple 7958-125 was electrically isolated from the N element and tested in a thermal gradient. Resistivity changes occurred in this element after 170 h which were analogous to the resistivity changes in the P element of couple 7958-109. Large fluctuations began to occur, and a step increase in resistivity resulted in the P element from approximately 7.5 milliohm-cm to ≥ 35 milliohm-cm. Operating at a T_H of 755°C, the segmented $(Cu,Ag)_2Se/Fe/(Bi,Sb)_2Te_3$ element has maintained a stable Seebeck coefficient measurement of $-220 \mu V/^\circ C$ for 380 test hours. The cap-to- $(Cu,Ag)_2Se$ joint apparently failed, probably because of differential expansion between the N and P legs of the couple which were transmitted by the too stiff collector.

Fig. 4-5. N leg of couple test 7958-109

Fig. 4-6. Transfer of stress through a too stiff current strap

4.3. TEST COUPLE 7958-133

A segmented couple 7958-133 was completed, as shown in Fig. 4-7. Copper used for the collector was nickel plated to provide elevated temperature stiffness. It was also coated with an organic liquid base spray coat of graphite to improve its emissivity.

The couple was put on test and heated to nominal test temperatures of $T_H = 750^\circ\text{C}$ and $T_C = 160^\circ\text{C}$. The corners of the collector gradually sagged as it was heated. Attempts to compensate for the sagging only aggravated it. As the heat source temperature increased, the region near the element hot cap became hotter and the collector corner sagged more. The greater the corner sag, the colder and stiffer the corner tips became. The corners unavoidably touched the rigid multifoil insulation. The slightly hotter collector on the N side of the couple was the first to touch the insulation. Slight power fluctuations caused small amplitude thermal cycles to occur. Locked to a fixed length at high temperature, the N element failed at the gold-to- $\text{NdSe}_{1.5-x}$ joint in one of the cooling portions of the mini-thermal cycle. The P element continued to function. The couple was then cooled to room temperature for a more detailed examination. The tensile load from the differential thermal expansion of materials was transmitted from the insulation to the P-type element through the stiffened collector. This caused the P element to fail in the $(\text{Bi,Sb})_2\text{Te}_3$ layer.

Fig. 4-7. Module test 7958-133

5. SUMMARY - ISOTEC TECHNOLOGY PROGRAM

Experimental work on selenide thermoelectric materials development has now been terminated.

1. Segmented P-Type Selenide Material

- a. $(\text{Cu,Ag})_2\text{Se}$ was reproducibly hot pressed into P-type thermoelectric material.
- b. Metallurgical contacts between $(\text{Cu,Ag})_2\text{Se}$ and MoRe hot caps were developed through a WRe wire mesh joint. Graded $(\text{Cu,Ag})_2\text{Se}/\text{Fe}$ cold cap joints were also developed.
- c. Operation of $(\text{Cu,Ag})_2\text{Se}$ at hot cap temperatures above 700°C requires vaporizing Se_2 to be suppressed.
- d. Current flow through P-type $(\text{Cu,Ag})_2\text{Se}$ significantly increases Se_2 vaporization.
- e. Vapor suppression in $(\text{Cu,Ag})_2\text{Se}$ was accomplished by a multiple baffle system which consisted of an ion plated glass plus Nd_2O_3 coating, a quartz sleeve mechanical barrier, and mechanical baffling by molybdenum-opacifier quartz paper washers.
- f. Techniques were developed for bonding $(\text{Cu,Ag})_2\text{Se}$ to PbSnMnTe-3P and $(\text{Bi,Sb})_2\text{Te}_3$ to form more efficient doubly and triply segmented P-type thermoelectric elements.
- g. Thermal gradient testing of a segmented P-type, $(\text{Cu,Ag})_2\text{Se}/\text{Fe}/(\text{Bi,Sb})_2\text{Te}_3$ element has exceeded 6300 h in a $755^\circ\text{C}/160^\circ\text{C}$ thermal gradient at an iL/A of 7.4 A/cm through the $(\text{Cu,Ag})_2\text{Se}$ segment.

2. Segmented N-Type Selenide Material

- a. Techniques were developed for preparing $\text{GdSe}_{1.5-x}$ and $\text{NdSe}_{1.5-x}$.
- b. $\text{GdSe}_{1.5-x}$ was found to undergo cubic to orthorhombic transformations at temperatures of 1000° to 1100°C with slight volume and thermoelectric property changes.
- c. Techniques were developed for controlling and monitoring the Se/Nd ratio in $\text{NdSe}_{1.5-x}$. This was found to be critical to the friability and thermoelectric properties of this material.
- d. Processes were developed for hot pressing $\text{GdSe}_{1.5-x}$ and $\text{NdSe}_{1.5-x}$ into elements.
- e. A process for making a hot cap contact to $\text{NdSe}_{1.5-x}$ was developed using a gold foil intermediate diffusion-bonded to the $\text{NdSe}_{1.5-x}$ and welding the gold to the nickel hot cap.

- f. Techniques were developed for joining $\text{NdSe}_{1.5-x}$ to 2PbNTe to form more efficient segmented N-type elements.
 - g. Life testing of a segmented N element in a $750^\circ\text{C}/100^\circ\text{C}$ thermal gradient showed stable thermoelectric properties despite thermal cycles and variations in current flows in a 918-h test (This test was terminated to life test a couple).
3. All-Bonded Selenide Couple
- a. An all-bonded selenide couple can be fabricated. The elements are strong enough to withstand thermal shocks and handling during thermocouple attachments, laser welding of the hot cap to the collectors, and silver soldering of the cold end radiator buttons and cold straps.
 - b. Elements pulled apart in short-term, thermal gradient life tests. Their failure was due to differential-thermal expansion-induced stresses transferred between elements through the current strap. Funding ended before this problem could be properly examined. From previous experience, this should not be a difficult problem to overcome.

APPENDIX A
A PHENOMENOLOGICAL EQUATION TRANSPORT
MODEL OF THE STABILITY OF P-TYPE $(\text{Cu,Ag})_2\text{Se}$
AS A THERMOELECTRIC MATERIAL