**Post-Test Analysis of Components
from Selenide Isotope Generator
Modules M-7, M-15, and M-18**

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POST-TEST ANALYSIS OF COMPONENTS FROM SELENIDE ISOTOPE
GENERATOR MODULES M-7, M-15, AND M-18

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ABSTRACT

Several critical components removed from SIG (Selenide Isotope Generator) thermoelectric modules M-7, M-15C, M-15D, and M-18 were examined. These modules failed to show the predicted stability and conversion efficiency. Understanding the degradation and identifying means for preventing it necessitated detailed post-test examinations of key parts in the modules.

Steel springs, which provided pressure for contacts at the hot and cold ends of P- or N-legs, relaxed more than expected. Beryllium oxide insulators had dark deposits that caused electrical shorts. The $\text{GdSe}_{1.49}$ N-leg exhibited cracking. The $(\text{Cu,Ag})_2\text{Se}$ P-leg lost weight or sublimed excessively in module M-7 and more than expected in the other modules.

Analyses of the steel springs indicated that the Cr-Si steel was marginal for the design conditions. Reactions with selenium vaporized from the P-leg might have aggravated spring load relaxations. Higher temperature alloys that resist selenium attack should be used for springs. Examination of BeO disks revealed braze contamination on as-made samples. The brazing alloy reacted with selenium evaporated from the P-leg to form a conductive layer, causing the observed electrical shorting. Proper control of the brazing process to eliminate contamination is necessary for BeO disks to maintain insulation during service. Analyses of cracked N-legs showed a massive phase transformation in the hot end and massive scale at surface cracks. As-made N-legs have many defects including internal flaws, surface cracks, large pores, pore agglomerates, large grains, and fine grain agglomerates. Such defects provided stress concentrations and crack initiation sites. Crack propagation was due to a combination of thermal stresses generated from nonlinear radial and axial thermal gradients and inhomogeneities and the stresses produced by the phase transformation. To solve the cracking problem requires fabrication of N-legs that are homogeneous, defect-free, and thermodynamically stable at service temperatures. Isostatic hot-pressing of suitable powders at appropriate temperatures may serve this purpose. Post-test studies of P-legs indicated gaps between the wrap and the hot part of the P-leg as well as localized cracks in the wrap, which could be eliminated by proper drying and removal of organic binders in the wrap and possibly by the use of thermal-expansion-matched wrap or seal materials. The bond between the W-Re top cap or partition and the P-leg should be strengthened so that handling or assembly operations will not cause bond separation. Sublimation of the $(\text{Cu,Ag})_2\text{Se}$ P-leg may be minimized by using a proper glass seal in the hot region.

In summary, this work indicated that the power output degradation of these modules was related to several extrinsic factors that prevailed at the time of their construction. These include improper selection of materials, inadequate brazing process, unsatisfactory fabrication, insufficient knowledge about equilibrium phase relationships, a lack of appropriate quality assurance procedures and specifications, and insufficient seal to suppress sublimation. These problems, however, are by no means insurmountable.

INTRODUCTION

Recently, the ground demonstration system (GDS) and several thermoelectric modules including M-7, M-10, M-12, M-15C, M-15D, and M-18 of the Selenide Isotope Generator for the 1981 Galileo Mission* all showed unexpected power output declines, increases in internal resistance, and erratic power outputs after various test durations.¹⁻⁴ These thermoelectric modules had different hardware designs and were tested under different thermal and environmental conditions to verify the adequacy of hardware, establish a data base of long-term stability, and define the degradation rate by accelerated tests. Among these modules, M-18 is the closest to the present flight system design. Table 1 summarizes the test conditions and operating parameters of these modules along with the most recent design of the flight system. These modules failed to meet the projected power output and life long before the planned termination of tests and caused serious concern about the past and present designs and materials of the SIG thermoelectric modules. Typical pretest thermoelectric modules are sketched in Fig. 1. Dissassembly of these thermoelectric modules after test revealed dramatic and totally unexpected alterations in materials and hardware. Virtually none of these problems were recognized as potential problem areas at the numerous review meetings held before September 1978 and attended by representatives of various organizations. The copper follower at the cold end of the P- or N-leg adhered to the aluminum rail.

*Note: In January 1979, the U. S. Department of Energy decided to use the Silicon-Germanium Generator for the 1981 Galileo Mission because of problems with the performance of the selenide thermoelectric converter of the Selenide Isotope Generator.

Table 1. Test Conditions of SIG Converter Modules and Related System Designs

Module	Number of Couples	Steady-State Temperature, °C		Environment	P-Leg Features	N-Leg Features	Follower	Test Time	
		Hot End ^a	Cold End					(Ms)	(h)
M-7	10	850	125 ^b	101 kPa Xe (1 atm)	Partitioned Unwrapped	Gd foil Ta gimbal	Square	68.4	19,000 ^c
M-15C	2	900	150	Vacuum	Partitioned Wrapped Large cap	Fe foil Ta gimbal	Square	3.96	1,100
M-15D	2	900	150	Vacuum	Partitioned Wrapped Thick cap	Fe foil Ta gimbal	Square	3.96	1,100
M-18	18	850	150	Vacuum	Partitioned Wrapped Thick cap	Gd foil Ta gimbal	Square	6.84	1,900
ATT583	6	850	150	Vacuum	Unpartitioned Wrapped Thick foil	Ni foil Mo gimbal	Compliant	3.6	1,000
GDS	168	850	150	40% Xe, 60% He 91 kPa (0.9 atm)	Partitioned Unwrapped	Gd foil Ta gimbal	Square	6.8	1,900
Flight Systems	336	825	150	Vacuum	Unpartitioned Wrapped Stepped cap Mo gimbal Pt foil	Ni foil Mo gimbal Segmented with PbTe at cold part	Compliant	180	50,000

^aHeat-up rate 0.028°C/s (100°C/h) except for Module M-7, which was less.

^b200°C for 0.774 Ms (215 h).

^c11,000 h before and 8000 h after open circuit.

Fig. 1. One Segment of a Typical SIG Thermoelectric Module.

Steel springs relaxed excessively. Dark deposits appeared on the BeO insulating disks, cold current straps, and followers. Misalignment of P-legs or N-legs with hot shoes or cold current straps occurred and consisted of lateral translation and/or tilting. Copper precipitated at the cold end of the P-legs; $(\text{Cu}, \text{Ag})_2\text{Se}$ bridged around the tungsten-rhenium partition; the hot ends of both P-leg segments (partitioned) bullet-nosed, mushrooming just below the partitions, and the P-leg hot segment had a larger diameter than the cold segment. The N-legs had longitudinal and transverse cracks, and orange-colored rings were formed around the upper portions. Following disassembly of thermoelectric modules, we began to seek the cause of failures and potential solutions. It is useful to analyze materials and hardware that have been used in the failed thermoelectric modules and exhibit accelerated degradation or unusual appearance. The analytical results provide insight into reasons for power output

decline and guide development, selection, and correct use of materials to improve performance. The materials analyzed in this report consist of four categories: steel springs, BeO insulating disks, $\text{GdSe}_{1.49}$ N-legs, and $(\text{Cu,Ag})_2\text{Se}$ P-legs.

DESCRIPTION OF COMPONENTS

Steel Springs

The springs are important and critical components of thermoelectric modules because the electrical contact at the hot and cold ends of the elements is achieved primarily by the pressure exerted on the copper follower through the preset springs at the cold end. Therefore, loss of load, load relaxation, or excessive creep of the springs could lead to poorer contact between the current straps and thermoelectric elements, thus increasing module internal resistance and decreasing power output. The steel springs used in thermoelectric modules M-7, M-15C, M-15D, and M-18 are fabricated of ASTM A 401 chromium-silicon steel. It contains⁵ 0.5-0.6 wt % C, 0.5-0.8 wt % Mn, 1.2-1.6 wt % Si, and 0.5-0.8 wt % Cr, and the balance is Fe. These springs relaxed severely. The relaxation ranged from 90% to 15% for different thermoelectric modules. Dark deposits were also formed on the surfaces of the spring wires.

BeO Insulators

The BeO disk was used in the cold end assembly as an electrical insulator as well as a thermal conductor. As-made BeO disks were metallized with molybdenum-manganese on the two flat faces, which were subsequently furnace brazed or soldered to the copper current straps with a Ag-Cu or Pb-Sn-Ag brazing alloy. The BeO disks must maintain electrical insulation during converter operation because any electrical shorts developed across the BeO disk may cause electrical subsystem failures and ultimately converter power failure. The dark deposits on the edges of some of the BeO disks disassembled from module M-18 caused shorting.

GdSe_{1.49} N-Legs

The N-leg, which is a key component of the SIG thermoelectric converter, is a cold-pressed and sintered composition, GdSe_{1.49}, with densities ranging from 97% to 98% of theoretical (7.3 Mg/m³). Cold-pressing involves dry compacting GdSe_{1.49} powder with a particle size distribution ranging from submicron to about 50 μ m in a WC-lined hardened tool steel die under uniaxial pressure without use of binders. The cold-pressed green body typically has a density 80% of theoretical. It is sintered in a tungsten resistance-heated furnace at 1600 to 1650°C under 101 kPa He for about 11 ks (3 h). The GdSe_{1.49} powder is obtained by ball-milling ingots cast from melts that had been derived from a sponge-like GdSe_{1.49} material synthesized via a low-temperature reaction of high-purity gadolinium with selenium in a vitreous carbon crucible placed in an evacuated quartz capsule at about 1000°C for about 0.6 Ms (170 h).

GdSe_{1.49} ingots are cast in a vitreous carbon crucible. The low-temperature-reacted GdSe_{1.49} material is melted in a vitreous carbon crucible in a tungsten resistance-heated furnace at 1800°C under 101 kPa He. Ball-milling is performed dry with WC balls and a WC-lined stainless steel container. An insulating second phase, GdSe_{1.50}, was reported^{3,4} to be present in the large GdSe_{1.49} ingots. The GdSe_{1.50} phase has a lower melting point than the substoichiometric GdSe_{1.49} and probably forms a liquid during the sintering of GdSe_{1.49} and aids its densification^{3,4}. However, the GdSe_{1.50} forms a continuous interconnected insulating layer surrounding the GdSe_{1.49} grains and causes a high extraneous resistance in the otherwise homogeneous GdSe_{1.49} N-legs. It should be noted that the GdSe_{1.49} in the form of the low-temperature-reacted material is an orthorhombic phase (U₂S₃ structure), whereas the cast ingots, milled powders, and sintered pellets have a cubic lattice (Th₃P₄ structure), which reportedly transforms to the orthorhombic lattice accompanied by a volume expansion during long anneals at 600° to 900°C in vacuum.⁶ The cylindrical surfaces of the as-sintered N-legs are then smoothed with emery paper. In the present flight system design, the hot end of the N-leg is coated with sputtered nickel and bonded to a nickel

foil, which in turn is in contact with a molybdenum gimbal. Earlier designs used a gadolinium foil and a tantalum gimbal, and in modules M-15C and M-15D, iron foils were accidentally used.

All the N-legs in modules M-7, M-15C, M-15D, and GDS and one-third of the N-legs in module M-18 had longitudinal and/or transverse surface cracks. In the module ATT583, the use of molybdenum gimbals and compliant copper followers imparted a certain mobility to the N-leg assembly. This perhaps reduced the severity of mechanical and thermal stresses to a certain extent and thus caused less cracking, as evidenced in the six-couple cold-end temperature difference test ATT583. Arguments were made that even cracked N-legs could be used in the generator because N-leg cracking did not directly cause converter failure or even significant power degradation. One single-couple vibration test demonstrated the vibration survival of N-legs that had been operated in a typical temperature gradient. However, the many potential generator problems resulting from N-leg cracking are considered to be significant. Cracking is considered a very serious problem from the viewpoint of materials performance, durability, and reliability. The present status of N-leg material processing is considered by the authors to be less than satisfactory, and much development is necessary before the $\text{GdSe}_{1.49}$ can be considered as an engineering material. The present design of the 1981 SIG flight system calls for a segmented N-leg with a $\text{GdSe}_{1.49}$ hot segment and a PbTe cold segment in order to alleviate some of the aforementioned problems. The potential advantage of this concept is twofold: to avoid the $\text{GdSe}_{1.49}$ cracking, which seems to heal in the hotter region but not in the cooler region, and to utilize the well-developed PbTe material, which has a higher efficiency than $\text{GdSe}_{1.49}$ in the temperature range from 150 to 400°C. Thermoelectric modules using the segmented N-legs are scheduled to be tested by the contractor starting in May 1979.

$(\text{Cu},\text{Ag})_2\text{Se}$ P-Legs

In the SIG converter P-legs are made of $(\text{Cu},\text{Ag})_2\text{Se}$. They are fabricated by casting a $(\text{Cu},\text{Ag})_2\text{Se}$ melt into a semiconductor-grade graphite mold, which is then slowly cooled under 101 kPa (1 atm) forming gas

(5–15% H₂ in N₂). The (Cu,Ag)₂Se melt is derived from elemental Cu, Ag, and Se in a vitreous carbon crucible in an evacuated quartz capsule held at 1200°C for a few hours. The residual stresses were minimized and the microstructure of the cast P-leg was controlled by using proper molds and vertical casting. To minimize the sublimation of P-leg material during operation, a baffle consisting of several wraps of Astroquartz* yarns impregnated with ground Min-K† powder was wound around the cylindrical surface of the P-leg. In the flight system design, a tungsten-rhenium stepped foil is used as a seal at the hot end. A thick tungsten-rhenium foil or oversized foil was used in modules M-15C, M-15D, and M-18. Early designs used a tungsten-rhenium foil partition about one-third the length of the P-leg from the hot end to control the local selenium chemical potential and thereby reduce the sublimation.⁷ The tungsten-rhenium foil partition also served as a barrier for the migration of copper and silver under a thermal gradient. An equivalent weight loss of about 16 mg per P-leg for 3.6 Ms (1000 h) was reported in module M-18, which used top-capped, partitioned, and wrapped P-legs. The relationship between weight loss due to P-leg sublimation and the converter power output decline was 6 W(e) power loss for 50 mg weight loss. Because of the volume change associated with the phase transformation⁷ of (Cu,Ag)₂Se at about 110°C, the cold end of the P-leg should be operated above 130°C, and fewer than 20 thermal cycles should encompass 110°C to prevent cracking and internal resistance buildup. In the present study, we analyzed as-made P-legs and tested P-legs from disassembled module M-18. Thermoelectric module tests on unpartitioned, top-capped, wrapped, and contact-improved P-legs will commence in May 1979.

OBJECTIVES

ORNL has been active in the SIG flight program as well as the technology program. Thermal insulations and refractory metals include areas in which we have been involved.⁸ As a member of the SIG flight program, we began post-test investigations on materials from various disassembled

*Astroquartz, product of J. P. Stevens Co., New York.

†Min-K, product of Johns-Manville Co., Denver, Colo.

thermoelectric modules to identify the causes for the observed test anomalies and failures to provide viable constructive corrective actions. Results presented in this report include chemistry, metallography, scanning electron microscopy, electron microprobe, microhardness, and ion microprobe analyses of selected materials plus interpretation of material degradation mechanisms based on results from these analyses and other observations reported in the literature. The analytical procedures are presented in the Appendix.

The objective of the present work is to identify the basic physical and chemical changes underlying the degradation processes operative in the steel springs, BeO disks, $\text{GdSe}_{1.49}$ N-legs, and $(\text{Cu,Ag})_2\text{Se}$ P-legs. We attempt to delineate the intrinsic and extrinsic nature of these degradations; that is, whether the problems of excessive converter power decline are due to some fundamental incurable nature of the key materials in the converter or extrinsic factors — such as material selection, fabrication, and contamination — which are solvable in an engineering sense. The ultimate goal of the present study is to provide input to DOE for its analysis and assessment of the potential for success of the SIG system.

SPECIMEN HISTORY

Steel Springs

Wire diameters ranging from 1.55 to 1.04 mm (0.059–0.041 in.) have been specified for the N-leg and P-leg springs. The hottest spring temperature can be estimated from the cold-end temperature shown in Table 1. The temperature varied about 30°C across the length of the spring during service. Except for the springs in module M-7, which might have been overheated to about 200°C for about 0.77 Ms (215 h), all the springs were at about 150°C. Table 2 lists the steel springs and their histories and relaxations. The load relaxations were measured at 3M Company by comparing the force required to compress the free-standing post-test springs to the original compressed length with the initial force corresponding to the original compressed length.

Table 2. Histories and Relaxations of Steel Springs

Sample	History	Relaxation
Cr-Si Virgin	Tempered	
Cr-Si M-7-11	200°C for 0.77 Ms (215 h) and 125°C for 67.6 Ms (18,785 h) in module M-7, 689 MPa (100 ksi)	90%
Cr-Si M-15D-1A	150°C for 3.96 Ms (1100 h) in module M-15D, 689 MPa (100 ksi)	20%
Cr-Si Assembly 2 No. 9	175°C for 0.90 Ms (250 h) in air, 517 MPa (75 ksi)	4%
Cr-Si Assembly 3 No. 11	175°C for 0.90 Ms (250 h) in vacuum with 1.33 mPa (1.00 E-05 torr) Se partial pressure, 517 MPa (75 ksi)	8%
17-7PH Virgin		
17-7PH Assembly 3 No. 9	175°C for 0.90 Ms (250 h) in vacuum with 1.33 mPa (1.00 E-05 torr) Se partial pressure, 689 MPa (100 ksi)	7%

BeO Insulators

The BeO insulators we analyzed were used in the thermoelectric module M-18. The samples were labeled and their room temperature electrical resistances are listed in Table 3. The odd numbers refer to P-leg and the even numbers to N-leg BeO assemblies. It should be noted that all six samples had dark deposits, but two of them remained insulating while the other four became conductive. The temperature of the copper current strap was monitored by a spot-welded thermocouple during module tests. Assuming that during service the temperature of the BeO disk was not too different from that of the copper current strap, the BeO disk temperature was raised from room temperature to 150°C at a rate much less than 0.028°C/s (100°C/h) and then kept at 150°C for about 6.8 Ms

(1900 h). The maximum and minimum temperatures during operation were 179 and 136°C, respectively. A copper-silver brazing alloy was used in these BeO assemblies.

Table 3. Room Temperature Electrical Resistance of Tested BeO Disks

Sample	Resistance (Ω)
As-made	∞
M-18-12B	∞
M-18-10B	∞
M-18-11A	15
M-18-14A	3000
M-18-2B	550
M-18-17A	10

GdSe_{1.49} N-Legs

We received ten N-legs from the 3M Company. These include one as-made N-leg (Lot N2651 T-6-19), one uncracked N-leg from the six-couple cold-end temperature difference test module ATT583 (Lot N 2651 T-4-10), three cracked and one uncracked N-legs from module M-18, one cracked N-leg from module M-15C, one cracked N-leg from module M-15D, and two cracked N-legs from module M-7. Table 4 lists these samples, their thermal histories, and the conditions of their surfaces upon visual examination. Except for module M-7, in which xenon was used as the cover gas, all the modules were under vacuum. The design load on the N-leg in all modules was 2.07 MPa (300 psi). The hot junction heat up or cool down was programmed at less than 0.028°C/s (100°C/h). Electrical current was increased from 0.10 A at room temperature to 4.0 A or the matched load condition when the hot junction temperature arrived at the design steady-state value. The rate of the current increase or decrease was less than 0.14 mA/s.

Table 4. Visual Examination Results and Histories of As-Made and Tested GdSe_{1.49} N-Legs

Sample	Module	Visual Appearance	Junction Temperature, °C		Module Test Duration		Hot End	
			Hot	Cold	(Ms)	(h)	Foil	Gimbal
As-made (N2651, T-6-19)		No cracks						
M-7-17	M-7	Broke into pieces	850	120-130 ^a	68.4	19,000	Gd	Ta
M-7-19	M-7	Broke into pieces	850	120-130 ^a	68.4	19,000	Gd	Ta
M-15C-2B	M-15C	Longitudinal and lateral cracks	890-925	146-163	3.96	1,100	Fe	Mo
M-15D-2B	M-15D	Longitudinal and lateral cracks	883-907	130-157	3.96	1,100	Fe	Mo
M-18-2A	M-18	Longitudinal and lateral cracks	850(877-837)	150(136-179)	6.84	1,900	Gd	Ta
M-18-2B	M-18	Longitudinal and lateral cracks	850(877-837)	150(136-179)	6.84	1,900	Gd	Ta
M-18-8A	M-18	No cracks	850(877-837)	150(136-179)	6.84	1,900	Gd	Ta
M-18-18A	M-18	Broke into pieces	850(877-837)	150(136-179)	6.84	1,900	Gd	Ta
ATT583 (N2651, T-4-10)	ATT583	No cracks	850	150	3.60	1,000	Ni	Mo

^aExcept 200°C for 0.77 Ms (215 h).

(Cu,Ag)₂Se P-Legs

Two as-made, partitioned, unwrapped P-legs and two partitioned, top-capped, wrapped P-legs from disassembled module M-18 were received. The transient and steady-state temperatures of the two P-legs removed from module M-18 were estimated to be the same as those of the N-legs listed in the previous section. The design pressure on the P-leg was 1.04 MPa (150 psi). The environment was vacuum and the average weight loss of the wrapped, top-capped P-legs was calculated to be 16 mg for an equivalent service life of 36 Ms (10,000 h) for flight systems.

RESULTS

Steel Springs

Chemical compositions of the springs were determined in several ways. The surface of some of the samples was subjected to x-ray analysis by means of the EDX attachment at the time of the scanning electron microscope (SEM) examination. Pieces of unmounted spring were submitted for carbon analysis by vacuum fusion and for spectrographic analysis for other alloying elements and impurities. Selected samples were examined in both the electron and ion microprobes, and semiquantitative measurements were made with these machines.

The results of SEM examinations of the spring surfaces are shown in the following. The surface of a virgin sample of chromium-silicon steel is shown in Fig. 2, the surface of a sample tested in module M-15D for 3.96 Ms (1100 h), M-15D-1A, is shown in Fig. 3, and the surface of sample M-7-11, tested for 68 Ms (19,000 h), is shown in Fig. 4. Energy-dispersive x-ray (EDX) analysis results, shown in Fig. 5, indicate that significant amounts of selenium were present on all examined areas of the spring exposed for 3.96 Ms (1100 h), M-15D-1A, but only a small amount of selenium was found on the sample exposed 68 Ms (19,000 h), M-7-11, and none on the virgin material. One sample of the 17-7 PH steel was examined with the SEM and EDX system. Figure 6 shows that this sample, which had been exposed in a selenium-containing environment for 0.90 Ms (250 h), had a small amount of selenium on the surface.

Fig. 2. Scanning Electron Micrograph of Natural Surface of Virgin Chromium-Silicon Steel Spring.

The results of the chemical analyses are given in Table 5 and compared with specifications for the two alloys. It is evident that all material analyzed satisfied the compositional requirements.

The electron microprobe was used to determine the constituents of the surface layer on the chromium-silicon steel sample from module M-15D. The area examined is compared in Fig. 7 with maps of the iron and selenium. The EDX spectra of chromium-silicon steel, both virgin and that exposed for 0.90 Ms (250 h) to selenium, are shown in Fig. 8. Any selenium present is below the detectable limit.

The ion microprobe was used to examine a spring from module M-15D, which operated 3.96 Ms (1100 h). The center coils of this spring appeared to have relaxed more than the outer coils. We analyzed spectra from both the center and near the edge of one of the relaxed coils and near the edge of one of the more normal end coils. The mass spectra are shown in Fig. 9. No selenium is apparent on any of the spectra, but it should be noted that the ion microprobe mass analysis is not especially sensitive to selenium. The ion microprobe was also used to make 400- μ m line scans across one of the relaxed center coils and across one of the

Fig. 3 Scanning Electron Micrographs of Natural Surface of M-15D-1A Chromium-Silicon Steel Spring. (a) (b) Two magnifications. (c) Inside of coil.

Fig. 4. Scanning Electron Micrograph of Natural Surface of M-7-11 Chromium-Silicon Steel Spring.

end coils. The area covered by the scans went from the edge to near the center of each wire examined. The analyses, which are shown in Fig. 10, were made for ^{12}C , ^{27}Al , ^{28}Si , ^{52}Cr , ^{55}Mn , and ^{56}Fe . The aluminum signal was very erratic across the sample, but we believe that was because pieces of polishing compound stuck in the sample. Both aluminum and silicon showed peaks at the surface, but we believe this was also related to the polishing compound. Otherwise, the concentrations of all elements checked were quite uniform.

Physical properties of the springs were measured to see if the relaxation could be related to some measurable property change in the steel. The diameter of four of the springs was measured, and the results of the measurements and a comparison based on exposure conditions are given in Table 6. The four samples we examined showed no clear correlation between exposure time and the ratio of the minimum diameter to the nominal diameter. Apparently some of the springs were significantly undersize. The effect of a reduction in wire diameter on the load-bearing properties of the spring will be covered in the discussion section of this report.

Fig. 5. Energy-Dispersive X-Ray Spectra of Chromium-Silicon Steel Springs. (a) Virgin spring. (b) Turn 1 of M-15D-1A spring. (c) Surface deposit on M-15D-1A spring. (d) Turn 1 of M-7-11 spring. (e) Turn 2 of M-7-11 spring. (Cu and Zn were from brass sample holder).

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Fig. 6. Steel Spring of 17-7 PH, Assembly 3 No. 9. (a) Scanning electron micrograph. (b) Energy-dispersive x-ray spectrum of turn 1. (c) Spectrum of turn 2.

Table 5. Chemical Analyses^a of Springs Compared with Specifications

Element	Chromium-Silicon Steel				17-7 PH Steel		
	Virgin Material	M-7-11	Assembly 3 No. 11	Specified	Assembly 3 No. 9	Virgin Material	Specified
Al, wt %	<0.02	<0.02	<0.02		1	1	0.75-1.50
B, ppm	20	20	20		10	20	
C, wt %	0.65	0.62		0.5-0.6			0.09 max
Co, wt %	<0.02	<0.02	<0.02		0.15	0.15	
Cr, wt %	0.8	0.7	0.6	0.6-0.8	17.8	17.5	16-18
Cu, wt %	0.05	0.03	0.03		0.35	0.35	
Fe	major	major	major	balance	major	major	balance
Mn, wt %	0.6	0.8	0.7	0.6-0.8	0.6	0.6	1.0 max
Mo, wt %	0.6	0.8	0.7		0.6	0.6	
Ni, wt %	0.2	<0.02	0.1		8.0	7.5	6.5-7.75
Se, ppm							
etched	<1	<1	<1		<1	<1	
unetched	<1	~5			10-500	<1	
Si, wt %	1.4	1.3	1.5	1.2-1.6	0.4	0.4	1.0 max
Ti, wt %	<0.02	<0.02	<0.02		0.08	0.09	
V, wt %	<0.02	<0.02	<0.02		0.05	0.05	

^aSpectrochemical, except for C, which was by vacuum fusion.

Fig. 7. Metallography and Electron Microprobe Analysis Identified FeSe_x on Surfaces but not Bulk of M-15D-1A Cr-Si Spring. 1000 $\times$.
(a) Optical micrograph. (b) Iron scan. (c) Selenium scan.

Fig. 8. Energy-Dispersive X-Ray Spectra of Chromium-Silicon Steel. (a) Virgin material. (b) Material exposed 0.90 Ms (250 h) to selenium in Assembly 3 No. 11. Note absence of selenium.

Fig. 9. Ion-Microprobe Mass Spectra of Coils of Spring Sample from M-15D. (a) Center of collapsed coil. (b) Edge of collapsed coil. (c) Edge of noncollapsed coil.

Fig. 10. Ion Microprobe Line Scan of Coils of Spring Sample from M-15D. (a) Collapsed coil. (b) Noncollapsed coil.

Table 6. Summary of Wire Diameter Data for Chromium-Silicon Steel Springs

Sample ^a	Exposure		Diameter, mm (in.)		Measured Nominal
	(Ms)	(h)	Minimum Measured	Nominal	
Virgin	0	0	1.38 (0.0545)	1.42 (0.056)	0.97
Assembly 3 No. 11	0.90	250	0.993 (0.0391)	1.04 (0.041)	0.95
M-15D-1A	3.96	1,100	0.991 (0.0390)	1.04 (0.041)	0.95
M-7-11	68.4	19,000	1.33 (0.0522)	1.32 (0.052)	1.00

^aIn modules M-1 through M-10, the specified wire diameters for the N-leg and P-leg springs are 1.32 mm (0.052 in.) and 1.14 mm (0.045 in.), respectively.

Microhardness measurements were made on all the springs that were examined in this study. Results are presented in Table 7. The springs that were aged longer and had the most relaxation also clearly had the lowest average hardness. Each spring showed some variation in hardness, but the variations were random and did not indicate a surface hardening or softening effect.

Table 7. Hardness of Springs

Specimen	Hardness at Each Position, DPH			Approximate Average Rockwell C Hardness
	Edge	Center	Edge	
<u>Chromium-Silicon Steel</u>				
Virgin	527	551	539	52
M-7-11	452	472	462	46
Assembly 2 No. 9	564	564	539	53
Assembly 3 No. 11	564	564	578	54
M-15D-1A	409	462	462	45
<u>17-7 PH Steel</u>				
Virgin	435	462	539	48
Assembly 3 No. 9	482	551		53

All samples were mounted in epoxy, polished, and examined metallographically. Fig. 11 shows photomicrographs of the edges of four of the springs. Some of the springs had an observable surface layer, but the thickness of the surface layer does not obviously correlate with the exposure time. Two unetched samples are shown in Fig. 12 at higher magnification to highlight surface features. As part of the metallographic examination, three samples were etched in nital to reveal the microstructure of the wires. The tempered martensitic structure of chromium-silicon steel is apparent in Fig. 13. Two of the springs were repolished then etched in a picral-HCl solution to reveal any retained ferrite. Figure 14 shows that at most only a small amount of ferrite was present.

Photomicrographs of the two 17-7 PH steel samples (Fig. 15) revealed internal cracks in both samples. This cracking probably occurred during fabrication of the springs and suggests that quality control procedures used by the contractor were not adequate for procurement of satisfactory springs.

BeO Insulators

Figure 16 shows an as-made BeO assembly, which has a Ag-Cu brazing alloy at the top and bottom flat faces of the BeO disk. It should be noted that a more recent design replaces the square follower in Fig. 16 by a compliant follower, and the Ag-Cu brazing alloy is replaced by a lower temperature Pb-Sn-Ag brazing alloy. Figures 17 through 22 show the tested BeO specimens taken from module M-18. A striking feature is the dark deposits on the cylindrical surfaces of the BeO disks. Polished sections of cutaways through the dark deposits were examined with optical microscopy. Microstructures of an as-made BeO disk and a typical shorted BeO disk are shown in Fig. 23. There was a columnar compound growing on the surface of the shorted BeO disk and copper hardware. The visible cracks in the as-made and tested BeO disks may have been introduced during their fabrication. Results of elemental mapping by electron microprobe wavelength dispersive analysis are shown in Figs. 24 and 25. The silver distribution in the dark deposits on shorted BeO disks was nonuniform, although the silver-containing compound could have formed a

Fig. 11. As-Polished Chromium-Silicon Steel Springs. (a) Virgin spring. (b) From assembly 3 No. 11. (c) From assembly 2 No. 9. (d) From M-15D-1A.

Fig. 12. High Magnification of As-Polished Chromium-Silicon Steel Springs. (a) From assembly 3 No. 11. (b) From M-15D-1A.

Fig. 13. Chromium-Silicon Steel Springs Etched with Nital to Show Tempered Martensitic Structure. (a) Virgin spring. (b) From M-15D-1A. (c) From M-7-11.

Fig. 14. Chromium-Silicon Steel Springs Etched with Picral and HCl to Reveal Ferrite. (a) Virgin spring. (b) From assembly 2 No. 9. (c) From M-15D-1A

Fig. 15. As-Polished 17-7 PH Steel Springs. (a) Virgin spring.
 (b) From assembly 3 No. 9.

Fig. 16. As-Made BeO Assembly.

Fig. 17. Beryllium Oxide Disk from M-18-12B.

Fig. 18. Beryllium Oxide Disk from M-18-10B.

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Fig. 19. Beryllium Oxide Disk from M-18-11A.

Fig. 20. Beryllium Oxide Disk from M-18-2B.

Fig. 21. Beryllium Oxide Disk from M-18-14A.

Fig. 22. Beryllium Oxide Disk from M-18-17A.

Fig. 23. Microstructure of Beryllium Oxide Assemblies. (a) As made. (b) Shorted, from M-18-2B. Note the columnar compound on the surface of the shorted beryllium oxide disk.

Fig. 24. Electron Microprobe Analysis of Unshorted BeO Disk Showed Only a Copper-Selenium Compound in the Dark Deposit and No Detectable Silver. (a) Optical micrograph. (b) Se scan. (c) Cu scan. (d) Ag scan.

Fig. 25. Electron Microprobe Analysis of Shorted BeO Disk Showed the Existence of a Ag-Cu-Se Compound in the Dark Deposit on BeO. (a) Optical micrograph. (b) Se scan. (c) Cu scan. (d) Ag Scan.

continuous network and contributed to electrical shorting. No silver was detected by electron microprobe in the unshorted BeO disks, which also had the dark deposits.

Scanning electron microscopy (SEM) and energy dispersive x-ray analyses of an as-made BeO disk revealed a very thin, discontinuous silver-copper layer distributed on the cylindrical surface. This is readily shown by the secondary electron image presented in Fig. 26. Typically, secondary electron images of an electrical insulator such as BeO appear extremely bright in the SEM because their lack of conductivity permits surface charge accumulation. Limited areas of the surface of the as-made BeO assembly did appear bright from charging, but a large portion of the surface appeared not to accumulate charges. Energy-dispersive x-ray analysis confirmed a thin layer of a silver-copper alloy on these noncharging areas. The silver-copper layer probably originated from contamination by the Ag-Cu brazing alloy applied to the two flat surfaces of the BeO disk. Scanning electron microscopy and energy dispersive x-ray analysis showed silver compounds with copper, selenium, or both in the dark deposits on shorted BeO disks [Fig. 27(a)] but only copper-selenium compounds in the dark deposits on unshorted BeO disks

Fig. 26. Scanning Electron Micrograph of As-Made BeO Disk (Secondary electron image, 20 kV, 1.0 nA).

Fig. 27. Scanning Electron Micrographs Showing Dark Deposits on BeO Disks. (a) Shorted disk from M-18-11A. (b) Unshorted disk from M-18-12B.

[Fig. 27(b)]. Analysis by SEM and EDX showed that the silver-containing compound in the dark deposit on a shorted BeO disk was not uniformly distributed. Some Fiberfrax* fibers were trapped in the deposits, and these had become coated with copper-selenium compounds.

The copper current strap in contact with the top flat face of the BeO disk was reportedly severely corroded in modules M-15C and M-15D. Metallographic examination of the current straps in module M-18 showed the presence of some small holes about 80 μm (0.003 in.) in diameter distributed in the 0.25-mm-thick (0.010-in.) copper current strap. The microstructure has eutectic appearance and contains a copper-silver phase, which is derived from the brazing operation (Fig. 28).

*Product of Carborundum Co., Niagara Falls, N.Y.

Fig. 28. Typical Tested BeO Assembly Showing Eutectic Materials in Copper Current Strap (M-18-17A).

$\text{GdSe}_{1.49}$ N-Legs

Figure 29 shows a typical as-made $\text{GdSe}_{1.49}$ N-leg. The cylinder is 8.00 mm (0.315 in.) in diameter and 7.62 mm (0.300 in.) long. Visual inspection of this specimen indicated no external cracks. The nickel sputter at the hot end and the lead-silver solder at the cold end spread over the corners and extended about 0.5 mm onto the cylindrical surface. Radiography of this as-made N-leg with a 200-kV x-ray source revealed no

Fig. 29. As-Made $\text{GdSe}_{1.49}$ N-Leg.

internal cracks within the detection limit. However, metallography (Fig. 30) of a cross section taken about 2 mm from the hot end of the as-made N-leg indicated one 0.25-mm-long (0.010-in.) crack, many small surface cracks, and many internal pores ($\sim 40\text{ }\mu\text{m}$ in diameter). The as-made N-leg reportedly had a density 97 to 98% of theoretical. The presence of internal pores is not surprising, but some internal pores are unexpectedly large, ranging up to $40\text{ }\mu\text{m}$. The cracks in the interior of the as-made N-leg as well as numerous surface cracks appear to have been introduced by nonuniform pressing stresses before sintering. These cracks are intergranular. Large pores are obviously inhomogeneous in size and distribution, and they are probably caused by agglomeration of the selenide powder during and before pressing. The pores are located at grain boundaries and within grains. Under polarized light, all the grains in the as-sintered N-leg appear isotropic. Segregation or the so-called "reddish second

Fig. 30. As-Polished Cross Section of As-Made N-Leg.

phase" was not detectable under optical microscopy. However, scanning electron microscopy (Fig. 31) of the external surface of the as-made N-leg showed large pores and pore agglomerates, which appeared to have been molten. The molten appearance of these grains suggests the existence of a low-melting second phase in the material during sintering. Sanding or machining marks are also evident on the external surface of the as-made N-leg [Fig. 31(b)]. Energy-dispersive x-ray analysis identified Gd, Se, and Cr on the external surface of the as-made N-leg. The minor amount of chromium was probably due to contamination introduced from furnace parts or the ball mill container during N-leg fabrication. No analysis was performed to confirm the stoichiometry and purity of the as-made N-leg material.

The two N-legs removed from module M-7 had been broken into pieces during service. Scanning electron microscopy and fractography of the fractured surfaces indicated the presence of a relatively thick layer believed to be an oxide of $\text{GdSe}_{1.49}$ (Fig. 32). This oxide layer masked

Fig. 31. Scanning Electron Micrographs of As-Made N-Leg.

Fig. 32. Scanning Electron Micrograph of Fractured Surface of M-7-17 N-Leg.

certain characteristics of fractured surfaces such as cleavages, which appeared as river patterns, and smooth areas. However, the mirror-like area near the hot end suggests fracture initiation at the hot end (Fig. 33).

Misalignment of thermoelectric elements with the hot or cold end hardware has been reported in all the thermoelectric modules.¹⁻⁴ One example is the N-leg from disassembled module M-15C (Fig. 34). The uneven dark deposit on the top tantalum gimbal is evidence of N-leg misalignment. Visual inspection revealed numerous external cracks. Metallographic examination of a longitudinal section of the M-15C-2B N-leg also revealed many internal cracks. The hot part of the tested M-15C-2B N-leg is anisotropic, whereas the cold part remained isotropic. Internal cracks are transgranular and they may have restricted the phase transformation (Fig. 35). Because the opposing faces of a crack in the anisotropic area in the hot part of this specimen have two different orientations, cracks seem to have been generated before the completion of the massive phase transformation in the selenide material, although these microcracks could have been generated during the early stage of

Fig. 33. Scanning Electron Micrograph of M-7-17 N-Leg Fracture Near Hot End.

the massive phase transformation. Scanning electron fractography (Fig. 36) of the external surface of the M-15-2B N-leg showed scale in crack surfaces. The scale presence in the crack extends from the hot end to about midway in the element. Crack surfaces near the cold end were relatively free from scale. The cracks are predominantly transgranular with many cleavages, river patterns, and occasionally smooth areas in large grains (Fig. 37). The presence of a large amount of scale on the crack surfaces indicated that the external cracks were formed during heat-up or steady-state operation and not during cool-down of the module.

The N-legs in module M-18 behaved somewhat better than those in previous selenide thermoelectric modules. Only one-third of the 18 N-legs showed external cracks upon visual examination. A typical cracked N-leg from the disassembled module M-18 is shown in Fig. 38. An orange ring, probably a gadolinium oxyselenide, is present on the surface in the hot part. The formation of this orange ring is believed related to the phase transformation from the isotropic

Fig. 34. N-Leg from M-15C-2B Showing the Uneven Dark Deposit on the Tantalum Gimbal and Macrocracks in the N-Leg.

Fig. 35. Structure of N-Leg from M-15C-2B.

to anisotropic phase. The sudden step or discontinuity in the orange ring across the external longitudinal crack shown in Fig. 38 probably resulted from the different degree of completeness of the phase transformations on the two sides of the crack, and perhaps also from the different oxidation rates of the isotropic and anisotropic $\text{GdSe}_{1.49}$ at a given temperature. Fractography by SEM confirmed the existence of scale on crack surfaces and also revealed (Fig. 39) that cracks typically penetrated deeper in the hot end than in the cold end. This could mean that higher stresses were present near the hot end and/or the N-leg was stronger at lower temperatures. Fractography by SEM also confirmed that most external cracks penetrated into the bulk at an angle between 45 and 90° with respect to the horizontal tangent to

Fig. 36. Scanning Electron Micrograph of an External Crack in the Hot Part of M-15-2B N-Leg.

Fig. 37. Scanning Electron Micrograph of the Cold Part of M-15C-2B N-Leg.

Fig. 38. N-Leg from M-18-2A.

Fig. 39. Scanning Electron Micrographs Showing Crack at Ends of M-18-2A N-Leg. (a) Hot end. (b) Cold end.

Fig. 40. Scanning Electron Micrograph of M-18-2A N-Leg Showing Shear by Relative Displacement of Two Sides of an External Crack.

the cylindrical surface at the crack. This suggested that cracks were formed during heat-up or steady-state operation.⁹ Evidence of a shear stress along the external crack is shown by the relative disregistry of the smoothing or sanding marks on the two sides of an external crack (Fig. 40).

Figure 41 shows another cracked N-leg (M-18-2B) removed from module M-18. External surfaces showed both longitudinal and circumferential cracks. Here also, SEM fractography disclosed that the external cracks

Fig. 41. Cracked M-18-2B N-Leg.

Fig. 42. Scanning Electron Micrographs of M-18-2B N-Leg. (a) Hot end. (b) Cold end. Note that crack path in end faces makes angle between 45 and 90° with tangent to edge. Angle appears smaller in (a) because of the viewing angle.

penetrated deeper into the bulk at the hot end than at the cold end, and the penetration angle was somewhere between 45 and 90° (Fig. 42). Internal cracks are present in the M-18-2B N-leg. Figure 43 shows the microstructure in the hot zone of the M-18-2B N-leg. Cracks are transgranular, and some cracks seem to have ended or started at the boundary between the isotropic and anisotropic areas. A U-shaped internal crack roughly followed the contour of the boundary between the anisotropic and isotropic phases, as shown in Fig. 43(a). Figure 43(b) clearly demonstrates the different crystallographic orientations of the two opposing sides of a crack running through the anisotropic area. This feature is shown at a higher magnification in Fig. 44. Cracks might have healed, as indicated by a narrowing of the crack width as shown in Fig. 44.

An example of an apparently noncracked N-leg taken from disassembled module M-18 is shown in Fig. 45. The presence of an orange ring deposition

Fig. 43. Hot Zone of M-18-2B N-Leg. (a) Note U-shaped crack between phases. (b) View under polarized light.

Fig. 44. Polarized Light View of the Anisotropic Phase in M-18-2B N-Leg.

scale on the surface of the hot part and the absence of surface cracks are noteworthy. However, metallography revealed many internal cracks in this specimen (Fig. 46). Here again, the cracks are transgranular and are quite narrow in the anisotropic area (Fig. 47). There are also numerous microcracks in the anisotropic area, as shown in Fig. 48 for a different N-leg. These microcracks appear to be intergranular and may be residues of healed cracks. Microcracks might also have been generated by large stresses resulting from the volume change associated with the phase change from the isotropic to anisotropic $\text{GdSe}_{1.49}$ form.

The thickness of the orange-colored ring is less than $0.1 \mu\text{m}$, too thin to be resolved by optical microscopy. The M-18-8A and as-made N-legs were analyzed by secondary ion mass spectroscopy (SIMS) using a beam of positive ^3He ions at a pressure of 5.3 mPa ($4.0\text{E}-05 \text{ torr}$) accelerated at 1 keV toward the sample surface. A depth of 100 to 1000 nm was analyzed. The net counts (for 64 s) for negative oxygen ions at the center and edge of the polished surface and the orange ring of M-18-8A N-leg were 870 , 380 , and 6500 , respectively. The corresponding count was 18 on the polished surface of the as-made N-leg. The much higher oxygen response from the orange band suggests gadolinium oxyselenide. Since the oxygen counts on

Fig. 45. Apparently Uncracked M-18-8A N-Leg.

the polished surface of the tested N-leg (edge or center) are greater than that of the as-made N-leg, oxygen contamination in the bulk of the tested N-leg cannot be ruled out. However, one should note that SIMS oxygen analyses are only qualitative.

Figure 49 is a drawing of one broken N-leg from the disassembled module M-18. This onion-skin fracture or spalling is very similar to the failure mode of sintered ceramic cylinders fabricated by uniaxial pressing with poor powder flow properties. Fractography by SEM [Fig. 50(a)] of the fractured surfaces showed an area characterized by agglomerates of fine pores near the hot end. These agglomerates of pores could be crack or fracture initiation flaws. The presence of fine whiskers on the surface of the hot part [Fig. 50(b)] indicated that fracture occurred during heat-up or steady-state operation.

Fig. 46. Low Magnification of As-Polished M-18-8A N-Leg.

A copper compliant follower was used in some six-couple cold end temperature difference tests to provide better contact and a lower temperature difference at the cold end. This compliant follower seems to alleviate the N-leg cracking to a great extent. The ATT583 six-couple cold end temperature difference test using compliant followers had no visible macrocracks in any of the six N-legs. Figure 51 shows one such uncracked N-leg. However, SEM examination did identify one crack near the cold end (Fig. 52). Metallography also revealed internal cracks similar to those in the M-18-18A N-leg.

Large variations in grain size and porosity were found among samples of the $\text{GdSe}_{1.49}$ isotropic phase. The average grain size at the edge is substantially smaller than at the center of the M-18-2B N-leg (Fig. 53). The center was also more porous than the edge of the M-18-2B N-leg. Other specimens including M-7-17, M-15C-2B, M-18-8A, M-18-2A, ATT583, and as-made $\text{GdSe}_{1.49}$ did not exhibit such variations in grain size and porosity, although two fine-grain agglomerates were found in

Fig. 47. As-Polished Microstructure of M-18-8A N-Leg.

Fig. 48. Anisotropic Area in M-18-2A N-Leg Showing Microcracks (Etched with Nital for 10 s).

Fig. 49. Sketch of Broken M-18-18A N-Leg.

Fig. 50. Scanning Electron Micrographs of M-18-18A N-Leg. (a) Pore agglomeration near the hot end. (b) Whiskers on crack surfaces.

the center of the M-18-8A N-leg (Fig. 54). The microstructural variation along the length of the N-leg region consisting of the isotropic phase was generally negligible, whereas the variation along the radial direction was easily observed by optical microscopy. No WC inclusions were observed. However, studies of similar samples at Battelle Columbus Laboratory revealed such inclusions.¹⁰

In the specimen region consisting of the anisotropic phase, grains were substantially larger than those in the isotropic $\text{GdSe}_{1.49}$. Grains are elongated, generally along the length of the N-leg, in the anisotropic phase, which has transformed from the original isotropic $\text{GdSe}_{1.49}$. Numerous intergranular and transgranular microcracks are present in the anisotropic phase. No significant changes in porosity or grain size are present anywhere in the anisotropic phase.

Fig. 51. N-Leg from ATT583.

Fig. 52. Scanning Electron Micrograph of the Cold End of ATT583 N-Leg.

Fig. 53. N-Leg from M-18-2B Etched 5 s with Nital to Show Grain Size. (a) Edge region with small grains and low porosity. (b) Central region with large grains and high porosity.

Fig. 54. Center of M-18-8A N-Leg, Showing a Fine Grain Agglomerate (Etched with Nital for 5 s).

$(\text{Cu,Ag})_2\text{Se}$ P-Legs

Figure 55 shows a typical, partitioned, top-capped, unwrapped, as-made P-leg. Visual inspection indicated no surface cracks. Scanning electron microscopy and EDX analysis showed the existence of numerous elbow-shaped macaroni-like Cu-Ag-Se crystals on the cylindrical surface of the as-made P-leg. Figure 56 illustrates the characteristics of the natural surface of as-made P-legs. Metallographic examination revealed some microcracks with copper and silver precipitated in the P-leg as well as copper precipitated on both sides of the tungsten-rhenium partition foil in the as-made P-leg (Fig. 57).

Two $(\text{Cu,Ag})_2\text{Se}$ P-legs, Figs. 58 and 59, from disassembled module M-18 were analyzed with SEM, EDX, and metallography. There were transverse and longitudinal cracks in the Astroquartz wrapping (Fig. 60). Analysis by SEM and EDX indicated selenium on the surface of the crack.

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Fig. 55. Typical Partitioned Unwrapped Thick-Foil-Capped As-Made P-Leg.

Fig. 56. Scanning Electron Micrographs of the Natural Surface of As-Made P-Leg.

Fig. 57. As-Polished As-Made P-Leg Showing (a) Microcrack and Copper-Silver Precipitate in the Crack and (b) Copper Precipitate on Both Sides of the Tungsten-Rhenium Partition.

Fig. 58. P-Leg from M-18-PlA.

Fig. 59. P-Leg from M-18-P5A.

Fig. 60. Scanning Electron Micrograph of the Wrap of M-18-P1A Showing (a) Longitudinal and (b) Transverse Cracks.

The cold end copper bond appeared to maintain integrity better than the hot end (Fig. 61). Metallographic analysis (Fig. 62) showed voids in the Astroquartz wrap. However, electron microprobe analysis detected no Cu, Ag, or Se in the wrap. The Min-K slurry cured fairly well with the Astroquartz yarns except for the voids occasionally found in the wrap. Figure 62 illustrates such voids between the wrap fibers. At the cold end of the leg, the wrap maintained an intimate contact with the P-leg (Fig. 63), but the wrap at the hot end, including areas above and immediately below the tungsten-rhenium partition, appeared to separate from the P-leg to produce a gap of about 40 μm (Fig. 64).

Copper and silver precipitated in nearly all the cracks at the cold end. These cracks were oriented along certain crystallographic planes of the $(\text{Cu,Ag})_2\text{Se}$ grains. They were similar to those observed in the as-made P-leg.¹¹ Figure 65 shows features of the cracks and the copper and silver precipitates in the colder region of the M-18-P1A P-leg.

Cracks in the tungsten-rhenium top cap of the M-18-P1A P-leg were observed by metallography. Electron microprobe analysis confirmed that the material lodged in these cracks was copper selenide.

Fig. 61. Scanning Electron Micrographs of M-18-P1A P-Leg. (a) Hot end. (b) Cold end.

Fig. 62. Voids in the Wrap of M-18-P1A P-Leg.

Fig. 63. Near the Cold End of M-18-PlA P-Leg. Note good contact between insulation wrap and P-leg.

Fig. 64. Hot End of M-18-PlA P-Leg, Showing Gap Between Insulation Wrap and P-Leg.

Fig. 65. Cold End of M-18-P1A P-Leg, Showing Cracks and Copper and Silver Precipitation.

DISCUSSION

Steel Springs

From the data available in this study, there is no obvious, single reason for the observed excessive relaxation of the chromium-silicon steel springs. On the basis of the results available, several possible explanations can be rejected while other explanations can be shown as plausible.

The results of the chemical analyses show that the measured compositions fall within the specifications for the alloy. Carbon is slightly high, but within the limits of accuracy of the measurement it satisfies the specification. Furthermore, the ion microprobe data indicate that no significant compositional gradient existed in the springs. Consequently, it appears that the weakening of the springs was not due to the absence or improper distribution of an element that was supposed to be present.

The chemical analysis did not detect any element that might be present and detrimentally affect the spring. Because of the close proximity of the selenide thermoelectrics to the springs, selenium was sought carefully by chemical analyses. Other studies¹² have shown that selenium can cause grain boundary embrittlement of a platinum-base alloy at 800°C, and at a partial pressure of 0.1 Pa (10^{-3} torr) selenium will react¹³ with molybdenum at temperatures around 300°C. Some of the electron microprobe results show the presence of iron and selenium in the deposits on the surface, but no evidence was found of any selenium inside a wire. The possibility of using Auger electron spectroscopy to look for selenium on a grain boundary was considered, but because even a sample fractured in liquid nitrogen showed a significant amount of ductility, the required grain boundary fracture of the specimen within the Auger spectrometer was not feasible. Reports¹⁴ from 3M Company that chromium-silicon steel springs exposed to selenium vapor had a larger relaxation than comparable springs exposed in air make strong evidence for some selenium effect, but no evidence confirming the presence of selenium could be found.

As has been described, in most cases the measured wire diameter was less than the assumed nominal diameter. According to the specification,⁵ for wire in the range of 0.813 to 1.83 mm (0.032–0.072 in.) in diameter, the permissible variation is 25 μm (± 0.0010 in.). So, either the wire diameter was out of tolerance or some process during aging uniformly removed material from the surface. Whatever the reason for the wire being undersize, it is important to note the effect of wire size on the stress. The formula for the stress in a statically loaded helical spring made from round wire and taking into account the Wahl correction factors is:¹⁵

$$S_k = \frac{71.9PD}{d^3} \left(\frac{4C-1}{4C-4} + \frac{0.615}{C} \right), \quad (1)$$

where

- S_k = "corrected" nominal shear stress in Pa
- P = spring load in N
- D = mean diameter of spring in m (outside diameter of spring minus the wire diameter)
- d = diameter of the wire in m
- C = spring index, D/d

The specifications for the springs are given in Table 8. Using Eq. (1) and the values from Table 8, the "corrected" nominal shear stresses are 511 MPa (74.1 ksi) for the P-leg spring and 640 MPa (93 ksi) for the largest wire used for the N-leg spring. If the diameter of the wire is less, the stress can be considerably higher, as is shown in Table 9. For the diameter measured for the N-leg spring from module M-7, if that spring carried the full 104 N (23.4 lb) load it was intended to carry, the corrected shear stress would be almost 900 MPa (130 ksi). These potentially high stresses illustrate that slightly undersize wire in the springs could result in permanent spring deformation or relaxation.

According to a number of references,¹⁶⁻¹⁸ chromium-silicon steel spring wire should have the properties listed in Table 10. Light service

Table 8. Nominal Specifications for Springs

Modules	Spring	Coil OD		Wire Diam		Load	
		(mm)	(in.)	(mm)	(in.)	(N)	(lb)
4-10	P-leg	6.6	0.26	1.14	0.045	38	8.5
	N-leg	6.6	0.26	1.32 ^a	0.052	104	23.4
11-19	P-leg	5.36	0.211	1.04	0.041	38	8.5
	N-leg	7.16	0.282	1.50	0.059	104	23.4

^aThe virgin chromium-silicon steel spring that was one of the specimens examined and six chromium-silicon steel springs that 3M recently furnished are 1.42 mm (0.056 in.) in wire diameter. This material was not used in any module or test assembly.

Table 9. Effect of Wire Diameter on "Corrected" Shear Stress

P-Leg Springs				N-Leg Springs			
Wire Diam		Calculated S_k		Wire Diam		Calculated S_k	
(mm)	(in.)	(MPa)	(ksi)	(mm)	(in.)	(MPa)	(ksi)
1.04	0.041	510	74	1.50	0.059	640	93
1.00	0.0395	565	81.9	1.42	0.056	745	108
0.97	0.038	627	90.9	1.37	0.054	814	118
0.93	0.0365	699	101	1.32	0.052	903	131
				1.27	0.050	1010	146

listed in the table covers a stable loading condition at room temperature. Two of the references^{16,18} give the maximum working temperature for chromium-silicon steel wire as 232°C (450°F). The *Tool Engineer's Handbook*¹⁷ lists the maximum permissible working temperature as 204°C (400°F) with a maximum stress of 483 MPa (70 ksi). The operating conditions of the modules from which we obtained the springs that have been examined called for a temperature of 150°C (~300°F). In at least one case, module M-7, the temperature was as high as 200°C (~390°F). Since the stress of both the N- and P-leg springs, when fabricated with the

Table 10. Properties of Chromium-Silicon Steel Spring Wire^a

Hardness, Rockwell C	49
Tensile strength of 0.89-mm-diam (0.035-in.) wire, GPa (ksi)	1.97-2.10 (285-305)
Modulus of elasticity, GPa (psi)	
Tension	210 (30 E+06)
Torsion	79 (11.5 E+06)
Allowable stress for helical Compression springs, GPa (ksi)	
Light service	0.68 (99)
Average service	0.61 (88)
Severe service	0.46 (66)

^aBased on refs. 16-18.

proper size wire, was greater than 480 MPa (70 ksi) the springs were clearly used beyond the recommended operating stress. Also the presence of selenium in the module environment may have produced operating conditions more severe than average service conditions. If this is so, the allowable operating stresses in the springs would be even lower than handbook-derived values (Table 10).

If, in fact, the springs were operated at temperature and stress levels beyond the recommended limits, the effect of these conditions on load relaxation is of major interest. Industry data⁹ indicate that the relaxation that might be expected in chromium-silicon steel springs at 230°C (450°F) and a stress level of 724 MPa (105 ksi) in 0.36 Ms (100 h) is about 9%. At 690 MPa (100 ksi), 200°C (400°F), and 3.6 Ms (1000 h), a 15% relaxation might be expected. For longer periods of time, the rate is greater, increasing as the logarithm of time.¹⁸ According to experienced engineers in the spring industry,^{19,20} 20% or more relaxation of these springs is conceivable. It should be noted that the greatest relaxation was always observed in the N-leg spring, which was more highly stressed than the P-leg spring within the modules.

The measured hardness values, which are shown in Table 7, were fairly limited in number, but the deviation from the values expected of

quenched-and-tempered chromium-silicon steel might be evidence of a problem. According to the *Metals Handbook*,²¹ the range of hardness values for chromium-silicon steel is 48 to 55 on the Rockwell C scale. Other references^{16,22} state that before tempering (this is assumed to mean the quenched condition) the expected hardness is R_C 50 to 53, while the hardness after tempering is nominally R_C 49. The measured diamond pyramid microhardness values, converted to the Rockwell C scale, indicate that the virgin material and the two springs that were exposed 0.90 Ms (250 h) at 175°C all had hardness values that were at the high end of the range for tempered material. The two springs that were aged longer and at a sometimes higher temperature both had low hardness values. The number of samples examined was small, so a conclusion drawn from our limited data must be regarded with some caution. A request to 3M Company was made for additional samples of the archive spring material, but none were available; however material from other spring batches was provided. From the limited data, we have concern about the tempering process used for the springs.

The photomicrographs of the samples that had been etched in picral-HCl solution²³ show a difference between the virgin material and two of the other samples, one that had been aged 0.09 Ms (250 h) in air and one that had been aged 3.96 Ms (1100 h) in a selenium-containing environment. The virgin material had a finer structure, while the structure of the aged material looked more like that expected²⁴ of tempered chromium-silicon steel. These results would tend to support the hypothesis that the springs were inadequately tempered, and this is consistent with the hardness results.

The internal cracks that were observed in the 17-7 PH steel were apparently not a result of exposure since they occurred in both the archive and aged material. Furthermore, since all cracks observed were parallel to the axis of the coiled spring, the cracking likely occurred during fabrication of the spring rather than as a result of over-drawing, which has been observed²⁵ to cause internal cracks in spring wire.

BeO Insulators

On the basis of post-test analysis of the BeO specimens taken from module M-18, the silver-copper brazing alloy contamination on the surfaces of the BeO disks seems to be responsible for the observed shorting. The braze alloy likely reacted with selenium sublimed from the P-leg to form conductive deposits across the BeO disk. Apparently, procedures used during brazing of the BeO disk were not sufficient to prevent spreading of the brazing alloy over the cylindrical surface of the BeO disk. This surface contamination occurred in almost every as-made BeO assembly. No effective procedure involving either mechanical or chemical cleaning to remove the contamination was used by the contractor.

The reaction kinetics between copper-silver alloy and selenium is unknown. The phase diagram of the copper-selenium binary system has been reported, but no reaction kinetics data could be found. In the present case, the copper-silver alloy on the surface of the BeO disk reacted with either selenium vapor, liquid, or solid and formed selenide compounds. It should be noted that not all the reaction products are conductive and lead to shorting. The dark deposits on the BeO disk became highly conducting only if a copper-silver-selenium compound was present in these dark deposits. In some deposits that contained only copper and selenium (no silver), no shorting was observed. Therefore, the formation of copper-selenium compounds alone did not cause shorting and the presence of a silver-copper-selenium compound seems to be a prerequisite for the shorting.

Cracks in the archive and tested BeO ceramic disks have been observed. Because no large stresses were present in the BeO disk during service, these cracks were believed to be due to fabrication problems. Cracks in the BeO disks are obviously undesirable. Crack-free BeO disks can be obtained from commercial vendors by use of proper specifications and inspection including nondestructive testing (NDT) or destructive testing of selected samples.

The voids in the copper current strap are not entirely surprising. Depending on the amount of brazing alloy used, the population of voids generated at the braze side during brazing can vary over a wide range. However, the voids or holes on the other side (the non-braze side) of the copper current strap are difficult to explain. Serious corrosion in the copper current strap was reported only in modules M-15C and M-15D. Several processes could contribute to the observed corrosion of copper hardware. Reactions of Se with the Cu-Ag braze of the P-leg BeO disk, reactions of Se with the Pb-Ag braze of the N-leg cold end, or reactions of Cu hardware and Cu-Ag or Pb-Ag braze with some other low-melting solid, liquid, or vapor species from other components in the system could result in the observed corrosion.

The use of a low-melting brazing alloy such as lead-tin-silver has the advantage that contamination or spreading of brazing alloy may be minimized by closer control of the brazing process, which is easier for lower melting brazing alloys.

GdSe_{1.49} N-Legs

The results of analysis indicated some unexpected phenomena in the as-made N-legs and dramatic alterations in the tested N-legs. The as-made N-legs are inhomogeneous. Post-test examination showed that a phase change occurred in the hot parts of the N-legs. Surface cracks and internal cracks, on both a macro and a micro scale, were routinely observed except in some M-18 N-legs that showed only internal cracks. An oxide layer in the form of an orange ring was observed on the cylindrical surface of the N-leg in the hot region. This discussion reviews the causes for the cracking.

Inhomogeneous As-Made N-Legs

The present fabrication techniques for GdSe_{1.49} N-legs include cold pressing and sintering cubic GdSe_{1.49} powder into the required cylinders. Internal cracks as large as 0.25 mm (0.010 in.) and numerous smaller surface cracks probably are introduced by uneven

pressure distribution within the powder compact during uniaxial pressing. One M-18 N-leg cracked in an onion-skin pattern on the hot end, which suggests incorrect pressing or sintering conditions had been used for this N-leg, resulting in nonuniform density distribution, internal cracks, and large residual stresses in the fabricated part. We feel that the large variation in grain size and porosity in M-18-2B occurred during pressing and sintering of the cylinder rather than during the module test. However, the particular as-made N-leg that we examined did not show such variations. Large pores, pore agglomerates, and fine grain agglomerates in tested N-leg microstructures provide numerous stress concentrations and fracture initiation sites. It is well known that such defects typically serve as crack initiation flaws in brittle ceramics.²⁶⁻³¹ In ceramic materials that are free of such flaws and defects, intrinsic strengths almost double or triple that of the inhomogeneous defective materials could be realized.²⁶

No red second phase was observed in the N-leg selenide within the resolution of optical microscopy. This, however, does not rule out the possible existence of this high-resistivity, reddish $\text{GdSe}_{1.5}$ phase, which reportedly⁴ degrades the efficiency of the selenide thermoelectric converter. If this phase is present as a grain boundary diluent, a high-resolution analytical technique such as transmission electron microscopy (TEM) is required. Thin foil preparation for TEM examination is very difficult for this material because chemical thinning or ion milling may inadvertently introduce trace oxygen impurities, which alter the original microchemistry and microstructure of $\text{GdSe}_{1.49}$. Development of a foil preparation technique for this material was not pursued because of lack of time. Conceivably, any second phase or impurity phases could not only alter the thermoelectric characteristics of this selenide but also cause cracking due to thermal tensile stresses generated from local Joule overheating due to non-uniform electrical conductivity. Additionally, thermal expansion mismatch between any second phase and the primary phase could cause stresses. Transformation of the second phase might also occur at an enhanced or retarded rate relative to the original phase. This might also bring about cracking under certain conditions.

Defects such as pores, pore agglomerates, and fine grain agglomerates may cause local stresses through nonuniform Joule heating and high local resistivity and thus give rise to cracking.

Since x-ray radiography failed to detect the 0.25-mm (0.010-in.) flaw in the as-made N-leg, other more sophisticated nondestructive methods including eddy currents and ultrasonics should be explored for future use on this material. However, the basic steps in N-leg processing should be carefully reviewed to clearly identify the mechanisms for the formation of initial flaws and to remove these from the process. Pressing and sintering of the selenide should be more closely controlled to assure uniform pressing stresses and a uniform sintering rate within the compact. An alternative route could involve radically changing the N-leg processing from cold pressing and sintering to uniaxial or isostatic hot-pressing. Hot-pressing has good potential for yielding a crack-free, homogeneous selenide N-leg. Selection of isolation canning material and minimizing oxygen contamination need to be demonstrated if isostatic hot-pressing fabrication is to be viable.

The large range of stoichiometry of GdSe_x over the stoichiometric $\text{GdSe}_{1.50}$ and the selenide vapor pressure over GdSe_x at high temperatures make high-temperature heat treatment difficult while maintaining the selenide composition. Selenium has a significant vapor pressure over GdSe_x at high temperatures and can easily result in stoichiometry variations between the center and surface of the N-leg cylinders. Because of the high oxygen affinity of the GdSe_x material, oxygen can readily contaminate GdSe_x at even modest temperatures. Literature reports³² of sintering studies of PZT (lead zirconium titanate) ceramics have demonstrated how a severe problem of lead evaporation was solved by sintering in a sealed ZrO_2 crucible containing some PbO -bearing powders. By this means, the partial pressure of the Pb -bearing vapor species equilibrated with the solid, and the stoichiometry of the PZT body could be controlled. To date N-leg material has been sintered at high temperature in a helium atmosphere. For control of its stoichiometry, GdSe_x might best be sintered in a protective atmosphere containing the proper vapor species at the correct pressures. Identification of the vapor species

over the selenide at the temperatures of interest would be very helpful in providing a data base for this development. An impervious GdSe_x crucible with cover to contain green compacts of GdSe_x for sintering may alleviate or reduce the degree of selenium evaporation and oxygen contamination. If this is not feasible, other refractory ceramics may function adequately for this purpose. Experimental work is definitely required to evaluate various sintering schemes.

Phase Transformation

Phase changes of the selenide from an isotropic structure to an anisotropic structure had occurred in the hot part of all tested N-legs. This agrees with reported cubic-to-orthorhombic phase transformations for this material.^{6,33} However, the phase transition temperature and the kinetics of the transformation are presently unknown. Even the volume change associated with the phase change has not been identified with high accuracy. The relationship of oxygen (or other impurities such as chromium) and stoichiometry with the phase change is also obviously important but unknown at present. In any case, the observed phase change and the about 5% volume expansion⁶ accompanying the cubic-to-orthorhombic transition could have generated tensile stresses in the cubic phase and caused some observed cracks. The magnitude of the stresses can be estimated³⁴ by

$$[E/(1 - \nu)](\Delta V/V) ,$$

where E is the elastic modulus, ν is the Poisson's ratio, and $\Delta V/V$ is the fraction volume change. Assuming $E = 0.21$ TPa (3.0×10^6 psi),³⁵ $\nu = 0.3$, the stresses would be about 14 GPa (2.0×10^6 psi). Such large stresses would probably generate cracks. An analogy exists between GdSe_x and ZrO_2 . It is well known³⁶ that ZrO_2 undergoes a phase change from a tetragonal to a monoclinic lattice with a 3 to 7% volume expansion at about 1200°C. This phase change severely limits the potential uses of pure ZrO_2 because the ceramic often fractures when cooling from the sintering temperature. The phase transformation problem is avoided

in zirconia ceramics by adding other elements such as Ca, Mg, Y, and Ce to ZrO_2 to form solid solutions and to enlarge the stability field of the cubic phase and eliminate phase changes at high temperatures. A similar technique might possibly work in GdSe_x , but such beneficial doping or alloying with other transition-metal or rare earth selenides must not impair the thermoelectric performance.

In the tested N-legs, the phase transformation occurred in areas from the top extending to about one-third of the length of the N-leg. More extensive transformation occurred in the edge of the cylinders than in the center. A rather sharp boundary that appears as a dome or U-shape in the longitudinal cylinder sections distinguishes the original and transformed areas. Viewing the N-leg cylinder with the hot end down, the U-shaped boundary appears with normal orientation. All material below the boundary — that is, between the boundary and the hot end surface — consisted of the orthorhombic phase. This could be explained by the typical nucleation of a new phase at grain boundaries and external surfaces. Oxygen or other contaminants might also play key roles in the nucleation process for the orthorhombic phase. The grain size of the orthorhombic selenide phase was about the same at the center and edge of the cylinder. The large, transformed grains at higher temperatures and fine, transformed grains at lower temperatures typically observed for phase transformations in metals or ceramics are not obvious in the present case.

The thermodynamics, crystal structure, phase metastability, equilibrium phase relationships, and transformation kinetics of the Gd-Se binary and Gd-Se-O ternary systems require thorough study before the GdSe_x material can be adequately understood. Mechanical and physical properties including elastic modulus, modulus of rupture, fracture toughness, Poisson's ratio, and thermal expansion, in addition to thermoelectric properties such as thermal conductivity, electrical resistivity, and Seebeck coefficient of the orthorhombic $\text{GdSe}_{1.49}$ should also be determined.

Oxygen contamination on the surface of the tested N-leg cylinder is obvious and could have influenced the phase changes at the surfaces. We did not observe phase changes of the oxyselenide. Since the oxygen content in the edge or center of the tested N-legs is several parts per million,³⁷ oxygen is unlikely to affect the transformation rate significantly in the bulk of N-legs.

Phase changes also complicate considerations of sintering of orthorhombic $\text{GdSe}_{1.49}$ powders. Because the average particle size of the orthorhombic $\text{GdSe}_{1.49}$ powder that can be obtained by grinding the low-temperature-reacted $\text{GdSe}_{1.49}$ sponges is about 10 μm , temperatures above 1400 or 1500°C are required for sintering, which puts the $\text{GdSe}_{1.49}$ in the cubic field and thus results in development of a cubic rather than orthorhombic lattice. Hot-pressing at temperatures lower than 1000°C could retain the orthorhombic phase but might not yield full densification. Sintered cubic $\text{GdSe}_{1.49}$ bodies could also be used as preforms and processed by uniaxial or isostatic hot-pressing at a temperature where the cubic to orthorhombic phase transformation is optimized. This could possibly achieve orthorhombic phase stabilization and densification simultaneously. This hypothesis is based on the assumption that acceptable phase transformation rates can be achieved in the selenide to produce the orthorhombic phase.

Thermal Stresses

Both axial and radial thermal gradients are present in N-legs during service. If such gradients are nonlinear, thermal stresses are generated. During heat-up or current loading, thermal transients might also have been high enough to generate thermal stresses. An order-of-magnitude calculation was made of these stresses. In steady-state conditions, the thermal stress can be estimated by

$$\sigma = [E/(1 - \nu)]\alpha(T_a - T) ,$$

where E is the elastic modulus, α is the thermal expansion, ν is the Poisson's ratio, T_a is the average temperature, and T is the local temperature.³⁴ If $E = 0.21$ TPa (30E+06 psi), $\alpha = 11\text{E-}06/^{\circ}\text{C}$,³⁵ $\nu = 0.3$, a radial temperature difference ($T_a - T$) of 100°C can generate tensile or compressive stresses of the order of 690 MPa (100 ksi), which very likely are larger than the modulus of rupture of the sintered body. Inhomogeneous defects such as pore agglomerates, flaws, and second phases may cause local overheating and generate such tensile stresses.

During heat-up or cool-down, the thermal stresses generated can be estimated³⁴ by

$$\sigma = \frac{E_a}{1 - \nu} \frac{\phi r_m^2}{3} \frac{\rho C_p}{\kappa} ,$$

where ϕ is the heating or cooling rate, $\kappa/\rho C_p$ is the thermal diffusivity, and r_m is the radius of the N-leg. If $\kappa/\rho C_p \leq 5\text{E+}07 \text{ m}^2/\text{s}$,³⁵ $E = 0.21$ TPa (30E+06 psi), $\alpha = 11\text{E-}06/^{\circ}\text{C}$, and $\nu = 0.3$, the specified heat-up rate of 0.028°C/s (100°C/h) and cool-down rate of 0.0056°C/s (20°C/h) could generate thermal stresses of about 10 MPa (1.5 ksi). This is probably less than the fracture strength of $\text{GdSe}_{1.49}$ (cubic or orthorhombic) N-legs. Therefore, the cracking observed in some tested N-legs was probably not due to thermal transients. The compliant copper follower was originally designed to minimize the temperature differences at the ends of the N-leg by better contact. Its use definitely reduced the cracking tendency in the selenide, perhaps because the improved contact minimized the radial thermal gradient at the hotter end.

A finite element computer program to solve the steady-state ($\nabla^2 T = 0$) and transient ($\rho C_p \dot{T} = \nabla \cdot \kappa \nabla T$) temperature distributions by using suitable boundary conditions and appropriate material property data is in progress at the 3M Company. However, results are not yet available.

Cracking

Basically four types of cracks are observed in most tested N-legs, namely surface macrocracks, internal microcracks, microcracks in the orthorhombic phase, and internal cracks in the orthorhombic phase, which appear to have healed.

Large longitudinal and circumferential macrocracks on external surfaces are all transgranular. The fact that essentially all the cracked surfaces have a surface ($<0.1 \mu\text{m}$) layer ruled out the possibility of cracking being caused by thermal expansion and/or thermal stresses during cool-down. Fracture characteristics such as mirrors, mists, and hackles are discernable in many cases, probably because of the lack of homogeneity in specimens.³⁸ Since most macrocracks seem to originate from the hot end and penetrate into the bulk at an angle between 45 and 90° , macrocracks are likely to have occurred through thermal stressing during steady state.⁹ Displacement of sanding marks on opposing sides of macrocracks also provided evidence of shearing. The macrocracking tendency was markedly reduced by use of a compliant follower, which improved contact and thus minimized radial thermal gradients. In short, catastrophic macrocracking in the N-legs appears to have been caused by thermal stresses.

Internal microcracks are transgranular and more abundant in the cubic phase. In many cases, they follow the contour of the boundary between the transformed and original phases. We have not observed but could not rule out oxide layers being present on internal crack surfaces. The internal cracks seem to initiate from the cubic phase in the cold part and propagate into the orthorhombic phase because crack width is larger in the cold part and the crack is discontinuous in the hot part. The cracks might have been initiated right at the interface between the two phases and propagated in a direction that depends on the relative fracture toughness of each phase. Thermal stressing further aggravates the cracking. Internal cracks are probably caused by a combination of phase-change-generated stresses and thermal stresses.

Numerous intergranular and transgranular microcracks ($<1.0 \mu\text{m}$) in the orthorhombic phase might actually impede or retard crack propagation

in a mode similar to that reported.³⁹ On the other hand, microcracks could obviously increase local resistivity and degrade the thermoelectric properties. From our results we conclude that microcracking in the orthorhombic phase is due to the phase transformation.

The internal cracks in the orthorhombic phase appear to have closed or healed. Crack healing conceivably can occur as a result of the generation of compressive stresses in the orthorhombic area due to the phase change. However, nonequivocal evidence of crack healing such as blunting of cracks⁴⁰ was not observed.

Misalignment

Misalignment, including tilting and lateral movement of the cylindrical legs, probably occurred during or before converter assembly because the nonuniform deposit on the molybdenum gimbal shows sharp rather than gradual changes as one moves from the uncoated to the coated surface of the gimbal. Effects of misalignment on cracking, phase changes, and oxidation are unknown. Obviously, elimination of misalignment within the module is necessary for precise determination of the causes of cracking.

Based on the results and discussion, potential ways to solve the cracking problem are: (1) eliminating crack initiation sites such as flaws, large pores, and pore agglomerates in the N-leg material; (2) strengthening the selenide by reducing the grain size, minimizing porosity, and eliminating surface flaws; (3) minimizing radial thermal gradients through better contact at the hot and cold ends; (4) hot-pressing the orthorhombic or cubic powder at or below the transition temperature or converting the cubic sintered $\text{GdSe}_{1.49}$ to the orthorhombic phase by proper processing; and (5) impeding or retarding catastrophic crack growth in the selenide N-leg cylinders under thermal stresses or phase-change-generated stresses, by intentionally introducing microcracks in the as-made selenide material.

$(\text{Cu,Ag})_2\text{Se}$ P-LegsMin-K and Astroquartz Wrap

The voids and cracks in the wrap appeared localized. Fast drying of the Min-K slurry might cause such defects. Such voids or cracks were probably present in the wrap of as-made wrapped P-legs because crack initiation and growth in the wrap during operation are not very likely since the numerous ultrafine pores in the Min-K can arrest crack growth. Decomposition of organic binders in Astroquartz yarns might also result in such defects. Closer control of the drying process and removal of the organic binders probably can solve this problem. Thermal expansion mismatch and the gap between the P-leg and the wrap in the hot part are of concern. Other wraps or seals that are impermeable, compatible, stable, and more closely matching the P-leg in thermal expansion should be developed.

Contact

Copper or silver migration to and precipitation in the cold end of the P-leg is normal. However, cold end contact with the copper disk might be impaired. Despite the exercise of a great deal of caution during sample handling and metallography specimen preparation, the tungsten-rhenium partitions and top caps all seemed to separate from the P-legs (as-made or tested). The compressive strengths of the bonds between the tungsten-rhenium partition or top cap and the P-leg were reportedly fairly high. However, their bend strengths might be unacceptably low, which could result in bond disintegration or separation because the assembly operation might somehow inadvertently introduce bending at the bond. Cracks in the tungsten-rhenium top cap with some copper-selenium compound lodged inside the cracks probably are caused by fabrication problems.

Similar to the N-leg, misalignment in the P-leg assembly is reportedly quite common.⁴ Here again, misalignment effects should be eliminated or minimized.

Creep or Deformation

Mushrooming and bullet-nosing of P-legs in GDS modules are clearly dramatic. Wrapped legs in M-18 have much less of this effect, presumably because use of wrap suppressed sublimation.

CONCLUSIONS

Steel Springs

Conclusions that can be made as a result of the examination of the chromium-silicon steel springs and the 17-7 PH steel springs are:

The composition of the two spring materials satisfied the specifications for the alloys, and no significant compositional gradients were found.

The examination did not produce any results to indicate that selenium was present internally in any of the springs. However, some degradation of the chromium-silicon steel by selenium cannot be ruled out.

According to wire diameter measurements, most samples of wire were undersized, some by more than the nominal limits.

For the expected temperature, time, and environmental conditions, chromium-silicon steel was, at best, a questionable material choice, and the design of the spring was such that the expected load would lead to significant relaxation.

Although the data are very limited, the steel may not have been tempered properly.

The 17-7 PH steel springs were probably damaged during fabrication.

BeO Insulators

Shorting across BeO disks was due to silver-copper braze contamination and its subsequent reaction with selenium evaporated from the P-leg and possibly copper from the P-leg or some other sources³⁷ (e.g., heater block) in the module to form a conductive layer on the BeO disk.

Such braze contamination occurred because the brazing process was not properly controlled. Corrosion in the copper current strap reported in modules M-15C and M-15D was possibly caused by reactions involving the silver-copper braze and selenium evaporated from the P-leg. Cracks in BeO disks probably resulted from ceramic fabrication problems.

GdSe_{1.49} N-Legs

As-made N-legs contained internal cracks, small surface cracks, large pores, pore agglomerates, and large grains. The grain size and porosity variation from the center to edge in some tested N-legs are probably present in as-made materials. These inhomogeneities can cause local tensile stresses during heat-up and steady-state operation from Joule heating and high local resistivity. They also act as stress concentrators and crack initiation flaws. During steady-state operation, nonlinear axial and radial thermal gradients produce thermal stresses. Thermal stress effects due to the heat-up or cool-down rates used are estimated to be small and thus probably do not cause cracking, but transient heating by rapid electrical current changes may produce high thermal stresses sufficient to crack the N-leg material. Massive phase transformations in the hot end resulted in compressive stresses in the orthorhombic transformed material and tensile stresses in the remaining original cubic phase because of the volume change associated with the phase transformation. The transformation might cause cracking, but the distinct evidence of shear strains in two opposing faces of a crack in the anisotropic phase and different crystallographic orientations indicated that these cracks were formed before or during the massive phase transformation.

Cracks in this material can be classified into four categories: (1) longitudinal and circumferential surface macrocracks, (2) long and large internal microcracks, (3) fine microcracks, and (4) discontinuous microcracks in the orthorhombic area. Oxygen-containing scale on the macrocrack surfaces suggests that cracks are formed during heat-up or steady-state operation rather than during cool-down. These surface cracks

are transgranular and seem to initiate from the hot end, probably because of higher thermal stresses and the initiation of the phase change at the hot end. Compliant contact possibly reduces thermal gradients and such cracking. Long, large, and transgranular internal microcracks are more abundant in the cubic than in the orthorhombic phase because presumably the latter is largely under compression. Such cracks probably are formed by a combination of phase change and thermal stresses. However, no direct evidence of phase-change-induced large cracks was identified. Numerous fine microcracks caused by the phase change in the hot end might impede catastrophic crack propagation in the orthorhombic phase. Segments of large internal microcracks in the orthorhombic phase appear discontinuous and closed or healed. However, blunting of cracks was not observed.

Oxidation on the surface of the hot end might have affected the nucleation of the orthorhombic phase, which in turn affected the cracking. However, the bulk oxygen content is low and is not expected to significantly influence the phase transformation.

(Cu,Ag)₂Se P-Legs

The Astroquartz-Min-K wrap impeded P-leg sublimation reasonably well except for the gap between the wrap and the hot part of the P-leg, which was caused by thermal expansion mismatch, sublimation, or creep, and the localized cracks in the wrap caused by improper drying or organic binder removal. The as-made bond of the tungsten-rhenium top cap or partition with the P-leg is very weak. Defects in the wrap and bond might result in misalignment of the P-leg assembly during module assembly and excessive selenium sublimation during module testing. The copper-selenium compound lodged in the tungsten-rhenium top cap is evidence of the sublimation and transport of copper and selenium away from the P-leg during service. Precipitation of copper and silver at the cold end of the tested P-legs was expected, but the accompanying cracks might cause imperfect contact with the copper disk at the cold end.

RECOMMENDATIONS

Steel Springs

The selection of chromium-silicon steel for the N- and P-leg springs in the SIG GDS and other converter modules was not a good choice, especially when the spring design is considered. We recommend that the spring design be reviewed by engineers of a prominent spring manufacturer. The conditions under which the springs will be used should be thoroughly specified. The material for the spring should be changed. The 17-7 PH steel that we evaluated might be suitable if a better fabrication technique and a design that gives lower stresses are used. Selection of a material more suited for elevated-temperature service in an oxidizing environment would provide a greater margin of safety. Because of the susceptibility of nickel-base alloys to sulfidation and perhaps selenium attack it would be better to avoid Inconel-type alloys. Cobalt-base alloys are more resistant to sulfur attack and possibly selenium attack, so we would recommend the Haynes* alloys, 25 or 188, as spring material.⁴¹ Haynes alloy No. 25 has been used in coil springs at temperatures up to 650°C (1200°F) in air.⁴² Other alloys that might be considered are René 41 and alloy A286.

BeO Insulators

The brazing process should be closely specified and controlled to minimize contamination of the cylindrical surface of the BeO disk to eliminate the subsequent formation of any conductive substances. Effective mechanical or chemical removal of braze contamination is required if surface deposits occur. A lower temperature solder may be advantageous because of relative ease in temperature control. However, the melting point of the solder cannot be too low and should provide enough margin if the P-leg cold end were to overheat and exceed 150°C. Residues of

*Trademark of Stellite Division, Cabot Corp., Kokomo, Ind.

brazing fluxes, if used, should be completely removed from the BeO disks. The testing module components should be reviewed and potential sources of contaminants should be eliminated. Proper specifications for the BeO ceramic disks are required to obtain crack-free as-made material.

GdSe_{1.49} N-Legs

To minimize the presence of cracks, surface and internal defects including flaws, large pores, and pore agglomerates, which are typical stress concentrators and crack initiation sites, should be eliminated by improving the powder compaction and pressing of the N-legs. Sieving through fine-mesh screens (e.g., -400 mesh) and isostatic cold- or hot-pressing or uniaxial hot-pressing are desirable alternatives. However, oxygen or other extraneous contamination must always be minimized. Hot-pressing the orthorhombic powder below about 1000°C to achieve greater than 99% of theoretical density and retain the stable phase for subsequent service temperatures is an alternative to fabrication by cold-pressing and sintering. The cubic-phase powder obtained from ball-milling cast ingots can also be hot-pressed at a temperature such that the maximum transformation rate occurs to yield fully dense and stable forms. Reducing porosity and increasing density will increase the elastic modulus, which can in turn increase thermal stresses. However, the tensile strength will be significantly improved by achieving high density, particularly if the grain size is kept as small as possible. Fracture strength can also be increased by using finer starting powder, which under proper fabrication conditions results in finer final grain size. An effective nondestructive testing technique in addition to bulk density, resistivity, and Seebeck coefficient measurement should be established to assure that fabricated N-leg cylinders are essentially crack-free. Finally, mechanical and physical properties including diametral tensile strength, bend strength, elastic modulus, and thermal expansion coefficient of the cubic and orthorhombic GdSe_{1.49} should be measured, correlated with microcompositional and microstructural properties, and reasonably well documented.

$(\text{Cu,Ag})_2\text{Se}$ P-Legs

Cracks in the wrap should be eliminated. A slower drying rate and proper removal of organic binders may yield crack-free wraps. Thermal expansion mismatch between the wrap and the P-leg can be solved by using different wrap or slurry materials. Crack-free tungsten-rhenium caps can be obtained through proper specification and inspection. The design load 1.03 MPa (150 psi) on the P-leg can be increased to improve contacts at the hot and cold end, but creep should be minimized. The use of a gimbal can impart mobility to the P-leg assembly and thus partially solve misalignment problems.

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REFERENCES

1. 3M Company, "SIG/Galileo Program Status," presented at SIG Review Meeting, DOE Headquarters, Germantown, Md., Jan. 9, 1979.
2. J. D. Hinderman, *SIG Technology and Converter Hardware Schedule Status as Applicable to Galileo Flight Program*, 3M Company, St. Paul, Minn., Dec. 29, 1978.
3. 3M Company, "Preliminary Design Review for the Galileo Program," presented at SIG Review Meeting, DOE Headquarters, Germantown, Md., Nov. 28-30, 1978.

4. 3M Company, "SIG/Galileo Conceptual Design Update," presented at SIG Review Meeting, DOE Headquarters, Germantown, Md., June 21-22, 1978.
5. "Standard Specification for Chromium-Silicon Alloy Steel Spring Wire," ANSI/ASTM A 401-77, *1978 Annual Book of ASTM Standards*, Part 3, American Society for Testing and Materials, Philadelphia, 1978.
6. M. Guittard, M. A. Benacerraf, and J. Flahaut, "Les Sélénures L_2Se_3 et L_3Se_4 des Eléments des Terres Rares," *Ann. Chim.* 9: 25-34 (1964).
7. E. F. Hampl, Jr., et al., "TPM Material Performance Characteristics," Paper 729040, presented at 7th Intersociety Energy Conversion Engineering Conference, San Diego, Calif., September 1972.
8. See for example, ORNL's presentation, "Status of CBCF Insulation Optimization and Qualification," SIG Review Meeting, DOE Headquarters, Germantown, Md., June 21-22, 1978.
9. F. H. Norton, *Refractories*, 4th ed., p. 247, McGraw-Hill, New York, 1968.
10. Private communication, C. A. Alexander, Battelle Columbus Laboratories, Columbus, Ohio, December 1978.
11. Private communication, C. A. Alexander, Battelle Columbus Laboratories, Columbus, Ohio, January 1979.
12. J. R. Keiser, *Compatibility of Pt-3008 with Selected Components of the Selenide Isotope Generator System*, ORNL/TM-6660 (in press).
13. J. R. Keiser, unpublished results.
14. Private communication, P. Hogerton, 3M Company, St. Paul, Minn.
15. *Metals Handbook*, 9th ed., Vol. 1, *Properties and Selection: Irons and Steels*, p. 306, American Society for Metals, Metals Park, Ohio, 1978.
16. J. T. Milek, "Materials for Springs," *Mater. Des. Eng.* 48: 115-26 (August 1959).
17. F. W. Wilson, ed., *Tool Engineer's Handbook*, 2nd ed., McGraw-Hill, New York, 1959, pp. 98-2, -3.

18. International Nickel Company, Inc., "Spring Materials for High Temperature Service," p. 318 in *Spring Design and Application*, N. P. Chironis, ed., McGraw-Hill, New York, 1961.
19. Private communication, E. Ritter, Associated Spring Co., Bristol, Conn., Feb. 5, 1979.
20. Private communication, D. Dancik, Eiler Company, Minneapolis, Minn., Feb. 7, 1979.
21. *Metals Handbook*, 9th ed., Vol. 1, *Properties and Selection: Irons and Steels*, p. 284, American Society for Metals, Metals Park, Ohio, 1978.
22. J. E. Shigley, *Mechanical Engineering Design*, 2nd ed., pp. 361-62, McGraw-Hill, New York, 1972.
23. G. L. Kehl, *The Principles of Metallographic Laboratory Practice*, p. 412, McGraw-Hill, New York, 1949.
24. *Metals Handbook*, 8th ed., Vol. 7, *Atlas of Microstructures of Industrial Alloys*, American Society for Metals, Metals Park, Ohio, 1972.
25. *Metals Handbook*, 9th ed., Vol. 1, *Properties and Selection: Irons and Steels*, p. 290, American Society for Metals, Metals Park, Ohio, 1978.
26. R. W. Rice, "Fractographic Identification of Strength-Controlling Flaws and Microstructures," pp. 323-45 in *Fracture Mechanics of Ceramics*, Vol. 1, R. C. Bradt, D.P.H. Hasselman, and F. F. Lange, eds., Plenum, New York, 1974.
27. A. G. Evans and R. W. Davidge, "The Strength and Fracture of Stoichiometric Polycrystalline UO_2 ," *J. Nucl. Mater.* 33: 249-60 (1969).
28. A. G. Evans and R. W. Davidge, "The Strength and Oxidation of Reaction-Sintered Silicon Nitride," *J. Mater. Sci.* 5: 314-25 (1970).
29. J. R. McLaren, G. Tappin, and R. W. Davidge, "The Relationship Between Temperature and Environment, Texture, and Strength of Self-Bonded SiC," *Proc. Br. Ceram. Soc.* 20: 259-74 (June 1972).
30. A. G. Evans and G. Tappin, "Effects of Microstructure on the Stress to Propagate Inherent Flaws," *Proc. Br. Ceram. Soc.* 20: 275-97 (June 1972).

31. B. Molnar and R. W. Rice, "Strength Anisotropy in Lead Zirconate Titanate Transducer Rings." *Am. Ceram. Soc. Bull.* 47: 505-09 (1973).
32. R. B. Atkin, R. L. Holman, and R. N. Fulrath, "Substitution of Bi and Pb Ions in Lead Zirconate-Titanate," *J. Am. Ceram. Soc.* 54: 113-15 (1971).
33. N. B. Elsner et al., GA's presentation at SIG Review Meeting, DOE Headquarters, Germantown, Md., June 21-22, 1978.
34. W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics*, 2nd ed., Wiley, New York, 1976.
35. Private communication, J. Hinderman, 3M Company, January 1979.
36. C. T. Lynch, F. W. Vahldiek, and L. B. Robinson, "Monoclinic-Tetragonal Transition of Zirconia," *J. Am. Ceram. Soc.* 44: 147-48 (1961).
37. Private communication, R. B. Ericson, 3M Company, January 1979.
38. H. P. Kirchner and R. M. Gruver, "Fracture Mirrors in Polycrystalline Ceramics and Glass," pp. 309-21 in *Fracture Mechanis of Ceramics*, Vol. 1, R. C. Bradt, D.P.H. Hasselman, and F. F. Lange, eds., Plenum, New York, 1974.
39. D.P.H. Hasselman, "Unified Theory of Thermal Shock Fracture Initiation and Crack Propagation in Brittle Ceramics," *J. Am. Ceram. Soc.* 52: 600-04 (1969).
40. T. P. Gupta, "Crack Heating in Thermally Shocked MgO," *J. Am. Ceram. Soc.* 58(3-4): 143 (1975).
41. Private communications, T. K. Roche and D. A. Canonico, ORNL, and R. B. Herchenroeder, Cabot Corp., January 1979.
42. R. A. Harlow, *Properties of Cold Worked 25 Alloy*, AFML-TR-67414 (January 1969).

APPENDIX

ANALYTICAL PROCEDURES

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APPENDIX

ANALYTICAL PROCEDURES

Chemical Analyses

Steel springs were analyzed by spark source mass spectroscopy. An Associated Electrical Industries Ltd. type MS-702 spark source mass spectrograph was used.

Atomic absorption and emission spectroscopy were also performed to identify the concentrations of certain elements. The carbon contents of the springs were determined by vacuum fusion analysis. All the chemical analyses were carried out by the ORNL Analytical Chemistry Division.

Metallography

In the metallographic preparation of specimens of steel springs, BeO disks, $\text{GdSe}_{1.49}$ N-legs, and $(\text{Cu,Ag})_2\text{Se}$ P-legs, the entire sample was placed in a hollow cylindrical mounting mold. The specimen was then covered with a mixture of an epoxy resin (Araldite 502)* and Hysolt† hardener 3416, and the mold and specimen were placed in a vacuum chamber to impregnate the sample with epoxy. Lucite was not used because of its solubility in ethanol and acetone.

Since the $\text{GdSe}_{1.49}$ N-leg and the $(\text{Cu,Ag})_2\text{Se}$ P-leg assembly including the wrap are extremely fragile, the samples were not cut or sectioned. Despite use of a great deal of caution during handling and mounting, the tungsten-rhenium partition and top cap still separated from the P-leg after mounting. The mounted specimen was ground with successively finer silicon carbide abrasive papers (180, 320, 400, and 600 grit) using Hyprez‡ lubricant as a coolant. The ground specimen was placed on a Syntron§ vibratory polishing bowl using a Pellon|| cloth with a slurry of

*Product of Ciba-Geigy, Ardsley, N.Y.

†Product of the Dexter Corp., Olean, N.Y.

‡Product of Engis Corp., Morton Grove, Ill.

§Product of FMC/Syntron Co., Homer City, Pa.

||Product of Pellone Co., New York, N.Y.

alumina (Linde-A,* 0.3 μm) and ethylene glycol. A time of 22 to 29 ks (6-8 h) was usually required to remove the scratches from the grinding operation. Final polishing started with vibratory polishing with the use of 0- to 1.0- μm diamond paste on a nylon cloth with ethylene glycol as a vehicle. Usually a time of 22 to 29 ks (6-8 h) was required for this step. The polished specimen was washed with 200-proof ethyl alcohol and dried by warm air. After drying the specimen was examined with a reflected-light metallurgical microscope, Leitz Model MM6.† Both bright field and polarized light illumination conditions were used.

Scanning Electron Microscopy and Energy-Dispersive X-Ray Analysis

A JSM-U3‡ scanning electron microscope was used to examine both the original and fractured surfaces of the samples. An energy-dispersive x-ray analysis (EDXA) unit is connected to the SEM and is capable of detecting elements with atomic numbers of at least 11. The detection limit is about 0.5 wt %. Springs, BeO disks, and $\text{GdSe}_{1.49}$ N-legs were secured to a brass sample holder with a brass screw. The wrapped $(\text{Cu,Ag})_2\text{Se}$ P-legs were coated with carbon and then chromium by vacuum evaporation because the Astroquartz-Min-K wrap is electrically nonconductive

Electron Microprobe

A Material Analysis Co. (ETEC, Hayward, Calif.) model 400S electron microprobe equipped with a wavelength-dispersive x-ray analyzer and an EDX analyzer was used. It is capable of detecting elements with atomic numbers of at least 11 (Na), and the detection limit is about 0.5 wt %. Elemental mapping was accomplished by the wavelength-dispersive x-ray analyzer.

*Product of Union Carbide Corp., New York, N.Y.

†Product of Leitz Wetzlar Co., West Germany.

‡Product of Jeol, Bedford, Mass.

Microhardness

A Kentron* microhardness tester was used. The load was 0.1 kg (0.98 N) and the diamond pyramid hardness (DPH) was calculated from the formula $H = (1854.4 \times P)/d^2$, where H is the DPH number, P is the load in grams, and d is the diagonal length in micrometers.

Ion Microprobe

The ion microprobe used in this work was manufactured by Applied Research Laboratories, Sunland, Calif. The instrument has two mass spectrometers. A magnetic analyzer of one spectrometer focuses a mass-analyzed primary beam onto the sample surface. The minimum primary beam diameter is about 2.0 μm , allowing resolution of surface spatial detail of that size. Ions formed by various mechanisms in the sputtering process are collected by an extraction electrode and directed by an electrostatic lens into a double focusing mass spectrometer, where mass analysis is accomplished.

Secondary Ion Mass Spectroscopy

An ion-scattering spectrometer-secondary ion mass spectrometer, model 610, made by 3M Company, was used for oxygen surface analysis of gadolinium selenide. A beam of positive ^3He ions at a pressure of 5.3 mPa ($4.0\text{E-}05$ torr) was accelerated at 1 keV toward the sample surface. A depth estimated as 0.1 to 1 μm was analyzed. A 64-s counting time was used.

*Product of Riehle Co., East Moline, Ill.

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