GENERAL ATOMIC

GA-A13426

RADIOISOTOPE SPACE
POWER GENERATOR
— ANNUAL REPORT —

FOR THE PERIOD JULY 1, 1973
THROUGH JUNE 30, 1974

by
N. B. ELSNER and J. CHIN

Prepared under
Contract AT(04-3)-943
for the San Francisco Operations Office
U.S. Energy Research and Development Administration

MASTER

DATE PUBLISHED — JULY 15, 1975

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General Atomic Project 3236
(Formerly 4020)

Date Published
July 15, 1975

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FOREWORD

The Isotec Technology FY 1974 annual summary report is an account of several different efforts:

1. Completion of the first ring converter segment, which was fabricated from N-type PbTe and P-type segmented PbSnMnTe/BiSbTe.
2. Testing of the ring converter segment at Jet Propulsion Laboratory (JPL).
3. Continuing studies on the interaction of SiMo and SiGe with candidate insulations. Si and Ge vapor species react with the SiO₂ insulation producing volatile SiO and GeO, which can condense out on the cooler areas causing electrical shorting. Qualification of Si₃N₄ as an insulating material and deposition of Si₃N₄ on SiGe couples by ion plating techniques.
4. Continuing development in the alloying and characterization of TAGS.

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ABSTRACT

During the Isotec Technology Program in FY 1974, fabrication of the first ring converter segment was completed. In subsequent performance testing at Jet Propulsion Laboratories it demonstrated good agreement with the expected performance. The segment has accumulated over 7000 hours at a T_H of 450°C and the degradation rate over the last 5000 hours has been 0.1%.

In the area of SiGe technology, continued compatibility tests between candidate insulation materials and SiGe, SiMo, and Si_3N_4 were conducted. Si_3N_4 in all cases continued to perform satisfactorily as a high temperature insulator. Low temperature Si_3N_4 coating development on SiGe thermocouples was performed by ion plating. While the ion plating process was successful in coating a whole couple, the Si_3N_4 deposited was silicon rich. Further process control of the stoichiometry of the material being deposited is required.

The development of a more stable TAGS type alloy did not result in any alloys that had enhanced thermal stability; however, it may be possible to use one of the developed alloys in segmenting with TPM-217.

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1. FABRICATION OF FIRST RING CONVERTER SEGMENT

The ring converter design for the Economic Radioisotope Thermoelectric Generator Study is given in Ref. 1. Its fabrication and performance testing are covered in Refs. 2 and 3.

In summary, the ring converter is designed to be a lightweight, low-cost system fabricated from many readily available off-the-shelf materials. It can be efficiently employed as a relatively low-temperature device using the PbTe and Bi_2Te_3 family of thermoelectric alloys. High-temperature materials such as the selenide alloys can also be used in the ring converter since the radiator structure would still operate at the same cold side temperature.

The ring converter segment was constructed of N-type PbTe and P-type segmented PbSnMnTe/BiSbTe.

The multifoil insulation was excess transit insulation. Since this insulation had been punched to accommodate elements in a flat panel configuration, the holes had to be opened up slightly to accommodate the elements that were now configured in a circular cross section. This slight opening up of the holes did not appear to contribute to any significant heat loss.

A cross section of the ring converter segment, giving the materials employed, is shown in Fig. 1-1.

Fig. 1-1. Schematic of ring converter thermal electric couple cross section

2. PERFORMANCE TESTING OF THE RING CONVERTER SEGMENT

Performance testing of the ring converter segment was carried out by using transit excess top and bottom covers and heat source. The performance testing was carried out at JPL by both GA and JPL personnel. The results are given below.

A maximum electric power output of 14.4 W was measured for hot and cold cap temperatures of 445°C and 174°C, respectively. By comparison, a transit equivalent* ring RTG would produce 55 W at a cold junction temperature of 140°C (expected space conditions). This represents greater than a 50% increase over the approximately 36 W produced by the transit. This increase in power output is due to the enlarged and segmented P-element and to the increase in hot junction temperature with the extended mesh bonded elements. Power output comparisons between ring and transit panels are shown in Fig. 2-1.

Since the heat loss out of the ends could not be accurately measured, the test was not intended to characterize the thermal efficiency of the device. Attempts were made to estimate the heat balance and infer the heat flow through the ring. These calculations showed a ring efficiency of 5.3% and a material efficiency of 5.8% at a hot cap temperature of 445°C and corrected cold cap temperature of 153°C. End closure losses for the ring converter test were approximately 25% of the total heat input, compared to 7% for the transit. The ring end closure losses were large because the covers overlapped the outside dimensions of the ring and exposed nearly 30% of the hot insulation surface area to the coolant shrouds.

*The ring contained 144 thermoelectric couples, which was one-third the number on the transit radioisotope thermoelectric generator (RTG).

Overall, the performance of the ring converter section was in good agreement with the expected performance. The power output was uniform around the circumference of the ring to within 2%, and the temperature variation around the surface was within 3%. The temperature drop across the radiator was 3°C and, between the cold cap and radiator surface, the total temperature drop was 7°C maximum. The corresponding panel configuration temperature drop was approximately 10°C.

The ring converter segment continues on test at JPL and as of the end of 1974 it had accumulated over 7000 hours at a T_H of 450°C (versus 400°C for the transit). The degradation rate over the past 5000 hours was 0.1%, which represents an extremely stable generator.

Fig. 2-1. Power output comparisons between ring and transit panels

3. SILICON - GERMANIUM

3.1. COMPATIBILITY AND VAPORIZATION

Vaporization control is a necessary requirement for the first stage of a cascaded generator. Much of the Isotec materials development work at General Atomic has been directed toward the study of material compatibility of N and P type 80 Si 20 Ge and N and P type SiMo in contact with candidate insulations. The work performed to date is reported in Refs. 1 and 2. The objectives of these early studies were to determine:

1. How the SiGe and SiMo alloys vaporized and what the resultant effects were on the alloys when they did vaporize.
2. What means of vaporization suppression and electrical isolation will enhance the lifetime of the thermoelectric generator.
3. What insulators can be used with SiGe and SiMo alloys.

Some of these objectives still applied to work done in the past year. Additional materials being examined now include N and P SiMo alloys in contact with proposed electrical insulation materials. Material vaporization studies included:

1. N and P SiGe and N and P SiMo resting on molybdenum.
2. N and P SiGe and N and P SiMo in contact with two forms of Astro quartz.
3. SiGe and SiMo, N and P, in contact with Si_3N_4 .
4. SiGe and SiMo, N and P, in contact with two forms of Al_2O_3 .

The results of these experiments are summarized in Figs. 3-1 through 3-18. The rate of evaporation of N SiGe is higher than P SiGe; similarly, the rate of N SiMo evaporation is higher than P SiMo at 1000°C in a 10^{-9} torr ion-pumped vacuum system. Evaporation rates for N and P SiMo are lower than corresponding N and P SiGe.

Wrapping of N and P SiGe or N and P SiMo in Astro quartz caused a marked increase in their rates of evaporation. These weight changes were not repeated when either slab quartz or layered quartz was used.

Rates of evaporation of SiGe and SiMo in contact with Al_2O_3 slabs were approximately the same as the controls. Similar evaporation rates for SiGe and SiMo in contact with Si_3N_4 slabs were lower than the controls. These results suggest Si_3N_4 forms a mechanical barrier to the evaporation of SiGe or SiMo. There are no apparent adverse reactions between Si_3N_4 and SiGe or SiMo. A slight reaction between the Al_2O_3 and SiGe or SiMo is occurring which nullifies the mechanical barrier to the evaporation effect by the Al_2O_3 slabs. Also, the enhanced evaporation of the SiGe and SiMo in contact with the quartz slabs is not compensated by the quartz slab as a mechanical barrier to SiGe and SiMo evaporation.

3.2. Si_3N_4 EVALUATION

Weight loss measurements at GA (Ref. 4) and JPL (Ref. 5) have shown Si_3N_4 is an effective barrier to vaporization losses in SiMo at 1050°C. One goal of this year's effort was to determine the feasibility of depositing Si_3N_4 on SiMo in an ion plater. A second goal was to evaluate the effectiveness of this deposition as a barrier to SiMo evaporation and an inhibitor to internal electrical shorting of the thermoelectric couple.

3.2.1. Si_3N_4 Deposition Studies

The properties of an ion-plated deposit depend on the following process variables:

1. The chemical composition, purity, and form of the evaporated source material.
2. Electron beam power and focus.
3. The reactant gases surrounding the substrate, and their chemistry and partial pressures.
4. The shape of the substrate and its physical relationship to the electron beam heated source.
5. The shape and magnitude of the RF field surrounding the substrate.
6. The substrate temperature.

Silicon and Si_3N_4 were used as evaporation sources. Silicon nitride as a source material was difficult to control. Wild fluctuations in the chamber pressure resulted which automatically shut down the electron beam. The electron beam drilled a hole in the Si_3N_4 evaporation source material, which made it difficult to sustain a long deposition run. Contaminants within the Si_3N_4 source were frequently deposited along with the Si_3N_4 on the substrate. Silicon as a source was also difficult to control. The silicon melt splattered during the deposition without warning. Several steps were taken to eliminate this problem. First, arc-melted silicon of high purity was purchased to eliminate included oxygen. Second, the silicon was premelted at the start of every deposition to eliminate porosity. The most important parameter to control splatter was the electron beam power input to the source material. Above a critical power setting (Ref. 6) the heat input to the molten silicon source is more rapid than heat removal by conduction to the copper-cooled crucible and evaporation from the silicon surface. When these conditions occur, splatter results.

The reactant gases used in these experiments included nitrogen, NH_3 , and $\text{NH}_3 + \text{SiH}_4$ mixtures. The nitration of silicon with either N_2 or NH_3

is thermodynamically feasible. Nitriding with NH_3 is more favorable than similar reactions using nitrogen because of the larger free energy of formation of ammonia and the large bond energy in the nitrogen molecule. This was verified in early depositions using nitrogen. These deposits, which were nonuniform, were mainly silicon with sporadic nitrogen inclusions.

Ammonia and ammonia plus 1% SiH_4 reactant gases were used in coating outgassed and nonoutgassed SiMo substrates. Both N and P SiMo samples were coated with these gas mixtures and compared. The intent of the SiH_4 was to increase the available Si by means other than increasing the beam power. The increase in H/N ratio was not expected to interfere with the deposition since only 1% SiH_4 was added. It was also hoped that the SiH_4 would react with residual oxygen in the ion plating system during the sputter cleaning of the substrate to minimize SiO inclusions in the Si_3N_4 deposit. Substrate temperatures for these depositions were maintained at 300°C with bias voltage RF heating.

Si_3N_4 deposits from both NH_3 and $\text{SiH}_4 + \text{NH}_3$ gas mixtures on nonoutgassed N-SiMo had small grains which were separated from adjacent grains. All of these coatings appeared porous and nonuniform. Deposits on outgassed N-SiMo had larger grains than deposits on nonoutgassed samples. These grains were frequently clustered together with no apparent grain boundary separation. The deposition rate for Si_3N_4 was increased by the addition of SiH_4 to the deposition gas.

Examination of scanning electron photomicrographs showed the presence of islands of molybdenum in uncoated N-SiMo (Fig. 3-19). These inclusions had no apparent effect on the uniformity of the final deposits (Figs. 3-20 through 3-23).

The generation of surface-connected columnar deposits is likely due to the outgassing of phosphorus during the deposition process.

To verify this, samples of Si_3N_4 -coated N-SiMo were annealed at 1100°C in a Knudsen cell connected to a mass spectrometer. The results of these

examinations are plotted in Figs. 3-24 through 3-26. An uncoated N-SiMo sample is shown in Fig. 3-27 for comparison. The results verify the large P_2 partial pressure in nonoutgassed specimens. N-SiMo, outgassed 200 hours at 1100°C and 10^{-9} torr and then coated with Si_3N_4 , had higher SiO partial pressures than uncoated N-SiMo and the same SiO partial pressures as non-gassed but Si_3N_4 -coated N-SiMo. These results suggest the formation and adsorption of SiO during the Si_3N_4 deposition. Partial pressures of SiO were slightly lower after 5 hours of annealing in coatings deposited from $\text{NH}_3 + 1\% \text{SiH}_4$ than from NH_3 only.

Si_3N_4 was also deposited on P-SiMo. The microstructure of Si_3N_4 -coated outgassed and nonoutgassed P-SiMo (Figs. 3-28 through 3-32) did not show the same microstructural differences as N-SiMo. This is reasonable since P-SiMo contains no phosphorus. Specimens coated in gas mixtures containing $\text{NH}_3 + 1\% \text{SiH}_4$ appeared approximately the same as those coated in NH_3 only.

3.2.2. Mass Spectrometric Studies

Knudsen cell measurements (Figs. 3-33 and 3-34) showed no volatile boron or boron oxides. SiO partial pressures for an uncoated control and a coated outgassed sample coated from $\text{NH}_3 + 1\% \text{SiH}_4$ were approximately the same as equivalent N-SiMo samples. Thus the results again suggest the adsorption of oxygen during Si_3N_4 deposition. These results led to the conclusion that oxygen is present during ion plating and must be removed if SiO is to be eliminated from the coating.

Two sources of oxygen are possible in the ion plating system. Either the system is not leak tight and/or adsorbed oxygen within the chamber is sufficient to cause the SiO formation. A partial pressure analyzer was attached to the system to determine if leaks were occurring. The results were indefinite. Attempts were made to remove adsorbed water by wrapping heater tapes around the chamber. The effectiveness of this tactic could be seen indirectly in the lower electron beam power settings needed during

the deposition. Quantitative evaluation of the effectiveness of this pre-heating has not been obtained.

3.2.3. Si₃N₄, Geometry Effects During Deposition

Substrate coverage in all vapor deposition processes is dependent on the geometry of the substrate. Trial depositions of Si₃N₄ were made on glass plates with separations equivalent to those of thermoelectric couples. Throwing power of the Si₃N₄ was determined by measuring the coating thickness as a function of penetration depth into the gaps. The results (Figs. 3-35 and 3-36) show that the penetration depth is not only a function of the substrate geometry but also a function of the orientation of the gap relative to the vaporizing silicon source. Line-of-sight depositions are a factor of 10 thicker than backside depositions. Side penetration is more shallow than vertical penetration.

3.2.4. Vaporization of Si₃N₄-Coated SiMo

Weight loss measurements have been made on Si₃N₄-coated N and P-SiMo. Samples were in the form of plates and cubes. Anneals were 1100°C in vac ion pumped, molybdenum resistant heated furnaces. Pressures were maintained below 10⁻⁸ torr during the annealing.

Weight loss rates for early Si₃N₄ specimens coated are shown in Figs. 3-37 and 3-38. These are compared with uncoated SiMo and hot pressed Si₃N₄ from Norton in Fig. 3-39. As noted, coated Si₃N₄ samples show an initial high release in SiO which decreases in a few hours. This SiO release causes an initial weight loss rate in coated SiMo samples which is greater than that of uncoated samples. One possible explanation for this loss is the chemical composition of the Si₃N₄ in these early coatings. Microprobe examinations of these surfaces showed the coatings to be substoichiometric in nitrogen. After this initial high release rate, coated samples showed smaller vaporization rates than the control. Evaporation rates in N-SiMo samples are higher than P-SiMo. This can be attributed to phosphorus

outgassing, which contributes to weight loss and an increased surface area available for evaporation. Scanning electron photomicrographs of typical N and P SiMo samples coated by early techniques with Si_3N_4 are shown after 0, 745, 800, and 3000 hours at 1100°C in Figs. 3-40 through 3-48. In these examinations the coatings were not obvious after 3000 hours at 1100°C .

3.3. RESISTIVITY MEASUREMENTS

Two questions persist in the study of SiGe couples:

1. How can weight loss in the SiMo hot shoe be inhibited?
2. How can vapor phase loss of Si from the SiMo be prevented from decreasing the overall resistivity of the SiGe couple?

The results, given in Section 3.1, show the rate of weight loss in Si_3N_4 -coated SiMo samples is reduced but not stopped. If Si is escaping through the coatings, it is reacting with SiO_2 to form SiO and is being deposited over the SiGe couple. If a conductive film is being deposited over the Si_3N_4 coating, then the limiting resistivity of the couple would be the resistivity of the Si_3N_4 film. Since SiO decomposes at lower temperatures to form Si + SiO_2 , the unknown variable is the resistivity of Si + SiO_2 composites. To obtain more quantitative data, resistivity measurements on Si_3N_4 coatings and Si + SiO_2 bodies are being made as a function of temperature.

The first measurements on Si_3N_4 coatings were made with the apparatus shown in Fig. 3-40. A Si_3N_4 coated Mo sample was clamped between molybdenum foil electrodes and placed in a diffusion pumped vacuum system. The sample (0.251 in. diameter x 0.531 in. long) was heated to 1000°C and cooled to room temperature while monitoring changes in resistance with an ohmmeter. The Si_3N_4 coated sample exhibited an expected decrease in resistance with temperature as shown in Fig. 3-41. However, the anomalous increase in

resistance of the sample at 800-900°C is apparently a reordering of the as-deposited material.

Several weaknesses in the first experimental resistivity measurements are being corrected by the apparatus shown in Fig. 3-42. First, the mechanically held contacts are only good if the SiMo thermal expansion coefficient is greater than the jig fixture. Then, the clamps must elastically yield so that contact is maintained during the cooldown. This is corrected in the modified furnace with a dead-weight molybdenum slug maintaining ceramic-to-metal contact. In the first apparatus, an ohmmeter was used for resistance measurements. In the modified apparatus, a Wheatstone bridge circuit will be used for resistance measurements. Finally, in the first apparatus, a diffusion pumped system was used which limited pressures to greater than 10^{-6} torr. An ion pump, bakeable vacuum system is being used for the modified resistivity measurements. The test environment thus more closely simulates the operating environment of the thermal electric generator. This apparatus is a two-terminal setup similar to that used by Wallace and Ruh (Ref. 7).

The two-terminal electrical resistivity apparatus was calibrated by measuring the electrical resistivity of polycrystalline alumina (Lucalox) from GE. The major impurity in this Al_2O_3 is 0.25 wt % MgO. The results of these calibration tests with and without an evaporative Mo film on the Al_2O_3 are essentially the same and are shown in Figs. 3-43 and 3-44. These results agree with those reported by Schemmel and Gordon (Ref. 8) for polycrystalline Al_2O_3 in a four-terminal measurement.

Resistivities of 50:50 and 90:10 GeO_2 -Ge hot-pressed mixtures were also measured. The 90:10 results are shown in Fig. 3-45. The test was repeated several times with no evidence of resistivity changes due to chemical reactions between the GeO_2 and Ge. The 50:50 GeO_2 -Ge sample (Fig. 3-46) suffered extensive weight loss in nonelectrode areas during the test. The resistivities measured from this sample were understandably inconsistent.

Resistivities of 90:10 SiO_2 -Ge are shown in Fig. 3-47. The repeatability of the tests shows that in short-term anneals electrical characteristics of 90:10 SiO_2 -Ge are not affected by a reaction between these materials.

3.4. SiGe COATED COUPLES

Twelve SiGe couples were coated with Si_3N_4 for life testing at JPL. These coatings were prepared in groups of four with the technology current at the time. For this reason, the results of some of these life tests are not necessarily representative of current coating technology.

Fig. 3-1. Weight loss rates for N-SiGe and N-SiMo vs time at 1000°C and 10^{-9} torr

Fig. 3-2. Weight loss rates for Si_3N_4 coated N-SiMo vs time at 1000°C and 10^{-9} torr

Fig. 3-3. Weight loss rates for P-SiGe and P-SiMo vs time at 1000°C and 10⁻⁹ torr

Fig. 3-4. Weight loss rates for Si_3N_4 coated P-SiMo vs time at 1000°C and 10^{-9} torr

Fig. 3-5. Weight loss rates for N-SiGe and N-SiMo wrapped with Astro quartz vs time at 1000°C and 10⁻⁹ torr

Fig. 3-6. Weight loss rates for P-SiGe and P-SiMo wrapped with Astro quartz vs time at 1000°C and 10⁻⁹ torr

Fig. 3-7. Weight loss rates for N-SiGe and N-SiMo in contact with layers of Astro quartz vs time at 1000°C and 10⁻⁹ torr

Fig. 3-8. Weight loss rates for P-SiGe and P-SiMo in contact with layers of Astro quartz vs time at 1000°C and 10⁻⁹ torr

Fig. 3-9. Weight loss rates for N-SiMo in contact with clear quartz vs time at 1000°C and 10⁻⁹ torr

Fig. 3-10. Weight loss rates for P-SiMo in contact with clear quartz vs time at 1000°C and 10⁻⁹ torr

Fig. 3-11. Weight loss rates for N-SiGe and N-SiMo in a molybdenum can covered with an Astro quartz lid vs time at 1000°C and 10⁻⁹ torr

Fig. 3-12. Weight loss rate for P-SiGe and P-SiMo in a molybdenum can covered with an Astro quartz lid vs time at 1000°C and 10⁻⁹ torr

Fig. 3-13. Weight loss rate for N-SiGe and N-SiMo in Al_2O_3 crucibles covered with Al_2O_3 wool vs time at $1000^\circ C$ and 10^{-9} torr

Fig. 3-14. Weight loss rate for P-SiGe and P-SiMo in Al_2O_3 crucibles covered with Al_2O_3 wool vs time at 1000°C and 10^{-9} torr

Fig. 3-15. Weight loss rate for N-SiGe and N-SiMo covered with an Al_2O_3 slab vs time at 1000°C and 10^{-9} torr

Fig. 3-16. Weight loss rate for P-SiGe and P-SiMo covered with an Al_2O_3 slab vs time at 1000°C and 10^{-9} torr

Fig. 3-17. Weight loss rate for N-SiMo covered with a slab of Si_3N_4 vs time at 1000°C and 10^{-9} torr

Fig. 3-18. Weight loss rate for P-SiGe covered with a slab of Si_3N_4 vs time at 1000°C and 10^{-9} torr

Fig. 3-19. Scanning electron photomicrographs of uncoated N-SiMo at 1500X (top) and 400X (bottom) showing connected porosity and islands of molybdenum

Fig. 3-20. Scanning electron photomicrographs of Si_3N_4 coatings on nonoutgassed N-SiMo deposited with a cover gas of ammonia at 1500X (top) and 400X (bottom). This fine grain columnar structure apparently has substrate connected porosity.

Fig. 3-21. Scanning electron photomicrographs of Si_3N_4 coatings deposited with a cover gas of ammonia on 200-hour, 1100°C , 10^{-9} torr outgassed N-SiMo at 1500X (top) and 400X (bottom). Intergranular-bonding is more evident here than in nonoutgassed samples, but some porosity still exists.

Fig. 3-22. Scanning electron photomicrographs of Si₃N₄ coatings on nonoutgassed N-SiMo, deposited with a cover gas of SiH₄ + NH₃ at 1500X (top) and 400X (bottom). A porous, fine grain columnar structure is equivalent to that deposited with a cover gas of NH₃ only.

Fig. 3-23. Scanning electron photomicrographs of Si₃N₄ coatings on 200-hour, 1100°C, 10⁻⁹ torr outgassed N-SiMo deposited with a cover gas of SiH₄ + NH at 1500X (top) and 400X (bottom). Large interconnected grains are noticed in this coating, but surface porosity is still evident.

Fig. 3-24. Partial pressures above nonoutgassed N-SiMo, coated with Si_3Ni_4 in ammonia, during 1100°C annealing in a molybdenum Knudsen cell

Fig. 3-25. Partial pressures above 200-hour, 1100°C, 10⁻⁹ torr outgassed N-SiMo coated with Si₃N₄ in ammonia, during 1100°C annealing in a molybdenum Knudsen cell

Fig. 3-26. Partial pressures above 200-hour, 1100°C, 10^{-9} torr outgassed N-SiMo, coated with Si_3N_4 in $\text{NH}_3 + 1\% \text{SiH}_4$ during 1100°C annealing in a molybdenum Knudsen cell

Fig. 3-27. Partial pressures above uncoated and nonoutgassed N-SiMo, during 1100°C annealing in a molybdenum Knudsen cell

(a)

(b)

Fig. 3-28. Scanning electron photomicrographs of P-SiMo at (a) 1500X and (b) 400X showing islands of molybdenum and notable porosity

(a)

(b)

Fig. 3-29. Scanning electron photomicrographs of ion-plated Si_3N_4 coatings deposited in an ammonia gas on nonoutgassed P-SiMo at (a) 1500X and (b) 400X. Surface connected porosity is visible.

(a)

(b)

Fig. 3-30. Scanning electron photomicrographs of ion-plated Si_3N_4 coatings deposited in ammonia gas on 200-hour, 1100°C , 10^{-9} torr out-gassed P-SiMo at (a) 1500X and (b) 400X

(a)

(b)

Fig. 3-31. Scanning electron photomicrographs of ion-plated Si_3N_4 coatings deposited from $\text{NH}_3 + 1\% \text{SiH}_4$ gas mixtures on nonoutgassed P-SiMo at (a) 1500X and (b) 400X

(a)

(b)

Fig. 3-32. Scanning electron photomicrographs of ion-plated Si_3N_4 coatings deposited in $\text{NH}_3 + \text{SiH}_4$ gas mixtures on 200-hour, 1100°C , 10^{-9} torr outgassed P-SiMo at (a) 1500X and (b) 400X

Fig. 3-33. Partial pressures above P-SiMo, uncoated and nonoutgassed during 1100°C annealing in a molybdenum Knudsen cell

Fig. 3-34. Partial pressures above 1100°C, 10^{-9} torr, 200-hour, outgassed P-SiMo, coated with $\text{Si}_3\text{N}_4 + 1\%$, during 1100°C annealing in a molybdenum Knudsen cell

Fig. 3-35. Si_3N_4 deposition thickness vs penetration into a vertically oriented 0.050 in. gap, 6 in. from the molten silicon source

Fig. 3-36. Si₃N₄ deposition thickness vs penetration into a horizontally oriented 0.050 in. gap, 6 in. from the molten silicon source

Fig. 3-37. Evaporation loss rate at 1100°C and 10^{-9} torr for Si_3N_4 -coated P-type SiMo

Fig. 3-38. Evaporation loss rate at 1100°C and 10^{-9} torr for Si_3N_4 -coated N-type SiMo

Fig. 3-39. Evaporation loss rate at 1100°C and 10^{-9} torr for Norton centered Si_3N_4

Fig. 3-40. Experimental apparatus for 1000°C, 10^{-6} torr Si_3N_4 coating resistivity measurements

Fig. 3-41. Electrical resistance measurement Si_3N_4 coating on Mo

Fig. 3-42. Two-terminal resistivity measurement apparatus showing a Lucalox standard sample in place. Electrodes are molybdenum slugs with smooth places and imbedded thermocouples

Fig. 3-43. Electrical resistivity measurements, polycrystalline Al_2O_3 (Luclox) control sample with evaporative molybdenum electrode interfaces

Fig. 3-44. Al₂O₃ sample (no coating)

Fig. 3-45. GE + GE O₂ 10/90 wt % molybdenum coated both sides (0.75 in. diameter)

Fig. 3-46. GE + GE O₂ 50/50 wt % molybdenum coated both sides (0.75 in. diameter)

Fig. 3-47. GE + SiO₂ 10/90 wt % (no coating)

4. TAGS ALLOY DEVELOPMENT

4.1. INTRODUCTION

As brought out in Ref. 9, TAGS [which is an acronym for $(\text{AgSbTe}_2)_{15}(\text{GeTe})_{85}$] suffers from an instability in thermoelectric properties and a high vaporization rate. The work reported upon in this report has been devoted to understanding the changes in properties and attempting to modify the alloy so it would not only produce improved thermoelectric properties but would retain these properties as a function of time.

From a programatic standpoint it was desirable to develop a new TAGS-type alloy that could be utilized in the ring converter. During this contract year, the first ring converter segment was to be fabricated and evaluated. In January 1973, the selection of the P-leg material for the ring converter had to be made, and the segmented combination of $\text{PbSnMnTe}/\text{BiSbTe}$ was chosen. Because of this decision and the limitation on funding, the work on TAGS alloy development was essentially terminated. From the results obtained on these experimental alloys, it appears that a TAGS-type alloy of improved thermoelectric properties can possibly be developed with further studies.

4.2. BACKGROUND

Three modified TAGS-type alloys, designated T-35, T-36, and T-37, were fabricated and evaluated. Their performance indicated a possibility for improvement. With all three alloys, the α and R increased with time just as with the conventional TAGS alloy; this data is given in Ref. 9. The reason for the change in properties of these alloys with time is presumed to be the same as for TAGS: a change in composition with time.

Alloys T-35, T-36, and T-37 continued to be life tested during this contract year. The basis for their selection is given in Ref. 9.

4.3. NEW ALLOYS

4.3.1. Design

The alloys initially developed were basically along the following lines:

1. In the first group, the Ag to Sb to Te ratios that were utilized were those of Ref. 10; namely ($\text{Ag}_{0.82} \text{Sb}_{1.18} \text{Te}_{2.18}$). The amount of GeTe alloyed with the Ag-Sb-Te was then varied over a range as noted in Table 4-1.
2. In the second group of alloys, the same procedure was utilized; however, the Ag to Sb to Te ratios were those of Ref. 11, namely $\text{Ag}_{0.82} \text{Sb}_{1.25} \text{Te}_{2.244}$.
3. The third group, composed of only one alloy, contains a $\text{Ag}_2\text{Te}/\text{Sb}_2\text{Te}_3$ ratio that is midway between that used in conventional TAGS and that used in the alloys of Refs. 10 and 11. As with alloys T-36 and T-37, this alloy was life tested to 8600 hours.
4. The makeup of the fourth group of alloys investigated was based upon microprobe examination of conventional TAGS that was run in gradient for 18,000 hours.
5. The fifth group is composed of two additional alloys that were prepared inadvertently (their weighed out composition was in error). The data generated is reported here because it is of interest.

SnTe was used in the area of the mesh since it readily extrudes into the mesh and is compatible with both TAGS and the Fe mesh/cap material.

TABLE 4-1
TAGS ALLOY STUDY

Alloy	Composition	Weight (%)				Seebeck Coeff. ($\bar{T}=80^{\circ}\text{C}$)	Resistance (RT)	α^2/R	X-ray Diffraction Results	Seebeck Coeff.	Resistance ($\bar{T}=280^{\circ}\text{C}$)	α^2/R	Remarks
		Ag	Sb	Ge	Te								
T-30	(Ag _{1.0} Sb _{1.0} Te _{2.0}) _{0.15} (GeTe) _{0.85}	6.66	7.52	25.40	60.42	110	3.00	4.0	Rhombohedral - may or may not have cubic	164	4.5	6.0	GA conversion based on isotopes composition
T-35	Ag _{0.82} Sb _{1.18} Te _{2.18} Series	6.34	7.56	25.55	60.55	105	2.60	4.2		159	4.4	5.8	
T-60	(Ag _{0.82} Sb _{1.18} Te _{2.18}) _{0.10} (GeTe) _{0.90}	3.83	6.21	28.26	61.70								
T-59	(Ag _{0.82} Sb _{1.18} Te _{2.18}) _{0.12} (GeTe) _{0.88}	4.47	7.26	26.91	61.36								
T-50	(Ag _{0.82} Sb _{1.18} Te _{2.18}) _{0.13} (GeTe) _{0.87}	4.78	7.76	26.26	61.19	148	5.32	4.1	Mostly rhombohedral, 20-30% cubic	213	8.9	5.1	
T-58	(Ag _{0.82} Sb _{1.18} Te _{2.18}) _{0.14} (GeTe) _{0.86}	5.08	8.26	25.63	61.03								
T-36	(Ag _{0.82} Sb _{1.18} Te _{2.18}) _{0.15} (GeTe) _{0.85}	5.38	8.74	25.01	60.88	130	3.60	4.6		180	5.9	5.5	
T-47	(Ag _{0.82} Sb _{1.18} Te _{2.18}) _{0.16} (GeTe) _{0.84}	5.66	9.20	24.41	60.72	125	4.30	3.6	Mostly rhombohedral, 20-30% cubic	201	7.3	5.5	
T-48	(Ag _{0.82} Sb _{1.18} Te _{2.18}) _{0.17} (GeTe) _{0.83}	5.94	9.66	23.82	60.57	132	4.50	3.8	Mostly rhombohedral, 20-30% cubic	208	7.7	5.4	
T-49	(Ag _{0.82} Sb _{1.18} Te _{2.18}) _{0.19} (GeTe) _{0.81}	6.48	10.53	22.69	60.29	142	5.15	3.9	Mostly rhombohedral, 20-30% cubic	209	8.3	5.2	
	Ag _{0.82} Sb _{1.25} Te _{2.244} Series												
T-62	(Ag _{0.82} Sb _{1.25} Te _{2.244}) _{0.10} (GeTe) _{0.90}	3.80	6.53	28.06	61.61								
T-61	(Ag _{0.82} Sb _{1.25} Te _{2.244}) _{0.12} (GeTe) _{0.88}	4.43	7.63	26.68	61.26								
T-39	(Ag _{0.82} Sb _{1.25} Te _{2.244}) _{0.13} (GeTe) _{0.87}	4.74	8.15	26.02	61.08	115	3.88	3.4		209	6.9	6.4	
T-38	(Ag _{0.82} Sb _{1.25} Te _{2.244}) _{0.14} (GeTe) _{0.86}	5.04	8.66	25.38	60.92	129	3.64	4.5		195	6.0	6.3	

TABLE 4-1 (continued)

Alloy	Composition	Weight (%)				Seebeck Coeff. ($\bar{T}=80^{\circ}\text{C}$)	Resistance (RT)	α^2/R	X-ray Diffraction Results	Seebeck Coeff.	Resistance ($\bar{T}=280^{\circ}\text{C}$)	α^2/R	Remarks
		Ag	Sb	Ge	Te								
T-37	(Ag _{0.82} Sb _{1.25} Te _{2.244}) _{0.15} (GeTe) _{0.85}	5.32	9.16	24.76	60.76	148	4.80	4.5		196	7.5	5.3	
T-40	(Ag _{0.82} Sb _{1.25} Te _{2.244}) _{0.16} (GeTe) _{0.84}	5.60	9.64	24.15	60.60	143	4.95	4.1		165	4.9	5.5	
T-51	(Ag _{0.84} Sb _{1.25} Te _{2.244}) _{0.17} (GeTe) _{0.83}	6.01	10.10	23.52	60.36	111	3.29	3.7	Mostly rhombohedral, <10% cubic	185	6.0	5.7	
T-52	(Ag _{0.84} Sb _{1.25} Te _{2.244}) _{0.19} (GeTe) _{0.81}	6.55	11.01	22.38	60.06	164	6.80	3.9	Rhombohedral and over 50% cubic	224	10.8	4.6	
	Synthesis of Alloys Based Upon Microprobe Exam- ination of Element Run in Gradient												
T-42		5.90	9.20	27.50	58.00	128	4.30	3.8		189	7.0	5.1	GA calculation of hot- end matrix
T-54		5.73	8.26	23.50	62.53	51	1.71	1.5	Rhombohedral but fuzzy, $\alpha \leq 90\%$, cubic may be hidden	89	2.3	3.5	Scripps calculation of hot-end matrix
T-43		5.90	7.00	30.00	59.00	97	2.77	3.3					GA calculation of cold- end matrix
T-56		6.74	8.18	23.71	61.37	60	1.70	2.1	Clean pattern, least rhombohedral, almost cubic fuzzy pattern	98	2.1	4.7	Scripps calculation of cold-end matrix
T-55		6.15	6.22	25.29	62.33	51	1.56	1.6	Same as T-54 but some slight shiftings	86	1.8	4.1	Scripps calculation of mid-section matrix
T-57		6.21	7.56	24.15	62.08	55	1.70	1.7	Same as T-55, fuzzy pattern	91	2.0	4.2	Scripps calculation of the average matrix overall
T-44		52.00	--	6.00	42.00	-133	High	--					GA calculation of the hot-end precipitate
T-53		49.15	0.58	4.74	45.54	+250	High	--					Scripps calculation of the hot-end precipitate

(a) Initial α very high (about 450) and then it drops off with time.

(b) The nominal dimensions of the elements allowed for an effective length of 0.170 in. and a diameter of 0.125 in.

4.3.2. Procedure

The alloys were prepared by weighing out the individual elements and melting them in sealed-off quartz vials. The alloys were typically cooled in a modified Bridgman cast furnace and annealed at 500°C for 16 hours. The whole ingot was then comminuted.

The alloys were measured for thermoelectric properties by vacuum warm pressing the powdered alloy with hot and cold end caps. For the hot-side bond, the mesh in cap type bond was utilized. For the cold-side bond, an iron powder end cap was joined to the TAGS material during the vacuum warm pressing operation. The processing steps for fabricating these elements are shown in Fig. 4-1.

The setup for obtaining the high temperature α and R is shown in Fig. 4-2. The element resistance was measured by passing 1 ampere through the element and measuring the voltage drop with the Fe leg of the thermocouple. The Seebeck coefficient was measured in the open circuit configuration. The T_H and T_C were measured with the Fe-Constantan thermocouples, and the Fe leg of the thermocouples was used to measure the voltage output.

4.3.3. Results and Discussion

The room temperature and high temperature α and R properties of the individual alloys in the as-fabricated condition are shown in Table 4-1 together with their respective crystal structure as determined by X-ray diffraction techniques.

Groups 1 and 2

The alloys investigated in groups 1 and 2 were essentially $\text{Ag}_{0.82}\text{Sb}_{1.18}\text{Te}_{2.18}$ and $\text{Ag}_{0.82}\text{Sb}_{1.25}\text{Te}_{2.244}$ with varying amounts of GeTe. In general, as more GeTe was added the structure was more rhombohedral and as less GeTe was added the structure was more face-centered cubic.

The earlier prepared alloys T-36 and T-37 accumulated 8612 hours in gradient operation at a T_H of 400°C. Although both of these alloys performed similarly to TAGS (increasing α and R), the rate of change for T-36 and T-37 was much less than that of TAGS. The power factor α^2/R for both of these alloys is essentially the same as TAGS after a few thousand hours, although TAGS started out slightly higher. The thermal conductivity of alloys T-36 and T-37 was not measured; however, it could be lower than TAGS since the electrical resistivity and Seebeck coefficient are higher. A comparison of α , R, and α^2/R of TAGS and alloys T-36 and T-37 at 0, 4940, and 8612 hours is given in Table 4-2. Individual performance curves for these three alloys are shown in Figs. 4-3, 4-4, and 4-5.

Two alloys (T-38 and T-39) yielded initial α , R, and α^2/R values (Table 4-2) that were somewhat improved over conventional TAGS. In life testing however, both alloys degraded worse than TAGS as shown in Figs. 4-6 and 4-7. Since both alloys started with high α s and high Rs, it was thought that both were in effect initially behaving as TAGS that had been operated for a while. Unfortunately, with both alloys, the α did not increase sufficiently (while R continued to increase) and after a while even the α started to decrease. This subsequent large decrease in α was surprising since the conventional TAGS, after undergoing an early large increase in α , tends to remain flat (in some instances the α has been observed to decrease but only slightly). Thus, from the performance of these particular alloys, the compositions prepared are metastable, as TAGS is, but are probably precipitating an additional phase as indicated by the decreasing trend in Seebeck coefficient.

Group 3

The one alloy in this group, T-35, has a reduced amount of Ag_2Te as compared to TAGS. The alloy was prepared to determine the effect of reducing the Ag_2Te in TAGS since metallographic and microprobe analysis showed Ag_2Te dispersed in the matrix. The alloy produced has closely resembled TAGS in performance and seems to offer no advantages. The

TABLE 4-2
COMPARISON OF TAGS TYPE ALLOYS

	α			R			α^2/R		
	0 hr	4940 hr	8612 hr	0 hr	4940 hr	8612 hr	0 hr	4940 hr	8612 hr
TAGS-85	164	208	204	4.47	10.18	10.38	5.97	4.28	4.05
T-35	159	202	197	4.36	9.61	9.98	5.76	4.28	3.92
T-36	180	211	213	5.90	10.62	11.30	5.49	4.22	4.01
T-37	196	220	--	7.47	12.19	--	5.26	4.20	--

performance of this alloy out to 8612 hours, given in Fig. 4-8, is compared with TAGS in Table 4-2.

Group 4

The TAGS alloy in the as-fabricated condition contains precipitates and, after the alloy is operated, further precipitation occurs. Presumably, if a detailed analysis of the matrix and the precipitating phases could be obtained, a single-phase material could be produced that exhibits stable thermoelectric properties as a function of time.

Microprobe analyses of as-fabricated and aged alloys were performed on conventional TAGS samples at both General Atomic and Scripps Institute of Oceanography. Considerable difficulty was encountered in performing the analyses since low-beam currents were required (if high-beam currents were used the precipitates were observed to melt) and, more importantly, large corrections to the raw microprobe data were required. Various computer code techniques available at both GA and Scripps for correcting raw microprobe data were utilized. Nevertheless, the alloys, whose preparation was based upon the microprobe corrected results (either that of GA or Scripps), were never single phase.

Group 5

The two alloys of this group were prepared inadvertently and one alloy, T-51, exhibited properties that are similar to the T-36 and T-37 alloys; i.e., the α^2/R is similar to TAGS but the rate of change with time is less than TAGS as shown in Fig. 4-9.

4.3.4. Recommendations

The TAGS type alloys (including conventional TAGS) have all indicated strong tendencies to behave in a metastable manner. The thermoelectric properties change as a function of time and the alloys examined have shown

precipitation. Thus, to obtain stable properties it is necessary to develop an alloy that will remain single phase.

Further efforts along this line could be accomplished by examining the microstructure of the alloys that have been run in gradient.

If the phases that are precipitating as well as the matrix that is being reformed during aging can be identified, then single-phase alloys can presumably be prepared. Although this approach was initiated with poor results in this study, it still seems that satisfactory analytical results could be obtained by using other analytical tools, such as the ion microprobe; then the problems encountered with the electron microprobe would not be present.

From a comparison of the figure of merit (Z) of P-type alloys (Fig. 4-10), presently configured TAGS has the highest Z over the range of 200 to 600°C. From a vaporization standpoint, however, its usefulness is probably restricted to $\leq 500^\circ\text{C}$. Above 500°C, the choice of P-type material is TPM-217. However, for high-performance, low-temperature systems, it seems that more efficient systems could be obtained if TAGS alloys that exhibited higher α^2/R values at the lower temperatures were segmented with TPM-217. A comparison of the materials efficiencies performed for various combinations of materials is given in Fig. 4-11. The thermoelectric properties of TAGS used in Fig. 4-11 are the published values and presumably the efficiencies would be increased if the lower temperature version of TAGS were utilized.

Fig. 4-1. TAGS element fabrication sequence

Fig. 4-2. Instrumentation for measuring both element resistance and Seebeck coefficient. (The element resistance was measured by passing 1 ampere through the element and measuring the voltage drop with the Fe leg of the thermocouple. The Seebeck coefficient was measured in the open circuit configuration. The T_H and T_C were measured with the Fe-Constantan thermocouples, and the Fe leg of the thermocouples was used to measure the voltage output.)

Fig. 4-3. Conventional TAGS, prepared by General Atomic

Fig. 4-4. Alloy T-36

Fig. 4-5. Alloy T-37. Instrumentation was lost after 5000 hours

Fig. 4-6. Alloy T-38

Fig. 4-7. Alloy T-39

Fig. 4-8. Alloy T-35

Fig. 4-9. Alloy T-51

Fig. 4-10. Figure of merit of P-type thermoelectric alloys

Fig. 4-11. Thermoelectric materials efficiency vs temperature

ACKNOWLEDGMENTS

The authors gratefully acknowledge the contributions of R. Akin, C. Morris, and C. Shearer for the sample preparations and experimental measurements, G. Staley for the mass spectrometer measurements, S. Liang for the scanning electron photomicrographs, and T. West for microprobe measurements.

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