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LIFE TESTING OF A NINE-COUPLE HYBRID THERMOELECTRIC PANEL

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SUMMARY

Life-test data are presented for a nine-couple thermoelectric panel of Hybrid couples operated at an average hot-junction temperature of 840° C (1113 K). In the Hybrid couple, a hollow cylinder of p-type silicon germanium (Si-Ge) is used to encapsulate a segmented lead telluride (PbTe)/Si-Ge n-leg. The output power and internal resistance of the panel, as well as the resistances of the individual Hybrid couples, are presented as functions of test time covering a period of more than 4200 hours. The performance characteristics are compared with those of a similar panel tested at an average hot-junction temperature of 926° C (1199 K).

Test results indicated good stability (about 7 percent total degradation during the first 4200 hr) compared to Hybrid couples tested at higher temperatures. Thermal cycling of the panel resulted in an order of magnitude increase in room temperature resistance. However, very little change in resistance at operating temperatures was noted following the thermal cycles. In general, the performance characteristics of the individual couples were identical.

INTRODUCTION

The thermoelectric (TE) materials most often considered for space power applications are alloys of lead telluride (PbTe) and silicon germanium (Si-Ge). Each material has its own unique advantages and disadvantages. In general, PbTe has superior thermoelectric properties but is limited to use temperatures below 600° C (873 K). The Si-Ge, on the other hand, exhibits somewhat lower TE properties than PbTe, but it has a useful temperature range extending to about 1000° C (1273 K). When operating over a large temperature difference, both materials can be used effectively in a single device called the Hybrid thermocouple. A detailed description of the design rationale and couple construction is given in references 1 and 2. Briefly, the thermocouple consists of a segmented Si-Ge/PbTe n-leg and a Si-Ge p-leg. The p-leg is fabricated in the form of a hollow cylinder and used to encapsulate the segmented n-leg.

Under contract NAS3-11843, the RCA Corporation of Harrison, New Jersey, designed and fabricated Hybrid couples for use at a hot-junction temperature of 926° C (1199 K) and an incident heat flux of 2 watts per square centimeter. In order to demonstrate the feasibility of the concept, two TE panels having nine Hybrid thermocouples each were assembled, instrumented, and delivered to the Lewis Research Center for testing.

The first of the two Hybrid TE panels was tested for 2600 hours at reference design temperatures, and the results are presented in reference 1. Because of the high degradation exhibited by the first panel, the second panel was tested at lower temperatures, that is, an average hot-junction temperature of 840° C (1113 K), an (estimated) n-leg interstage temperature of 500° C (773 K), and a cold-junction temperature of 200° C (473 K). The results of 4200 hours of life testing are presented herein. The tests were conducted to provide a first-order evaluation of the mechanical, thermal, and electrical behavior of the Hybrid couple.

DESCRIPTION

Hybrid TE Panel

The Hybrid TE panel consists of nine Hybrid thermocouples arranged in a three by three array and electrically connected in series. Photographs of the Hybrid couple and the nine-couple panel are shown in figures 1 and 2, respectively. A sketch of the Hybrid couple is included in figure 3. The dimensions of the hot surface of the panel are 7.5 by 7.5 centimeters resulting in a hot-shoe area of 56 square centimeters. Each Hybrid couple consists of a segmented PbTe/70 atomic percent Si - 30 atomic percent Ge alloy n-leg and an 80 atomic percent Si-20 atomic percent Ge p-leg. The p-leg is fabricated in the form of a hollow cylinder and used to encapsulate the segmented n-leg. The 3M Company's 3N alloy is used for the PbTe segment of the n-leg. A Si-Mo alloy (85 wt. % Si) heat receptor plate or hot shoe is bonded to the Si-Ge thermoelements at the hot end. (See ref. 2 for an expanded description of the bond systems.) At the cold end, the p-Si-Ge and n-PbTe elements are bonded through a series of compensating members (to accommodate thermal expansion mismatch) to a copper mounting stud. Copper straps are used to electrically interconnect the couples at the cold end. The thermocouples are mechanically fastened to an aluminum radiator plate. Two intersecting 0.635-centimeter-thick copper plates, 15.2 by 15.2 centimeters on a side, are mechanically attached perpendicular to the surface of the aluminum radiator adapter plate to provide the required radiative cooling. All radiator surfaces are coated with graphite to provide high emittance. Fibrous insulation (Johns Mansville, Min K 2020) is used between the thermocouples to minimize shunt heat loss. The gap between the segmented n-leg and the p-leg is filled with 99.5 percent purity aluminum oxide powder to minimize shunt heat losses through this space.

The p-Si-Ge cylinder is 3.17 centimeters long with a wall thickness of 0.117 centimeter. The n-PbTe and Si-Ge segment lengths are 0.798 and 1.87 centimeters, respectively.

A more detailed description of both the Hybrid couple and the test panel is given in reference 2.

Instrumentation

Each of the nine Si-Mo hot shoes was instrumented with tungsten-3-percent-rhenium tungsten-25-percent-rhenium thermocouples. The thermocouples were inserted in 0.084-centimeter-diameter holes provided near the corner of each hot shoe and potted in place with an alumina cement. In addition, ten type K thermocouples were positioned between the thermoelectric couples at the cold end (located on the copper connecting straps). The negative legs of these thermocouples were also used as voltage probes. Two copper straps were used, one at each end of the circuit, as power taps.

Test Fixtures

The test fixture (fig. 3) consists basically of a double-walled copper box (0.318-cm wall thickness). The heater, contained in the inner box, consists of five strips of 1.27-centimeter-wide graphite tape mounted on a 8.9-centimeter-square, 0.635-centimeter-thick ceramic (aluminum silicate) plate. Molybdenum extension leads (0.076 cm wide by 36 cm long) are used between the graphite heater and the external leads. Min K2020 thermal insulation is used between the heater and the inner box. Four ceramic spacers (0.953 cm wide and 1.27 cm long) are used to support the inner box from the base of the outer box. The surfaces between the inner and outer boxes are coated with graphite to provide a uniform emittance.

The Hybrid TE panel is placed in the test fixture such that the cold-junction surface is in the plane of the outer wall of the test fixture. The test fixture is mounted on the base plate of an oil-diffusion pumped vacuum system with the radiator fins viewing a 45.7-centimeter-diameter glass bell jar.

Testing Procedure

The nine-couple Hybrid TE panel was tested in the following manner. Room temperature resistance of the entire nine-thermocouple string was measured both before and after installation in the vacuum chamber. The panel was then connected in the load circuit (fig. 4). Three 0- to 2-ohm potentiometers, connected in parallel, were used as the variable resistance load and a 1-milliohm shunt was used to measure thermoelectric current.

After a vacuum pressure of 10^{-4} torr or less was reached, the heater power was turned on and was gradually increased to achieve operating conditions. Because of the rather large amount of min-K thermal insulation in the vacuum chamber, a relatively slow heat up procedure was used (about 24 hr) to ensure that the vacuum pressure never exceeded 10^{-4} torr (typically 10^{-5} at higher temperatures). When an average hot shoe temperature of 850° C (1123 K) was reached (corresponding to a hot-junction temperature of 840° C (1113 K)), the steady-state open-circuit voltage was recorded. The instantaneous current and closed-circuit voltage were then recorded by closing the circuit, and the internal resistance of the panel was determined using the relation

$$R_i = \frac{V_{oc} - V_L}{I} \tag{1}$$

where V_{oc} is the steady-state open-circuit voltage, V_L the instantaneous closed-circuit voltage, and I the instantaneous current. The instantaneous measurements were made within 0.2 second after closing the circuit. Since each of the nine Hybrid couples was instrumented at the cold-side with type K thermocouples, it was possible to measure the individual couple output voltages (using the negative leg of each type K thermocouple as a voltage probe) and thereby determine Hybrid couple internal resistance, again using the relation given in equation (1).

The Hybrid couple was life tested in the open-circuit condition with an input power fixed at 126±1 watts. Panel output power was recorded periodically using the relation

$$P = \frac{V_{oc}^2}{4R_i} \tag{2}$$

where P is the matched-load power.

The average hot-shoe temperature was determined using only seven of the nine W-3Re/W-26Re thermocouples, two being damaged during installation of the TE panel into the test fixture. The average cold-side temperature was based on nine type K cold-side thermocouples.

There were three unscheduled shutdowns during the 4200-hour test, all due to vacuum system malfunctions. The first two were at 740 hours while the third was at 1620 hours.

TEST RESULTS

The average hot-shoe temperature, matched load power, and internal resistance of Hybrid TE panel 2 (recorded at various times during the 4200-hour life test) are presented in figure 5. The average cold junction temperature throughout these tests was 200° C (473 K). The corresponding performance values for panel 1, tested at higher junction temperatures, are also included in figure 5 for comparison. Note that at zero hours the output power and resistance of panel 2 were about 6.05 watts and 235 milliohms, respectively, while at 1500 hours the power dropped to 5.75 watts and the resistance increased to 271 milliohms. This is consistent with the degradation (about 5 percent) expected as a result of phosphorus dopant precipitation in the n-Si-Ge segment at these temperatures (ref. 3). Between 1500 and 4000 hours the degradation rate decreased markedly, the power dropping from 5.75 to 5.6 watts, and the resistance increasing from 271 to 286 milliohms. Again, this is consistent with the degradation expected due to the diffusion limited process of dopant precipitation.

In comparison, the degradation rate of panel 1 was very severe, the power dropping about 16 percent (from 7.5 to 6.3 W) during the first 1500 hours of operation. As indicated in reference 1, the data suggest a possible degradation and/or partial separation of some of the metallurgical bonds in panel 1.

The sensitivity of Hybrid panel performance stability relative to operating temperatures is also indicated in figure 6, where normalized power is plotted against test time. Normalized power is defined as the ratio of the power at a given time to the initial power, that is, 6.05 watts for panel 2. Panel 1, tested at nominal hot-shoe and cold-junction temperatures of 940° C (1213 K) and 230° C (503 K), respectively, exhibited a drop in normalized power to about 0.76 in 2600 hours, while the normalized power of panel 2 decreased to only 0.93 in 4200 hours.

As indicated in figure 5, Hybrid TE panel 2 was thermally cycled three times during the 4200-hour test as a result of unscheduled shutdowns due to system malfunctions. Two shutdowns occurred at 740 hours and one at 1620 hours. The hot-junction temperature typically dropped 300° C during the first 20 minutes, decreasing gradually over the next 3 to 4 hours to room temperature. Following the first thermal cycle, an order of magnitude increase in room temperature panel resistance was observed, that is, from 130 milliohms to 1.3 ohms (measured external to the bell jar enclosure). However, as noted in figure 5, very little, if any, change in resistance at operating temperature occurred following the thermal cycle. Based on previous test experience, it appears that a deterioration in bond strength occurs at the PbTe - stainless steel hot-shoe interface after several hundred hours of operation. Subsequent tensile stresses, resulting from rapid cooldown, are sufficient to cause partial bond separation, hence increased resistance at room temperature. When heated to operating temperatures, sufficient compressive forces are generated to restore the low bond resistance.

In initially installing Hybrid panel 2 into the test fixture, two couples, 21 and 26, were damaged and subsequently replaced with spare couples 16 and 38, respectively. (Hybrid couple numbers as designated by vendor, see ref. 2.) Couple 16 had about the same room temperature resistance as couple 21 (viz., 10.7 compared to 10.6 mΩ). However, the room temperature resistance of couple 38 was much higher than couple 26 (viz., 14 compared to 10.1 mΩ). These were the only spare Hybrid couple available. Figure 7 shows the variation in Hybrid couple resistance at operating temperature for a test period in excess of 4000 hours. Note that eight of the nine couple resistances fall in a fairly narrow band of ±1 milliohm about the mean value while, as expected, the other (couple 38) exhibits a resistance value about 5 milliohms higher than the average of the eight. This resistance spread is probably due to slight variations in processing conditions from couple to couple which are to be expected in a developmental device. In addition, the resistivity of the PbTe and Si-Ge alloys used in making the couples may vary slightly from lot to lot due to variations in dopant concentration. In general, the behavior of couple resistance with time, exhibited by the Hybrid couples of panel 2, closely approximates that of "all-Si-Ge" couples. The nearly linear variation in resistance with time (fig. 7), after the first few hundred hours, is typical of a diffusion limited degradation mechanism (viz., the precipitation of phosphorus dopant in the n-type Si-Ge). Thus, at the reduced operating temperatures under which this test was performed, that is, 850° C (1123 K) hot shoe, 500° C (773 K) n-leg interstage, and 200° C (473 K) cold junction, the Hybrid couple exhibits relatively good stability.

COMPARISON OF PERFORMANCE OF HYBRID TE PANELS 1 AND 2

The severe degradation of Hybrid TE panel 1 (about 24 percent in 2600 hr) tested at a hot-shoe temperature of 940° C (1213 K) and cold-junction temperature of 230° C (503 K), was attributed to deterioration and/or partial separation of the metallurgical bonds (ref. 1). Visual inspection of the couples from panel 1 indicated, in a few cases, a separation in the bond between the n-type PbTe and the stainless steel hot shoe. Nickel was used as the bonding material in this region, and a tungsten diffusion barrier was used on the stainless steel hot shoe. Apparently, this bond system was not adequate for the thermal and mechanical conditions encountered in the Hybrid couple at the reference operating temperatures. At reduced operating temperatures (850° C (1123 K) hot shoe and 200° C (473 K) cold junction), however, the performance stability of the Hybrid TE panel improved dramatically. As shown in figure 5, after about 2000 hours of testing, the power output of panel 1 (940° C (1213 K) hot shoe and 230° C (503 K) cold junction) had degraded from 7.5 to 5.75 watts, the latter being about the same power level as that of panel 2 operating at much lower temperatures (850° C (1123 K) hot shoe and 200° C (473 K) cold junction). In terms of normalized power (fig. 6), panel 1 degraded from 1.0 to about 0.8 while panel 2 only degraded to 0.95 during the first 2000 hours.

Reference 1 indicated that the 10 to 15 percent performance gain, predicted for the Hybrid couple relative to "all-Si-Ge" couples, was realized during the first 600 hours of operation of panel 1. This fact, combined with the demonstrated stable performance of panel 2 operating at reduced junction temperatures, suggests that the combined objectives of improved performance and stability, relative to all-Si-Ge couples, might be achieved using the Hybrid couple concept.

Accordingly, it would appear that the feasibility of the Hybrid couple has been demonstrated but that additional improvement in the n-leg interstage bond strength is needed to allow satisfactory operation at the elevated temperatures. Due to the premature termination of the test program, the metallurgical examinations necessary to identify the bond degradation mechanism(s) were not performed. Hence, it is difficult to predict whether substantial improvements in the present bond system are possible.

SUMMARY OF RESULTS

Life testing a nine-couple Hybrid TE panel produced the following results:

1. The panel output power degraded from 6.05 to 5.6 watts, or about 7 percent, after 4200 hours of testing at an average hot-shoe temperature of 850° C (1123 K), an n-leg interstage temperature of 500° C (773 K), and an average cold-junction temperature of 200° C (473 K).

2. The resistances of eight of the nine Hybrid couples were generally grouped in a narrow band of about ± 1 milliohm, while the remaining couple resistance was about 5 milliohms higher than the average of the others.

3. Following a thermal cycle, in which the hot-junction temperature dropped at the rate of 900° C per hour during the first 20 minutes, a order of magnitude increase in room temperature panel resistance was noted, that is, from 130 milliohms to 1.3 ohms. However, after again heating the panel to normal operating temperatures, the panel re-

sistance returned to its original value (i.e., its value prior to the thermal cycle).

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, June 21, 1973,
503-25.

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3. Ekstron, L.; and Dismukes, J. P.: Precipitation of Phosphorus from Solid Solution in Ge-Si Alloy. J. Phys. Chem. Solids, vol. 27, 1966, pp. 857-863.

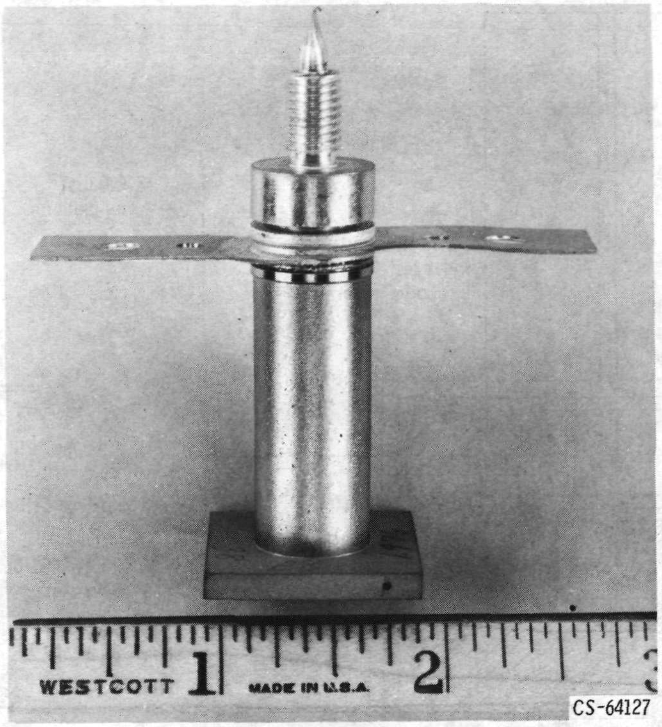


Figure 1. - Hybrid thermocouple.

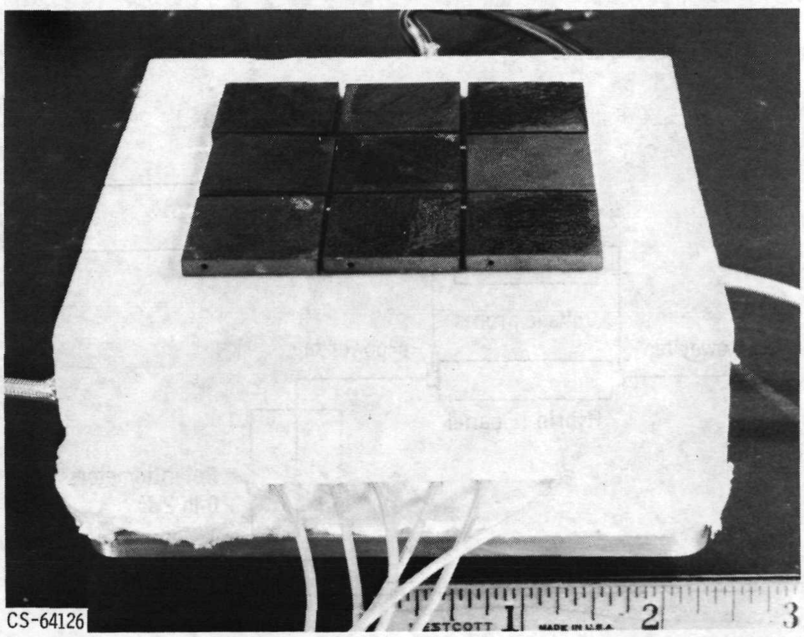


Figure 2. - Nine-couple Hybrid TE panel.

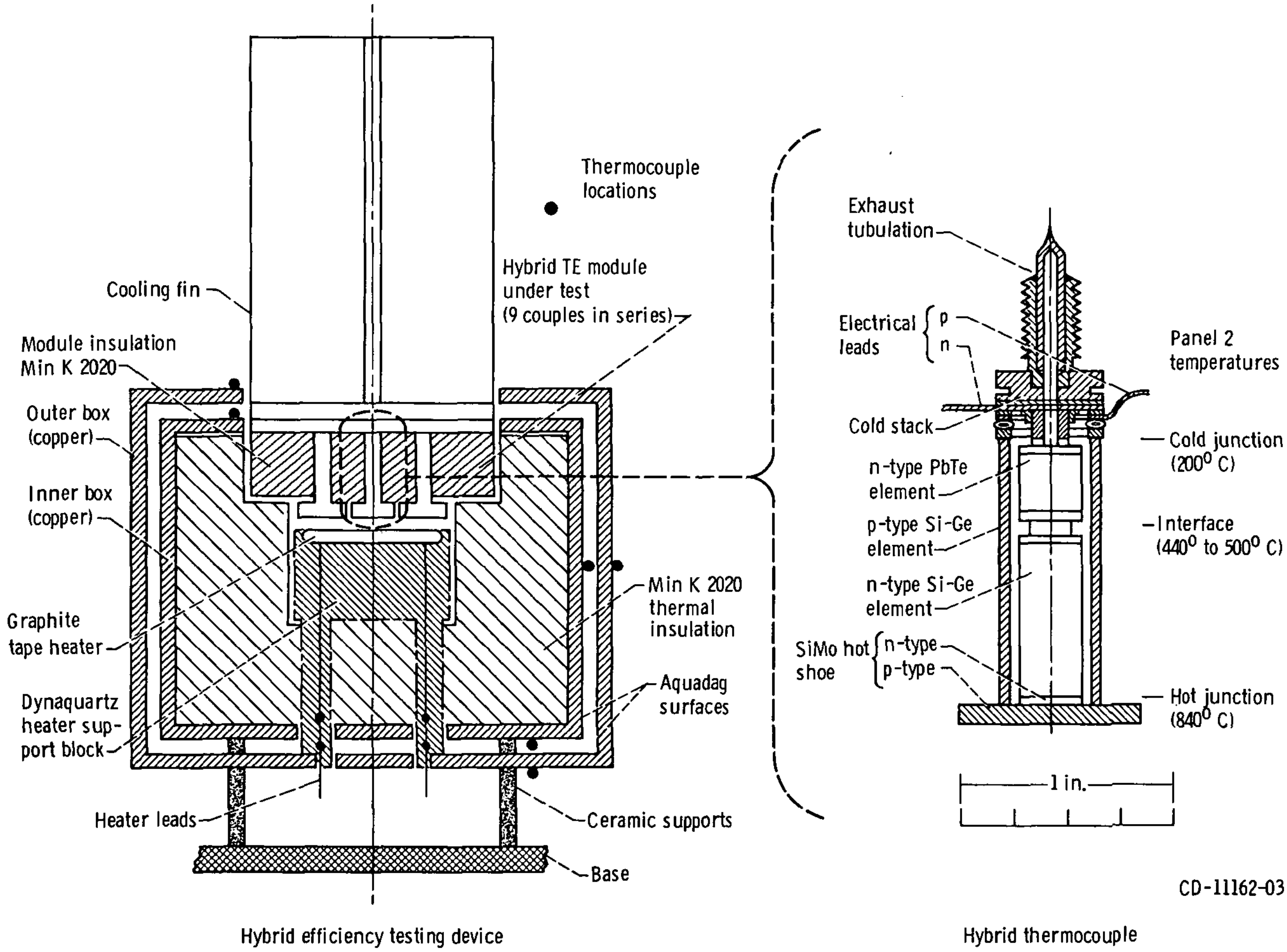


Figure 3. - Hybrid thermoelectric panel test fixture.

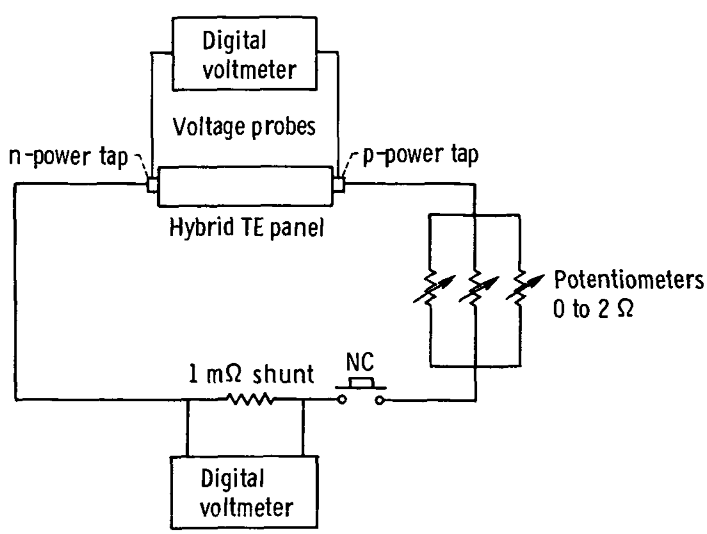


Figure 4. - Schematic of thermoelectric circuit.

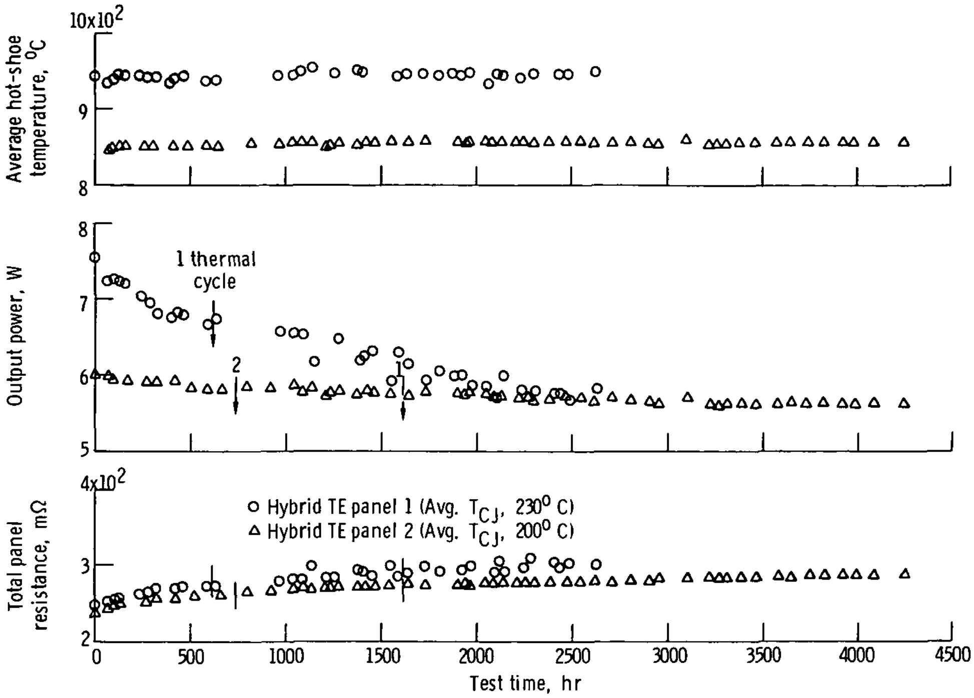


Figure 5. - Hybrid TE panel hot-shoe temperature, resistance, and matched load power plotted against test time.

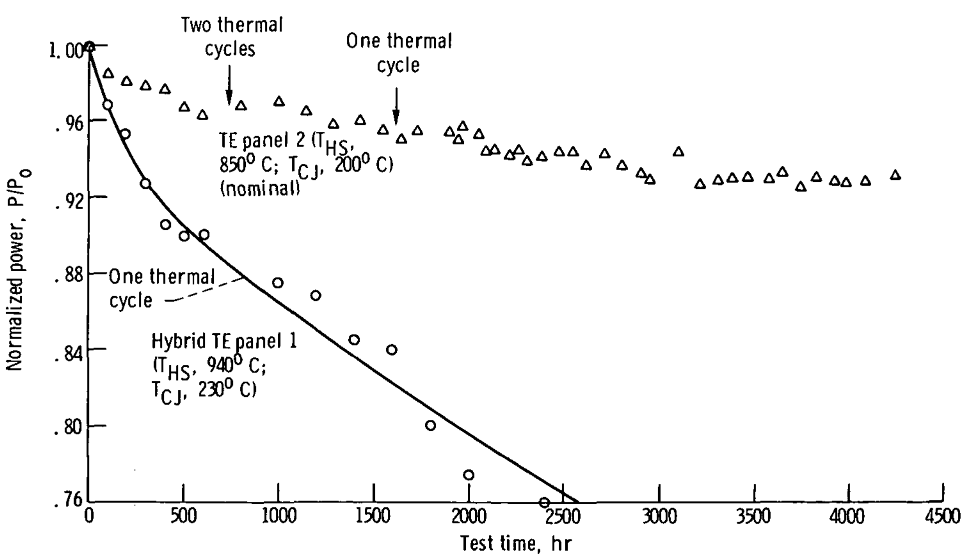
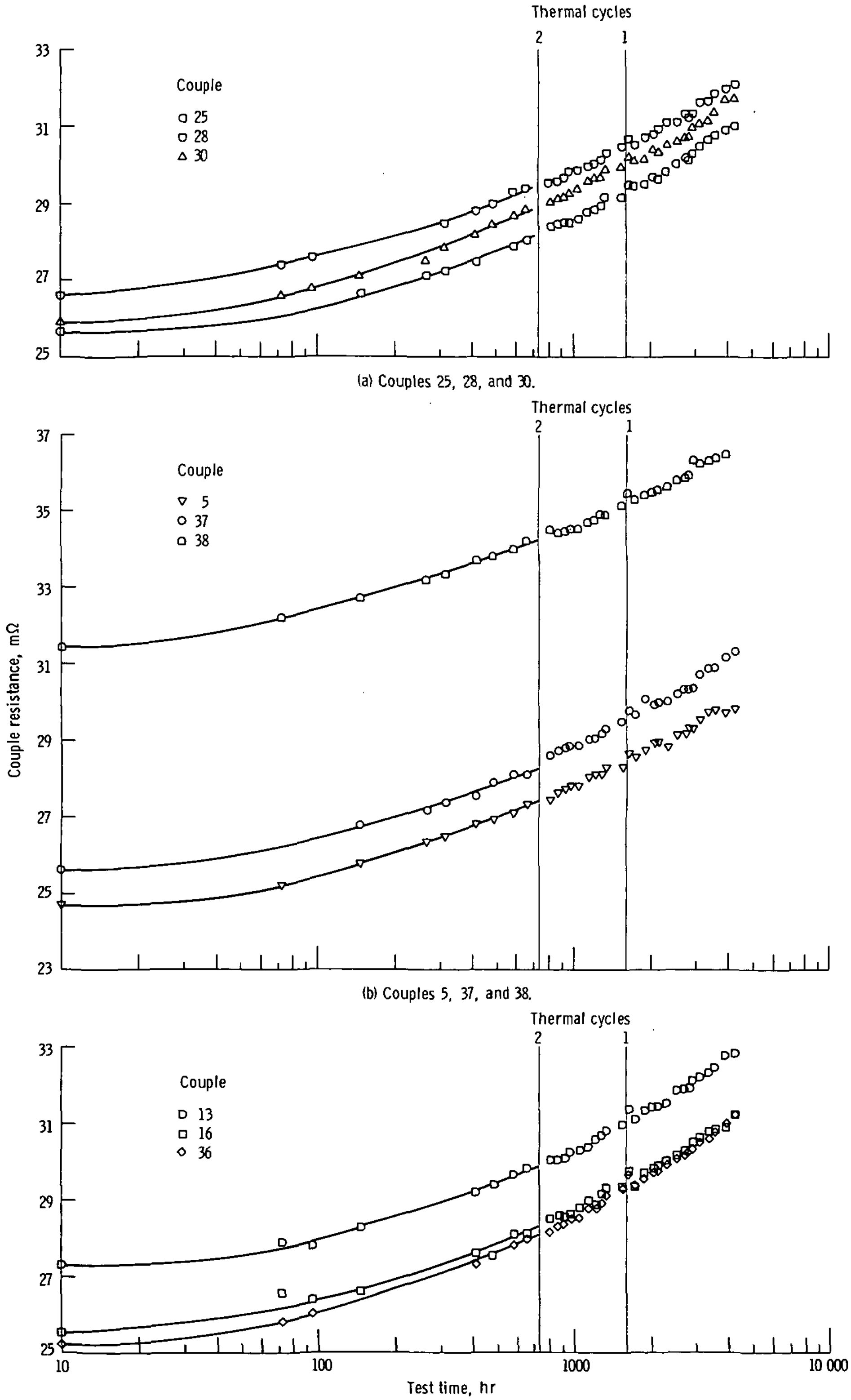


Figure 6. - Hybrid TE panel normalized power plotted against test time.



(c) Couples 13, 16, and 36.

Figure 7. - Hybrid couple resistance plotted against test time.

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