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Tests results of skutterudite based thermoelectric unicouples

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Abstract

Tests were performed of skutterudite based unicouples with (MAY-04) and without (MAR-03) metallic coating on the legs near the hot junction to quantify the effect on reducing performance degradation with operation time. The p-legs in the unicouples were made of $CeFe_{3.5}Co_{0.5}Sb_{12}$ and the n-legs of $CoSb_3$. The MAY-04 test was performed in vacuum ($\sim 9 \times 10^{-7}$ torr) for ~2000 h at hot and cold junction temperatures of 892.1 ± 11.9 K and 316.1 ± 5.5 K, respectively, while the MAR-03 test was performed in argon cover gas (0.051–0.068 MPa) at 972.61 ± 10.0 K and 301.1 ± 5.1 K, respectively. The argon cover gas decreased antimony loss from the legs in the MAR-03 test, but marked degradation in performance occurred over time. Conversely, the metallic coating in the MAY-04 test was very effective in reducing performance degradation of the unicouple. Because the cross sectional areas of the legs in MAY-04 were larger than those in MAR-03, the measured electrical power of the former is much higher than that of the latter, but the Beginning of Test (BOT) open circuit voltages, V_{oc} (204.2 mV) for both unicouples were almost the same. The peak electrical power of the MAY-04 unicouple decreased 12.35% from 1.62 W_e at BOT to 1.42 W_e after ~2000 h of testing, while that of the MAR-03 unicouple decreased 25.37% from 0.67 to 0.5 W_e after 261 h of testing at the above temperatures. The estimated peak efficiency of the MAY-04 unicouple, shortly after BOT (10.65%), was only ~0.37% points lower than the theoretical value, calculated assuming zero side heat losses and zero contact resistance per leg.

Keywords: Skutterudite; Thermoelectric conversion; Metallic coating; Performance tests; Space power

1. Introduction

Radioisotope Thermoelectric Generators (RTGs) with SiGe thermoelectric unicouples have powered numerous spacecraft for planetary exploration with remarkable success since the early seventies [1–3]. The General Purpose Heat Source (GPHS) in RTGs uses $^{238}PuO_2$ fuel for supplying thermal power from the ^{238}Pu radioactive decay by alpha particles with a half life of ~87 years. The thermal power for these systems decreases by ~4% after 5 years and is converted into electricity at <6% efficiency using SiGe unicouples operating at a hot junction temperature of ~1273 K. RTGs readily vent the helium gas generated by the radioactive decay of ^{238}Pu in the GPHS fuel modules into space.

Because of the limited supply of ^{238}Pu and the low conversion efficiency of SiGe, Radioisotope Power Systems (RPSs) with more efficient conversion technologies are being developed or considered for electrical power levels of 100–200 W_e. Others are being developed for much lower power levels, from milli-watts to just a few watts electric. These RPSs are *enabling* for deep space missions and long duration surface and subsurface exploration of Mars and other planets in the solar system. For some surface and subsurface missions, the GPHS could fully retain the helium gas generated by radioactive decay of ^{238}Pu when using a compact of coated fuel particles [4–6]. Energy conversion technologies considered for RPSs include free

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piston Stirling engines [7,8], thermophotovoltaic [9] and skutterudite based unicouples (SKUs) [10–13]. These unicouples with p-legs made of $CeFe_{3.5}Co_{0.5}Sb_{12}$ and n-legs of $CoSb_3$ can both reduce the mass of $^{238}PuO_2$ fuel and increase the specific electric power of the RPS [10]. These leg materials, however, are limited to a hot junction temperature of 973 K, at which it is important to suppress the sublimation of the volatile antimony from the legs near the hot junction, thus minimizing degradation in performance over time in multi-year space missions. For the SiGe unicouples used very successfully in RTGs during the last four decades [1–3], the sublimation of germanium from the legs near the hot junction (~1273 K) has been dealt with satisfactorily using thin Si_3N_4 coatings (a few to tens of microns thick), resulting in very little degradation in performance over time.

Recently, a thin metallic coating, which is compatible with the material of the legs of SKUs (p-$CeFe_{3.5}Co_{0.5}Sb_{12}$ and n-$CoSb_3$), has been developed at the Jet Propulsion Laboratory (JPL), the California Institute of Technology, Pasadena, California. This coating has been shown to reduce significantly the loss of antimony at higher temperatures (up to 973 K) in tests conducted at JPL and the University of New Mexico [11–16]. A number of tests involving segmented and non-segmented SKUs, with and without metallic coating, have been conducted in the high temperature vacuum facility at the University of New Mexico's Institute for Space and Nuclear Power Studies (ISNPS). These tests, conducted at hot and cold junction temperatures of ~973 K and 300 K, respectively, lasted for hundreds of hours [15–17] (Fig. 1). The purpose of the tests was to verify the Beginning-of-Life (BOL) performance relative to theoretical predictions.

As shown in Fig. 1, tests performed at ISNPS included segmented and non-segmented and coated and uncoated SKUs, both in vacuum and in argon cover gas (0.051–0.068 MPa). The non-segmented unicouples had p-legs made of $CeFe_{3.5}Co_{0.5}Sb_{12}$ and n-legs of $CoSb_3$. The segmented unicouples had p-legs made of $CeFe_{3.5}Co_{0.5}Sb_{12}$ and $Bi_{0.4}Sb_{1.6}Te_3$ segments and n-legs made of $CoSb_3$ and $Bi_2Te_{2.95}Se_{0.05}$ segments (Fig. 1) [15–17]. Although not designed as life tests, the obtained results provided valuable data on the performance of segmented and non-segmented SKUs and the effectiveness of the argon cover gas and the metallic coating on suppressing the loss of antimony and, hence, minimizing the decrease in the unicouples performance over time.

This paper presents the results of tests conducted at ISNPS involving non-segmented, coated (MAY-04) and uncoated (MAR-03 and JUN-03) SKUs (Fig. 1). The MAY-04 test, lasting for ~2000 h, was conducted in vacuum (~9.0×10^{-7} torr) at average hot and cold junction temperatures of 892.10 ± 11.90 K and 316.10 ± 5.50 K, respectively. To quantify the effectiveness of the metallic coating applied to the legs of the MAY-04 SKU near the hot junction, test results were compared with those from earlier tests of two uncoated SKUs (MAR-03 and JUN-03) using the same materials in the n- and p-legs. The cross sectional areas of the legs in the MAR-03 and JUN-03 unicouples were almost half those of the MAY-04 unicouple, but the total lengths of the legs in all unicouples were similar.

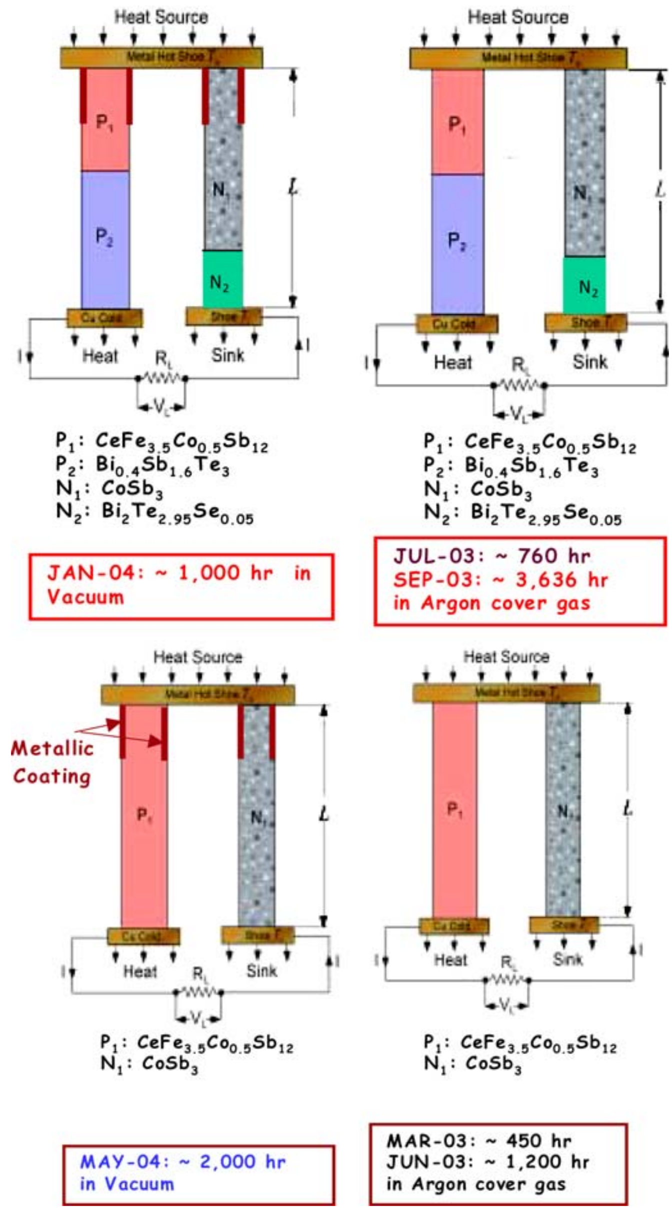

Fig. 1. Duration of coated and uncoated skutterudite based unicouples tests performed at the University of New Mexico.

2. Experiment setup

The MAR-03 and JUN-03 tests (Figs. 1–3) were performed in argon cover gas at 0.051–0.068 MPa in order to minimize the loss of the volatile antimony (Sb) by sublimation from the legs near the hot junction (~973 K). In previous tests performed in vacuum (~9.0×10^{-7} torr), extensive sublimation of Sb and deposit on the surrounding fiberglass insulation occurred above 600–700 K. Fig. 2