POST-IRRADIATION EXAMINATION OF THERMIONIC CONVERTERS*

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Post-irradiation results are reported on a number of single-cell in-pile converters (SCIP) and several three-cell thermionic fuel elements (TFE). All the SCIPs and TFEs had chemical vapor-deposited (CVD) tungsten emitters and bulk UO₂ fuel. Two of the SCIP emitters were vented and one was instrumented with thermocouples; all had nickel collectors. All of the TFEs had unvented emitters; two were a nominal one-inch diameter with niobium collectors, while a third TFE was 0.6 inch size with a composite nickel-niobium collector body. All of the TFEs had an outer Kovar sheath bonded in an inner sheath of alumina.

INTRODUCTION

The post-operational analysis of in-pile converters was performed in the Radioactive Materials Laboratory (RML). In general, the converters with long operating histories or those of advanced design are scheduled for thorough analysis and those tested for shorter duration usually receive partial examination. The information generated in the post-irradiation analysis is fed back to the design and fabrication engineers and necessary corrective measures are instituted to improve the life and performance of subsequent converters.

The major routine and specialized techniques used in the post-irradiation examinations of the in-pile converters were presented in the previous conference(1) and the reader is referred to that paper for detailed information.

The design, fabrication and testing of the SCIPs(2) and TFEs(3) are presented in other papers of this conference and therefore are not reviewed herein. Post irradiation examination was performed on the SCIPs and TFEs shown in Table I. The results of the post irradiation examination for each converter are discussed herein.

RESULTS AND DISCUSSION OF POST IRRADIATION EXAMINATION

SCIP-510: This converter operated for 3596 hours and upon puncturing the converter envelope, no fission gases were detected. This provided direct evidence that the chemical vapor deposited tungsten emitter operated with complete containment of fission gases to a measured UO₂ burnup of $2.8 \times 10^{20}$ fissions/cc. The electrical short that occurred in the converter was identified as an emitter-to-collector short that resulted from the localized swelling (0.007 inch) of the emitter body. A photograph of the emitter is illustrated in Figure 1. The surface of the emitter, in particular the area of the short, was

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observed at high magnifications. The microstructure is shown in Figure 2. This has the appearance of an eutectic structure; i.e., a lamellar microstructure; tungsten and nickel form an eutectic reaction at 1495°C.

Table 1 - Converter Description (UO₂ fuel, vapor deposited W emitters)

<table>
<thead>
<tr>
<th>Converter</th>
<th>No. Cells</th>
<th>Emitter Diameter (inches)</th>
<th>Collector Material</th>
<th>Electrode Gap-mils</th>
<th>Reason for test termination</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCIP-510</td>
<td>1</td>
<td>0.460</td>
<td>Ni</td>
<td>7</td>
<td>Diode Shorts</td>
</tr>
<tr>
<td>SCIP-512*</td>
<td>1</td>
<td>0.460</td>
<td>Ni</td>
<td>7</td>
<td>Diode Shorts</td>
</tr>
<tr>
<td>SCIP-513</td>
<td>1</td>
<td>0.460</td>
<td>Ni</td>
<td>7</td>
<td>Diode Shorts</td>
</tr>
<tr>
<td>TFE-605</td>
<td>3</td>
<td>0.460</td>
<td>Ni-diff. bonded on Nb</td>
<td>10</td>
<td>Diode Shorts</td>
</tr>
<tr>
<td>TFE-606</td>
<td>3</td>
<td>0.866</td>
<td>Nb</td>
<td>11.5</td>
<td>Gassy Tube</td>
</tr>
<tr>
<td>SCIP-509**</td>
<td>1</td>
<td>0.460</td>
<td>Ni</td>
<td>7</td>
<td>Envelope Leaks</td>
</tr>
<tr>
<td>SCIP-511**</td>
<td>1</td>
<td>0.460</td>
<td>Ni</td>
<td>7</td>
<td>Envelope Leaks</td>
</tr>
<tr>
<td>I-SCIP-1***</td>
<td>1</td>
<td>0.460</td>
<td>Ni</td>
<td>7</td>
<td>Envelope Leaks</td>
</tr>
</tbody>
</table>

*finned emitter **SCIP-509 - 20 mil vent hole in emitter ***emitter T/Cs
SCIP-511 - 5 mil vent hole in emitter

Observations of the collector body revealed a clean surface with evidence of large grains. A depression was noted in the area of the electrical short.

Puncturing of the emitter for fission gas measurements was unsuccessful and the emitter was prepared for metallographic analysis. A transverse section of the emitter in the region of the localized swelling is illustrated in Figure 3; the piece of UO₂ fuel in the center resulted from the preparation procedure. The fuel had redistributed and a typical columnar structure was evident. High magnification observations of the W-UO₂ interface revealed no evidence of interaction. The CVD tungsten experienced a change in microstructure; the columnar grain structure was essentially replaced by large equi-axed grains as shown in Figure 4, the area of the short. Also discernible is the grain boundary penetration of a metallic phase which is likely nickel pickup from the collector. The penetration of nickel and the subsequent formation of Ni-W eutectic in the grain boundaries of the tungsten would be expected to weaken the tungsten and result in the grain boundary cracking during the emitter preparation. A continuation of the metallic phase was observed on the internal diameter of the emitter.

The extensive grain growth in the CVD tungsten emitter wall may be related to the strain induced by the deformation. The fact that the tungsten in the area of emitter extending beyond the end caps did not experience any deformation and exhibited normal columnar grains provides evidence for this proposed mechanism of grain growth.

SCIP-509: The emitter of this converter contained a 0.020 inch vent for purposes of venting off the fission gases. In a previous paper the fission product migration was reported. In spite of the 2812 hours of operation, the emitter and collector surfaces remained clean and the emitter experienced essentially no dimensional changes. A transverse cross section of the emitter was prepared for metallographic observations. At high magnifications, the following observations were made: no UO₂-tungsten interaction; UO₂ fuel completely redistributed with characteristic columnar grains and lenticular voids; fine metallic particles detected in UO₂ by selective etching indicated that they were not free uranium; and grain growth had occurred in the tungsten with growth.
apparently initiated at the internal diameter of the tungsten. A photomicrograph of the tungsten wall with evidence of grain growth is shown in Figure 5.

**SCIP-511:** This converter operated for 885 hours before an envelope leak developed. The leak was located in the weld region between the nickel collector and the Kovar flange. In one area of the weld, incomplete weld penetration was observed. As a result of the envelope failure, some oxidation of the emitter occurred; a temper film was observed on the active emitting area of the emitter surface. Metallographic observations of the transverse and longitudinal sections of the emitter revealed: redistribution of the UO2 fuel; a ceramic type second phase in the UO2 concentrated at the outer rim of the fuel; and evidence of grain growth initiating at the inner diameter of the tungsten. The results of the fission product migration through the 0.005 inch vent hole in the emitter end cap were reported previously.\(^1\)

**SCIP-512:** The objective of this converter was to demonstrate an internally finned emitter and its effectiveness in reducing fission gas release by lowering the maximum operating temperature and reducing the thermal gradient in the UO2 fuel. SCIP-512 emitter consisted of a stacked array of ten 0.080 inch thick UO2 discs spaced with nine 0.010 inch thick tungsten members. Testing of the converter was terminated after 512 hours of operation because of an electrical short. This was identified as an emitter-collector short.

A black deposit was observed on the emitter and there was evidence of cracks in the emitter which permitted the escape of fission gases; the emitter also increased 6 mils in diameter. A gross gamma scan was performed on the emitter, and as shown in Figure 6, each of the 10 fuel discs are clearly visible and relative spacing appears unchanged from the fabrication dimensions. No gross fission product activity was found outside of the emitter.

Observations of the transverse and longitudinal metallographic sections of the emitter revealed: extensive grain growth and intergranular cracking of the emitter; the columnar grain structure remained in the overhang region of the emitter; the UO2 fuel discs, except those at the emitter end positions, showed evidence of equi-axed grain growth; a second phase, ceramic in characteristics, was observed in the UO2 fuel; and metallic particles, not free uranium, were distributed throughout the UO2. A typical microstructure of the UO2 fuel is illustrated in Figure 7; metallic particles are evident.

Analysis of fission gas revealed that approximately 20% release occurred; this compares to an 80% release for converters fueled with bulk UO2. Thus, based on this data and microstructure of the UO2, the objectives of the finned emitter were realized.

**SCIP-513:** After 1032 hours of operation, SCIP-513 exhibited characteristics of a permanent emitter-to-collector short. Post-irradiation examination revealed: dark deposits in two local areas of the emitter which were related to the short; no dimensional changes of the emitter; the UO2 solid pellet redistributed to form a central void and columnar grains; large equi-axed grains replaced the typical columnar grains in the CVD tungsten clad; cracks and localized porosity were evident in the region of the black deposit.

**I-SCIP-1:** This converter, instrumented with emitter thermocouples, operated for 57 hours at which time an envelope leak developed and the test was terminated. Post-test examination disclosed the following: the envelope leak occurred in a local area of the Kovar flanges because of insufficient weld penetration; the active emitting area of the emitter was covered with a dark film; no measurable dimensional changes occurred in the emitter; equi-axed grain growth initiated
at the internal diameter of the CVD tungsten; UO₂ solid fuel pellet only partially redistributed; a ceramic second phase concentrated in the outer rim of the UO₂ (Figure 8), and metallic particles, not free uranium, dispersed mostly in the outer rim of the fuel. The microstructure of the tungsten emitter and part of the UO₂ fuel is illustrated in Figure 9, the longitudinal section of emitter. Grain growth in the tungsten, metallic particles and the ceramic phase in the UO₂ are evident in this figure.

**TFE-605:** Testing of this 0.6 inch diameter TFE was terminated after 316 hours because of electrical shorts. The shorts were identified as emitter-to-collector contacts in the middle and bottom cells. The three emitter surfaces had evidence of surface cracks and increased in diameter by 3, 2, and 3 mils for the top, middle and bottom respectively. The solid fuel pellets had redistributed and characteristic columnar grains were evident. A second phase was observed at the UO₂-tungsten emitter interface. Extensive grain growth, grain boundary voids and intergranular features were evident in the tungsten emitter. A montage of the transverse cross section of the clad and fuel of the middle emitter is illustrated in Figure 10. The second phase had the appearance of an eutectic structure; attempts to identify this phase by x-ray diffraction were unsuccessful. The composite Nb-Ni collector maintained its diffusion bond integrity; however, inner diameter of the collectors decreased by 2.2, 3.9 and 1.9 mils for the top, middle and bottom respectively.

**TFE-606:** This TFE, the first to have a nominal outside diameter of 1 inch was tested for 450 hours. Characteristics of gas contamination were diagnosed and analysis of the gases in the envelope indicated that all three emitters had vented and some outgassing of the components had occurred. No envelope leak was detected. The top and bottom emitters were cracked on the side facing the reactor and had increased 5 and 2 mils in diameter respectively, while the middle emitter appeared integral with no dimensional changes. The relative input power levels for the emitter were 1.18, 1.00 and 1.12 for the top, middle and bottom emitters respectively. It is important to note that dimensional changes and degree of cracking parallel the input power level. Observations on the transverse metallographic sections of the three emitters revealed: an azimuthal variation in the UO₂ structure ranging from a fine grain equi-axed (as sintered) to large columnar grains that were oriented toward the reactor; metallic particles which exhibited etching characteristics of free uranium were found in the fine grain (cool) region of the fuel; evidence of a UO₂-ceramic phase eutectic at the tungsten interface; a very thin metallic type deposit discerned in local regions of the internal diameter of the tungsten; extensive grain growth in the emitter; cracks in the emitter with penetration of the ceramic-eutectic; thin metallic layer on some of the cracks and penetrating some of the tungsten grain boundaries; and localized grain boundary porosity in the tungsten. A macrograph of transverse section of the top emitter is illustrated in Figure 11.

The tungsten-25 w/o Re intercell lead between the top collector and middle emitter came loose at the region of the palco braze during disassembly. Metallographic examination revealed that the palco braze had not penetrated the joint, and resulted in a poor bond.

**EVALUATION OF TUNGSTEN AND UO₂ FUEL**

An investigation was initiated on the tungsten and UO₂ fuel materials to determine if the characteristics of the starting materials and/or processing history was related to the in-pile behavior of the fueled emitters.

**Chemical Vapor Deposited (CVD) Tungsten:** All of the CVD tungsten was produced by hydrogen reduction of tungsten hexafluoride. A proprietary additive, which
does not appear as a major impurity, was used to control the fluorine content to acceptable levels. The chemistry and microstructural analysis of the tungsten used in some of the in-pile converters was again reviewed in light of the post-irradiation results, this yielded the following: a deposit of material ~ 0.2 mil thick was detected on the i.d. of some of tungsten tubing (Figure 11); localized microcracks and blisters were found on the i.d. of some of the tungsten; and grain growth in the tungsten varied from lot to lot. X-ray analysis of the deposit revealed the presence of iron, nickel, and chromium, constituents of stainless steel; these were likely picked up from the stainless steel mandrel. Further, it was determined that the localized blisters were related to outgassing of the mandrel. To avoid these problem areas, the i.d. of the tungsten is honed to remove 1 mil, and molybdenum mandrels may be used in the future.

Tungsten produced with the additive exhibited greater grain growth than that without the additive. Also, the grain growth of the tungsten varied from lot to lot and some samples exhibited extensive grain growth at 1675°C after 300 hours. These results are not inconsistent with those obtained from the post-irradiation examination.

Uranium Dioxide (UO₂) Fuel: The chemistry and microstructure data of the starting fuel was re-examined in light of current requirements. Some of the UO₂ had impurities of aluminum (200 to 500 ppm), some with silicon (to 200 ppm), some with nickel (to 360 ppm) and some with iron (to 500 ppm). In some fuel, a combination of these impurities was present; these were introduced during pellet preparation. Aluminum and silicon impurities may exist as oxides which form low melting point eutectics with UO₂ at 1915°C and 1650°C respectively. Iron and nickel usually exist as alloyed metallic particles dispersed in the UO₂ as shown in Figure 12.

The oxide impurities in the UO₂ may have participated in the eutectic appearing structure observed in the irradiated fuel at the tungsten-fuel interface. If these oxides represent one of eutectic constituents, then they have gone through a process of concentration. It is hypothesized that this may occur during the process of UO₂ redistribution. In some of the emitters, the eutectic phase was observed penetrating the tungsten grain boundaries. The volume changes accompanying the eutectic reaction may, in part, explain the cracking of some of the emitters. In one of the as-processed UO₂ pellets, free uranium was detected by selective etching techniques; this may explain the presence of free uranium in the fuel of TFE-606.

In view of these results, the UO₂ fuel specifications have been further modified to reduce the impurities and additional quality control steps have been instituted during fuel processing.

SUMMARY

The post-irradiation examinations have identified various problem areas as envelope leaks, intercell lead braze integrity, effects of neutron flux gradients and problems associated with the characteristics of the starting materials, tungsten and UO₂. This information was fed back to the design, fabrication and material engineers and corrective measures were instituted in subsequent in-pile converters. Further work is necessary to determine the mechanisms that are responsible for some of the atypical behavior of the fueled emitters.
REFERENCES


1. SCIP-510 Emitter

2. SCIP-510 Emitter Surface at Short
3. SCIP-510 FUEL-CLAD CROSS SECTION

4. SCIP-510 POSSIBLE W-Ni PHASE IN W
5. SCIP-509 TUNGSTEN MICRO

6. SCIP-512 CROSS GAMMA SCAN
7. SCIP-512 FUEL MICRO

8. FUEL STRUCTURE I-SCIP-1
9. FUEL-CLAD INTERFACE I-SCIP-1

10. TFE-605 STRUCTURE OF MID-EMITTER
11. TFE-606 MID-EMITTER CROSS-SECTION
12. ETCHED MICRO OF DVD TUNGSTEN

13. ETCHED FUEL MICROSTRUCTURE