*Technical Information File
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UC-33, Propulsion Systems
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AEC Research And
Development Report

UNION CARBIDE CORPORATION

LINDE DIVISION

EVALUATION OF A MOLYBDENUM FOIL-ZIRCONIA CLOTH
INSULATION SYSTEM AFTER 10,000 HOURS AT A SOURCE
TEMPERATURE OF $\sim 1100^{\circ}\text{C}$

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DATE 10/27/72

SEPTEMBER 1972

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ALO 2832-45
UC-33, Propulsion Systems
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UNION CARBIDE CORPORATION

LINDE DIVISION

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INSULATION SYSTEM AFTER 10,000 HOURS AT A SOURCE
TEMPERATURE OF $\sim 1100^{\circ}\text{C}$ (2012°F)

SEPTEMBER 1972

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Contract No. AT(29-2)-2832
(Formerly Contract No. AT(30-1)-3632)

U.S. Atomic Energy Commission

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A B S T R A C T

This report presents the results of the molybdenum foil-zirconia cloth insulation system stability test performed by Linde Division of Union Carbide. The test and post test analysis were performed in the duration from November 1970 to August 1972.

The objectives of this program are to evaluate and demonstrate long term thermal performance stability of multi-layer insulations at source temperatures up to 1100°C (2012°F) for use in radioisotope power systems.

Two multi-layer insulation systems were selected for long term stability testing at a source temperature of 1100°C in high vacuum.

(1) Molybdenum Foil-Zirconia Cloth

This test system was maintained at stability test conditions for 10,000 hours. Upon completion of this test duration the system was disassembled for post test analysis. The results of the ensuing evaluation are documented in this report.

(2) Molybdenum Foil---Quartz Cloth

This system has over 15,000 hours at stability test conditions without indication of deterioration in thermal performance as of 9/8/72. The duration objective of this test is 20,000 hours. The results will be reported after completion of the test.

The information contained in this report should be supplemented with report ALO 2932-44 of May 1971.

INTRODUCTION

The objective of the current program is to demonstrate physical and thermal stability of multi-layer insulation systems at a maximum temperature of 2012°F for long term applications.

In order to provide stable long term thermal performance, insulation material, mechanical, chemical and physical stability becomes imperative. However, it is well known, that thermal and physical properties change with increase in temperature and also the reactivity between materials increases. The selection of insulation materials, thus, becomes quite critical. The materials chosen should not only be independently stable (low vapor pressure, etc) but should also be compatible with other materials in the insulation system.

From the results of prior testing and a review of other materials available molybdenum foil-quartz cloth and molybdenum foil-zirconia cloth systems were selected for testing at the 2012°F source temperature.

The molybdenum foil-quartz cloth insulation stability test is still in progress. The results will be presented upon completion of the test.

The molybdenum foil-zirconia cloth insulation stability test and the post test evaluation have been completed. This report documents the results of the evaluation. The molybdenum-zirconia system had been subjected to a source temperature of $\sim 2012^{\circ}\text{F}$ and a cold side temperature of 400°F for 10,000 hours. The vacuum level ranged from an initial value of 1×10^{-6} torr to a value of 3×10^{-8} torr at the completion of the test. As part of the post test analysis sections were removed from various locations for metallurgical evaluation.

This effort is being performed under the direction of the United States Atomic Energy Commission, Isotope Technology Branch, Division of Space Nuclear Systems. The AEC program director is P. A. O'Riordan at Washington, D.C.

The Linde project manager is D. J. Webster. Other Union Carbide personnel contributing to this test report are Dr. C. Angell, G. M. Faulring, Dr. W. Forgeng and D. H. Stellrecht.

CONCLUSION

1. The measured effective thermal conductivities between the source (2012°F) and cold wall temperature for both the molybdenum-zirconia and molybdenum-quartz systems are tabulated on the following page. These conductivities were corrected for 100°F cold wall so that they could be compared. Actual cold side temperatures were 390°F for the molybdenum-zirconia system and 230°F for the molybdenum-quartz system.

SYSTEM	DURATION AT STABILITY TEST CONDITIONS	K $\left. \begin{array}{l} 2012^{\circ}\text{F} \\ 100^{\circ}\text{F} \end{array} \right\}$	% CHANGE FROM INITIAL VALUE
	HOURS	BTU/HR FT $^{\circ}\text{F}$	- DENOTES IMPROVEMENT
Molybdenum-Zirconia	546*	3.03×10^{-3}	- 3.7
	10,000	2.92×10^{-3}	
Molybdenum-Quartz	0	2.10×10^{-3}	- 1.9
	15,000	2.06×10^{-3}	

2. Some degradation as determined by thermal conductivity data and the metallurgical evaluation occurred at temperatures above 1200°F during start up. However, the thermal conductivity values stabilized and did not degrade during the 10,000 hour test.

3. The primary cause of the insulation degradation during start up was believed to be the formation of molybdenum oxides. Offgassing from the zirconia cloth was believed to be the primary source of oxygen. The theory of volatile oxide formation was supported by the presence of molybdenum oxides and condensed molybdenum rich globules on cooler layers of the insulation package.

4. The overall condition of the molybdenum layers was considered to be satisfactory. All of the molybdenum layers remained ductile as recrystallization did not occur even at 2000°F in the hottest layers. Some deterioration occurred on the surfaces of the hottest layers as a result of the formation of volatile oxides and the resulting thermal etching as the oxide vaporized. On many of the intermediate layers the molybdenum oxide remained resulting in a decreased reflectance value. This is probably the primary reason why the thermal conductivity of the molybdenum-zirconia is about 40.% higher than the molybdenum-quartz system.

* System did not stabilize until 546 hours at test conditions. There was about 10% improvement in performance during the duration from 0 to 546 hours.

5. The overall condition of the zirconia layers was considered to be satisfactory. As the temperature to which zirconia layers were exposed increased, it was noted that the zirconia fibers lost strength and turned black. The black color is evidence of oxygen deficiency which can be induced in zirconia fibers exposed to a high vacuum at elevated temperatures according to the reaction:

It is believed that the above reaction was a source of oxygen needed for the formation of molybdenum oxides.

6. It appears that the drift in performance which occurred during the first 500 hours at stability test conditions was due to vaporization of molybdenum oxides from the hottest molybdenum layers.

PROCEDURE

A number of techniques were utilized during the investigation of the vacuum insulation test package. They included:

1. Determination of the effective thermal conductivity of the vacuum insulation.
2. Visual examination of samples of molybdenum and zirconia insulation layers at low magnifications (to 30X).
3. Micro-examination of molybdenum and zirconia layers at magnifications to 500X.
4. X-ray diffraction analyses of selected layers of molybdenum and zirconia from the end disc.
5. Electron probe scans of selected zirconia layers from the end disc assembly of the test package.
6. Examination of selected zirconia layers from end disc via X-ray image.
7. Reflectance measurements on various molybdenum layers removed from a selected end disc.

RESULTS/OBSERVATIONS

1. Temperature measurements which permitted calculation of the effective thermal conductivity of the insulation test package were made while the test was in progress. Figure 1a⁽¹⁾ shows a plot of the effective thermal conductivity as a function of maximum source temperature. In Figure 1a, it appears that a sudden increase in the thermal conductivity occurred above 1200°F. The next point on

the plot is at 1600°F. For reasons which become apparent later in the test it was theorized that the rapid change in thermal conductivity actually initiated in the 1300°F - 1400°F range.

Figure 1a also shows that the thermal conductivity continued to rise rapidly until the maximum hot face temperature of 2000°F was reached. The effective thermal conductivity then stabilized and essentially did not change for the balance of the 10,000 hour test. Upon conclusion of the testing one of the hot wall thermocouples was replaced with a new calibrated couple. The system was then returned to stability run conditions to calibrate the remaining test thermocouple. The calibration indicated that at test conditions the hot wall test couple was reading 44°F low. Based on this recalibration the effective thermal conductivity was found to be as follows at the 10,000 hour point.

$$K \int_{100}^{2012} = 2.92 \times 10^{-3} \text{ Btu/Hr-Ft-}^\circ\text{F} \quad (1)$$

The above value is corrected for a 100°F cold wall. This value is 3.7% lower than indicated near the beginning of the test at 546 hours.⁽¹⁾

Upon cooldown no sharp deviations in thermal conductivity were observed during the cooling period. Post test conductivity data was recorded at five source temperatures from 2000°F down to 800°F as shown in Figure 1a. Also noteworthy in Figure 1a is the thermal conductivity plot for the molybdenum-quartz system which is still in test. Up to 1200°F there was little difference between the molybdenum-zirconia and molybdenum-quartz system. Between 1200°F and 2000°F the performance of the molybdenum-zirconia system was somewhat inferior to that of the molybdenum-quartz system. It should be noted that with the exception of the spacer materials the two insulation test packages were identical.

2. The thermal conductivity plot for the molybdenum-zirconia system suggested that something unusual occurred above 1200°F which resulted in the sharp rise in thermal conductivity. It is common knowledge that molybdenum alloys will oxidize rapidly at temperatures above approximately 1300°F to 1400°F as shown in Figure 1b.⁽²⁾ Figure 1b shows the air oxidation case for molybdenum. It is obvious that the molybdenum oxidation plot in Figure 1b shows the same basic shape as the molybdenum-zirconia thermal conductivity plot in Figure 1a. In a vacuum, the oxidation plot for molybdenum would be similar to Figure 1b, the air case, although the magnitudes of the weight changes would be much less. Rapid oxidation of molybdenum surfaces above the 1300°F - 1400°F temperature range has been attributed to the formation of a volatile non protective oxide film.^(2,3) Up to this point data to definitely confirm a hypothesis of insulation deterioration through a mechanism involving molybdenum oxidation have not been presented.

3. After the completion of the 10,000 hour test and prior to thermocouple calibration the bottom end insulation disc were removed and submitted for metalurgical evaluation. Figure 2a indicates the location of the end disc, as shown by the arrow designated as #3 in that figure. The removed materials were replaced

by new materials for the thermocouple calibration. The end disc assembly consisted of six disc sets in a stepped miter joint. Figure 3 shows the test cylinder configuration. The six disc sets were labeled as shown in Figure 3 for convenience. End disc set "A" was the hottest set and had the smallest diameter, while set "F" was the coldest set and was the largest in diameter. These bottom end disc sets were a portion of the samples which were used in the investigation.

In addition to samples obtained from the end disc assembly, sections were also cut from the side of the test package after the thermocouple calibration cycle. Figure 2a shows the location of this sampling. The arrow numbered "4" in Figure 2a indicates the position of the first set of samples designated as set I. The insulation which was wrapped around the cylindrical walls of the high purity alumina tube consisted of a total of 104 alternate layers of molybdenum foil and zirconia cloth. A second set of layers was also cut from the side opposite to that of set I and at a lower position as shown by Figure 2b. The second set of layers, designated as set II also consisted of 104 alternate layers of Mo and ZrO_2 . The two sets of layers which were cut from the cylindrical wall of the test package along with the 6 sets of discs obtained from the bottom end of the test cylinder composed the group of samples which were utilized for metallurgical evaluation. No significant difference was noted between sample sets when comparing insulation materials from each of the three samples which occupied similar locations within the temperature profile.

A visual examination of the layers composing the end disc assembly and also the side wall of the vacuum insulation test package was performed at magnifications up to 30X. Table I tabulates the results of a visual examination of the end disc sets. Various trends were observed in the layers of the end disc as well as in the layers from sets I and II from the side wall of the test cylinder. The results of the visual examination on the layers from the side wall of the test package are tabulated in Tables II and III for the sets I and II respectively. Figures 4 and 5 are plots offering a qualitative assessment of the condition of the molybdenum and zirconia layers respectively.

The visual examination indicated that the hottest molybdenum layers were thermally etched, but there were no signs of recrystallization. In some isolated cases the nucleation stage of recrystallization could be observed but only on a very small scale. The hotter molybdenum layers showed some limited signs of a light violet discoloration, but the greatest discoloration was found on the "cooler" molybdenum layers in the 60 to 80 range. Thick dark violet films were noted on both the "hot" and "cold" sides of molybdenum layers in the 60 to 80 range as indicated in Figure 4. The coldest layers appeared to have no discoloration and appeared to have surfaces similar to an unused molybdenum foil which had been stored as a control sample.

3. An X-ray diffraction analysis was performed at the UCC-Mining and Metals Division on selected molybdenum layers from the end disc sets B and C in an effort to determine the identity of the violet-to-blue surface film observed on the molybdenum foils. The films appeared to be identical to those noted on the side wall foil samples. Table IV summarizes the results of the X-ray diffraction analysis on the molybdenum layers. The results showed the violet-blue films to be molybdenum oxides. These results were considered important since they

confirmed that oxidation of molybdenum foils occurred. Hence, oxidation became a more plausible mechanism for explaining the degradation of the insulation package.

It had been observed that the "hotter" molybdenum layers were thermally etched but had little if any oxides present and that "cooler" layers had evidence of heavy oxide coatings. The presence of heavy oxides on the cooler layers might be attributed to condensation of the volatile molybdenum oxides which were formed on the "hotter" molybdenum layers of the insulation.

4. For oxidation of the molybdenum foils to occur the presence of oxygen was a prerequisite. It was theorized that the three most likely sources of oxygen were as follows:

1. Inadvertent introduction of oxygen into the test package during heat up.
2. Offgassing of oxygen from the zirconia insulation layers.
3. Offgassing of oxygen from the alumina components of the system.

The last possibility was discounted immediately since with the exception of the spacer materials, the molybdenum zirconia system was identical to the molybdenum-quartz system still in test which did not exhibit the anomalous behavior above 1200°F. In view of the care taken during the test, the first possibility also must be discounted. Of the three possibilities, the second seemed to be the most likely.

The macro-examination revealed changes in the physical appearances of the zirconia cloth as a result of temperature and vacuum exposure. Figure 5 is a qualitative impression of these changes as they were noted in individual layers. The hotter layers between 2 and 85 were very black while the coolest layers between 86 and 105 were basically light in color. It was also observed that the hottest zirconia layers were very fragile. At this time it should be noted that the dark colors are typical of oxygen-deficient zirconia of the form ZrO_{2-x} . It has been reported that oxygen deficiency in zirconia can be induced through high temperature vacuum treatment according to the following reaction:⁽⁴⁾

The changes in the appearance of the zirconia layers are apparent in Figures 6 and 7a through 7d.

Figures 6 and 7a through 7d show the typical appearance of the zirconia cloth after 10,000 hours of thermal treatment. Figure 6 shows the difference between the "hottest" zirconia layers and the "coldest". The hottest layer which was sectioned from the side wall of the test cylinder is shown to be very dark and tattered as opposed to layer #103, one of the coldest layers, which shows limited signs of oxygen deficiency. Layer #51, which is shown in Figure 6, appeared to

be in better condition than the "hotter" zirconia also shown in Figure 6. Layer #51 still had a shiny appearance while the hotter layer #1 appeared fragile and dull.

The presence of oxygen-deficient zirconia in the insulation test package was of interest since it identified a source of oxygen which could have reacted with molybdenum layers to form volatile molybdenum oxides.

5. In addition to the molybdenum layers which were subjected to X-ray diffraction analyses, various selected layers of the zirconia layers from the end disc assembly were also subjected to X-ray diffraction analyses. Table V tabulates the results of X-ray diffraction analysis which indicated that a lattice transformation had occurred in the end disc sets A, B and C. The tetragonal zirconia structure appeared to be stable in the "hottest" layers and a gradual change to the cubic form was exemplified by the "cooler" end disc sets. An unused zirconia sample was also analysed and Table V indicates that the zirconia was initially in the cubic form. The X-ray diffraction data indicated that the temperatures experienced in the end disc sets D, E and F were not high enough to cause an allotropic change in the zirconia; and secondly, the tetragonal structure is a stable structure in the zirconia layers of the "hottest" end disc sets, since the tetragonal structure remained even after a very slow cool to room temperature.

6. Upon the completion of the X-ray diffraction analyses of molybdenum and zirconia layers, a more thorough macro-examination of the end disc assembly was performed. At this stage of the evaluation the significance of the molybdenum surface deposits and zirconia color changes was more fully appreciated.

Figure 8a shows the end disc assembly after thermal treatment at 2000°F for 10,000 hours. The six sets of differently sized discs can be seen stacked one upon another. This assembly was subsequently divided into the various sets for closer metallurgical examination. The hottest molybdenum layer in the A set had some evidence of a reaction as large sections of the hottest foil were missing. The sections that were missing were those that were exposed to the alumina heater core. The melting point of molybdenum is 4730°F and at 2000°F it has a low vapor pressure. It seemed inconceivable that the missing portion of the molybdenum foil could have simply melted or vaporized away.

The possibility of low melting or eutectic reactions were considered. A high purity alumina core was utilized. Surface examination of the alumina material revealed no evidence of a reaction between the alumina and the molybdenum. If the alumina were at fault, then a thermal conductivity rise would also have been observed in the molybdenum-quartz system which is still in test.

Eventually, the disappearance of the molybdenum was attributed to two very important phenomena which occurred simultaneously. The first phenomenon which was observed in the zirconia cloth was the inducement of oxygen deficiency in the zirconia cloth by means of high temperature vacuum treatment. In Figure 8b, the regions beneath the areas where the Mo foil was missing appear black. The black regions, as indicated by the arrows in Figure 8b, are portions of the zirconia cloth which were oxygen-deficient. Although the inducement of oxygen deficiency

does not explain why portions of the molybdenum foil in Figure 8b were missing it leads to the second phenomenon which will explain the disappearance of the Mo foil.

As a result of the high temperature vacuum heat treatment, oxygen deficiency was induced in the zirconia layers and oxygen was given off by the zirconia layers. The available oxygen reacted with the molybdenum layer shown in Figure 8b and formed a volatile oxide. A volatile oxide is a non protective oxide and continuously exposes the substrate to further oxidation. As the volatile oxide left the surface of the molybdenum, oxygen was allowed to continuously contact and react with the surface of the molybdenum. Thus, through the continuous production and availability of oxygen, the molybdenum continuously reacted and the degradation of the molybdenum layer, shown in Figure 8b, occurred. It is suspected, however, that eventually oxygen generation by zirconia would stop as an oxygen-deficient sub-stoichiometric zirconia was formed which was in equilibrium at temperatures up to 2000°F in a high vacuum. The hub and spoke appearance on the foil layer is the image of a molybdenum bracket which was in direct contact with the first hot side foil. This bracket sets on the end of the inner core to support the end cap insulation. It appears that this bracket retarded the degrading of the molybdenum foil underneath.

Figures 8c through 8g show the remaining end discs which were removed from the test package. A comparison of these figures among one another indicates that the molybdenum foils of end disc sets C, D, E and F show increased amounts of surface oxide deposits as opposed to the end disc sets A and B which appear to be somewhat shiny. The increased amount of oxide deposits on the colder end disc sets was due to condensation of the volatile molybdenum oxides which were produced in the hotter end disc sets (A & B). The oxide then deposited on the colder layers producing a dull violet-to-blue color.

7. Following the visual examination of the molybdenum foils and zirconia cloths at low magnifications up to 30X, selected layers were subjected to metallographic examination at magnifications up to 500X. The top molybdenum layer of end disc set A was examined at various locations. Figure 9a shows the hottest molybdenum layer from the end disc set A which had areas that showed evidence of severe reactions. Four locations are indicated in Figure 9a. These were examined at a magnification of 500X. The area referred to as area #4 in Figure 9a is shown in Figure 9b at a magnification of 10X. The edge of the reacted zone appeared to be jagged and had little if any change in color.

Figures 10a through 10e show the surface appearance of the molybdenum foil at various locations which are identified in Figure 9a. Figure 10a, which shows the "hot" side of the Mo foil from end disc set A, indicates that the nucleation stage of recrystallization had been reached. In studies previously performed on a molybdenum-zirconia system, extensive recrystallization occurred in the "hotter" molybdenum layers resulting in very brittle molybdenum foils which couldn't be handled.⁽⁵⁾ The molybdenum samples obtained from the insulation test package during the present study showed no signs of extensive recrystallization and remained quite ductile. The reason for the reduced tendency towards recrystallization in molybdenum foil used in this latter test is not clearly known; however,

the molybdenum foil used in this latter test could have been in the stress relieved condition. Thus, the driving force for recrystallization could have been reduced as a consequence of the stress relieving.

To test this hypothesis samples of the original as-received molybdenum foil were heat treated at 2000°F in an argon atmosphere. There was no evidence of recrystallization. The samples remained ductile. It is almost certain that if the molybdenum foils had any degree of residual stresses in them prior to the 2000°F exposure, recrystallization would have occurred. Recrystallization of molybdenum samples has been known to occur as low as 1652°F.⁽⁶⁾ The key variables in this instance are the prior mechanical working, heat treatment and the amount of residual stresses in the metal.

Figures 10b, 10c and 10d show the number 1, 2 and 3 locations respectively on the Mo layer #1 of the end disc set A. The various locations appeared to have experienced varied degrees of thermal etching. Figure 10d is a good illustration of the appearance of a molybdenum layer after fairly extensive thermal etching. The dark regions in Figure 10d are heavy oxide deposits.

8. Following the surface examination of layer 1 of end disc set A, additional selected molybdenum layers from end disc set A were examined at a magnification of 400X. The arrows in Figure 11a, which shows the "hot" side of layer #5 of end disc set A, indicate some evidence of the nucleation stage of recrystallization. Figure 11b which shows the "cold" side of the same layer #5 of end disc set A had a slightly different appearance than that of the "hot" side of the same layer. No evidence of any equiaxed grains, which are characteristic in a recrystallized structures, could be found. Evidence of duplex twinning was present.

Figures 12a and 12 b show molybdenum layer #15 of end disc set A. This layer appears to be slightly more thermally etched when compared with Figure 11a and 11b, which show the fifth layer of the same set. Figure 13a shows layer #45 of the end disc set A. This layer was one of the "cooler" layers. Yet, the appearance of this layer was very similar to the "hotter" layers of the same set. Figure 13b, shows the "cold" side of layers #45 from end disc set A. It indicates that an oxide deposit was present. These oxide deposits were different from other oxide deposits previously observed.

9. A micro-examination was also performed on selected layers from the remaining end disc sets. Figure 14a and 14b show the surface of molybdenum layer #7 from end disc set B. The B photograph shows the presence of an oxide very similar to that found on layer #45 of end disc set A (shown in Figure 13b). Figure 14b very clearly shows that the deposits had a straight sided appearance and also appeared to be oriented in the rolling direction of the molybdenum foils.

Some signs of oxide nucleation could be observed in Figure 15a which shows layer #47 of end disc set B. Very tiny equiaxed grains could be detected. The large light areas found in Figure 15a and also in 15b were probably a different form of oxide which either formed on the molybdenum surface or condensed from a vapor. Figures 16a and 16b show the surface of molybdenum layer #3 of set C.

The appearance of this layer was similar to the "cold" side of layer #47 of set B shown in Figure 15b.

10. The surface appearance of the "cooler" end disc sets are shown in Figures 17 through 19. Figure 17a and 17b show the "hot" and "cold" sides of molybdenum layer #3 of set D respectively. The surface appeared to be much darker than the "hotter" layers which are shown in Figures 10 through 16. The light areas in both Figures 17a and 17b were probably a different form of oxide deposit, possibly a MoO_3 type. The latter oxide has a white-to-yellow color.⁽⁷⁾ Figures 18a and 18b show layer #3 from end disc set E. Again, the appearance was very dark; characteristic of a heavy oxide deposition.

Figure 19 shows molybdenum layer #3 from set F, the "coolest" end disc set. Compare this photograph with Figure 20, which shows a unused sample of molybdenum foil, from the same lot of foil used in fabricating the vacuum insulation test package. It is apparent that the "coolest" layers of the test package are very similar to an unused sample of the molybdenum foil. The condition of the molybdenum layers and also the zirconia cloths from the end disc set F was very good. The molybdenum layers remained very shiny and ductile, while the zirconia cloth apparently remained in its stoichiometric form.

11. It has previously been mentioned that the molybdenum layers of the "coldest" end disc sets were very similar to an unused sample of the molybdenum foil. As the layers became progressively hotter, evidence of thermal etching had been detected. Thermal etching of the molybdenum foil had been a matter of concern because this effect theoretically could increase the emissivity of molybdenum foils thus increasing the effective thermal conductivity of the insulation package.

Evidence of thermal etching was much more substantial in the samples of molybdenum which were sectioned from the side wall of the test cylinder. Figures 21a through 21c show molybdenum layers that were subjected to various thermal conditions in the test package. Figure 21a shows layer #98 from set II which was removed from the sidewall. The surface was very similar to an unused molybdenum sample. Figure 21b which shows layer #34 from set I, indicates that some evidence of thermal etching was present, but not to the extent as that found in Figure 21c. The surface appearance had greatly changed from the relatively smooth surface of the "cooler" layers to the rough wrinkled appearance which was characteristic of the "hottest" molybdenum layers. The surface appeared clean and free of oxide deposits, but nevertheless had been severely thermally etched.

12. It was observed that the surface appearances of the various molybdenum layers had varied substantially. The surfaces ranged from the shiny smooth surface typical of the "coolest" molybdenum layer to a very dull, dark violet surface typical of molybdenum layers with heavy oxide films. Also, thermal etching effects had left many of the hottest layers very wrinkled and rough. Reflectance measurements were performed on selected molybdenum layers from the end disc sets A and B in an effort to evaluate any degradation from a reflectance point of view. Table VI tabulates the results of the reflectance measurements. It should be noted that the values listed in Table VI are all relative to an unused molybdenum foil sample which was assumed to have a reflectance of 100%.

Reflectance measurements indicated that the "cold" sides of all the molybdenum layers that were tested had a reflectance value of 100%. Therefore, any thermal etching along with any limited oxide deposition had no noticeable deleterious effect on the reflective properties of the "cold" side molybdenum layers. A gradual decrease in the reflectance on the "hot" side of the molybdenum layers was observed in the layers of sets A and B. The trend observed was decreasing reflectance on the "hot" side as the layers became "cooler". A reflectance value of 58% was exhibited by the "hot" side of layer #39 of end disc set B. It can be concluded that the presence of oxide deposits greatly decreased the reflectance, while thermal etching had little if any affect on the reflectance. The oxide deposits observed in end disc set B were not as heavy as those found on "cooler" molybdenum layers of sets C, D and E. Thus, the reflectance of the "cooler" layers of sets C, D and E would be expected to decrease on both the "hot" and "cold" sides.

13. Another occurrence which was quite common on the molybdenum layers of both the end disc sets and the sections removed from the cylinder wall was the presence of small areas of what appeared to be an oxide deposit of a different form. Figure 22a shows one of these deposits which in this particular instance had a yellow color. The majority of these spots were white in color as was indicated in some of the previously mentioned figures. A yellow deposit might be associated with MoO_3 . It has been theorized that the volatile MoO_3 was condensed on the "cooler" molybdenum layers resulting in many small spots scattered over the molybdenum surfaces. Figure 22b shows another type of deposit which was observed on layer #86 from set II of the cylinder wall. A small zirconia fiber can be seen adhering to the Mo foil in Figure 22b. A third example of a localized oxide deposit can be found in Figure 22c. This figure shows a much more severe case in which a very small hole appeared to have formed in the molybdenum foil. The arrows in Figure 22c indicate a region which had a yellow color, characteristic of MoO_3 . The large dark ring was blue in color which is typical for a MoO_2 type oxide. A possible reaction mechanism might involve the formation of a low melting eutectic between MoO_3 and MoO_2 . The melting point of the eutectic is 778°C (1432°F).⁽⁸⁾ Diffusion rates in liquid oxides may be very rapid in comparison to solid oxides. Therefore, liquid oxides are not effective diffusion barriers. Thus, a possible reaction mechanism would be one in which a low melting eutectic formed in this zone which allowed rapid oxidation and deterioration of the Mo foil.

14. Figures 23a through 23c show molybdenum layers which exhibited evidence of bonding with a zirconia cloth. The weave pattern can be observed in all three photographs and in Figure 23c, the "square" weave pattern of the zirconia cloth is observed. In view of the high temperature and vacuum levels of the test, intimate contact between the molybdenum and zirconia layers could have promoted solid state bonding between them. Such an occurrence might promote diffusion and indirectly result in an increase in the rate of molybdenum oxidation. Further evidence of zirconia fibers adhering to the molybdenum foils is shown in Figures 24a, 24b and 24c. The zirconia fiber shown in Figure 24b appeared to have a deposit on it which could possibly have been a molybdenum deposit. This would substantiate that a reaction between the molybdenum and zirconia was promoted by intimate contact between the two materials. Figure 23c shows an opposite type

of effect in which the molybdenum foil appeared to have experienced the formation of an oxide as a result of a zirconia fiber adhering to the surface of the molybdenum.

A more detailed study of the zirconia cloths was performed at a magnification of 500X followed by electron probe scans of the zirconia cloth in an effort to detect possible molybdenum deposits on the zirconia cloths. Figures 25a and 25b show zirconia layer #6 from end disc set B. Small globules lodged between zirconia fibers were detected and are shown in Figure 25a. These globules were subsequently identified as Mo deposits.

Figure 26a shows layer #14 from end disc set A. Deposits are clearly visible on the zirconia fibers. An electron image of the same zirconia layers was performed and is shown in Figure 26b. The X-ray image shown in Figure 26c indicated that these very same deposits shown in Figures 26a and 26b were indeed molybdenum deposits; and furthermore, many minute deposits were detected which could not be observed at a magnification of 500X using an optical microscope. Figure 26d shows an X-ray image indicating the strong presence of yttrium in the zirconia fibers. This was to be expected since yttria, the oxide form of yttrium, is used as a stabilizer in zirconia. A typical analysis for zirconia cloth is presented in Appendix A and the actual as received analysis for the molybdenum foil utilized is presented in Appendix B.

DISCUSSION

In previous studies on the molybdenum-zirconia vacuum insulation system evidence of high temperature vacuum induced oxygen-deficient zirconia was limited and its effects on the performance were not felt. In the present test the harder vacuum was probably responsible for the extensive inducement of zirconia oxygen deficiency. Thus, a source of oxygen was present as a result of the inherent nature of zirconia to become oxygen-deficient under conditions of high temperature and vacuum. As a consequence of the oxygen deficiency the oxidation of the molybdenum foils occurred. Thus, the two important reactions were as follows:

It was believed that these reactions were responsible for the major portion of any deterioration which had occurred in the vacuum insulation.

Oxygen is the most critical interstitial element where molybdenum is concerned. Above 795°C (1463°F) molybdenum forms a volatile non protective oxide which allows O₂ to continuously contact and react with the surface. Thus, oxygen which was present, due to ZrO₂ changing to the oxygen-deficient ZrO_{2-X}, was able to react the Mo foil and form a volatile oxide.

Visual observations along with X-ray diffraction data confirmed that the oxidation of the "hotter" molybdenum layers resulted in volatile oxides which eventually condensed on "cooler" molybdenum layers. As a result, the thermal conductivity increased as a consequence of increased emissivity and decreased reflectance of intermediate molybdenum layers.

Oxidation of molybdenum foils would continue as long as oxygen was available. It seems probable that after zirconia layers reached substoichiometric compositions that were in equilibrium with the ambient temperature and vacuum levels, oxygen offgassing would stop. That the effective thermal conductivity of the test package did not change substantially during the 10,000 hour test after the maximum hot face temperature of 2000°F was reached might be evidence in support of this contention. The minimum pressure level that was obtained in this test was 3×10^{-8} torr. Possibly in the harder vacuums of outer space, oxygen offgassing from zirconia layers might occur for a longer period. Thus additional oxidation of molybdenum layers and further degradation in thermal conductivity might occur in outer space.

A very desirable result of the test was that the molybdenum layers remained ductile, for all practical purposes. The ductility of the molybdenum is strongly influenced by recrystallization. It has been observed in previous studies that the molybdenum had a tendency to recrystallize resulting in a brittle foil which could not be handled. In the present tests no recrystallization was observed and the molybdenum layers remained ductile. A possible explanation for the observed ductility of the molybdenum foils could lie in the fact that molybdenum foil used in the present test was in a stress relieved condition. The thermodynamic driving force available to promote recrystallization is less in stress relieved materials than as-formed materials.

In general the overall performance of the present molybdenum-zirconia system was considered to be satisfactory, despite an initial degradation in the thermal conductivity of the system which was observed during the heating stage. The thermal conductivity of the system was stable over the duration of the 10,000 hour test.

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TABLE I

General Comments on Results of Visual Examination
Of Insulator Layers From The Bottom End Disc⁽¹⁾

<u>Set</u>	<u>Layer Numbers</u>	<u>Description</u>	<u>Comments</u>
A	Even numbers, Layers 2-48	Zirconia Cloth	Color of all layers is very dark gray, brittle, layers tear when folded.
A	Odd numbers, Layers 1-49	Mo foil	Both sides of layers have a dull appearance on the hotter layers of the set, colder layers have a light deposit on the interior of the "Hot" sides, ductility is fair, layers crease when bent, no sign of recrystallization.
B	Even numbers, Layers 2-48	Zirconia Cloth	Color of layers are dark gray, brittle, layers break when bent.
B	Odd numbers Layers 1-49	Mo foil	"Hot" sides of layers are violet in color indicating a Mo oxide deposit. "Cold" sides are dull with very light deposits, ductility is slightly reduced, layers crease when bent, no sign of any recrystallization.
C	Even numbers, Layers 2-48	Zirconia Cloth	All zirconia cloths are discolored, colors range from dark gray characteristic of the "Colder" layers to a medium gray characteristic of the "hotter" layers. "Hotter" layers tear when bent. "Colder" layers crease when bent, all layers appear to be ductile.
C	Odd numbers, Layers 1-49	Mo foil	All "Hot" sides of all the layers are a light violet color, characteristic of MoO ₂ ; ductile, crease when bent, "Colder" layers have a light violet appearance on the "Cold" side of the layers, violet color lightens towards the hotter layers, no sign of recrystallization.
D	Even numbers, Layers 2-46	Zirconia Cloth	Appearance is very similar to zirconia layers of the C series. All zirconia layers appear to be similar in color, very dark gray, cloths crease when folded, ductile.

TABLE I

(Continued)

<u>Set</u>	<u>Layer Numbers</u>	<u>Description</u>	<u>Comments</u>
D	Odd numbers, Layers 1-47	Mo foil	"Hot" sides of layers have a light violet color, "Cold" sides are slightly lighter than "Hot" sides in color, ductile, crease when bent, many shiny spots can be detected on both sides of the layers, no sign of recrystallization.
E	Even numbers, Layers 2-48	Zirconia Cloth	Hotter layers are medium gray in color, Colder layers have a medium gray border with a light gray color in the interior of the layers, ductile.
E	Odd numbers, Layers 1-49	Mo foil	"Hot" sides of layers are a light violet color characteristic of the hotter layers. The colder layers have a shiny border with light violet interiors. The shiny borders match the gray borders of the zirconia cloths which are between the Mo layers. "Cold" sides are very similar to "Hot" sides for each layer, ductility has increased slightly, no sign of recrystallization.
F	Even numbers, Layers 2-46	Zirconia Cloth	Hotter layers are very very light gray in color, color gradually lightens to a tan color, tan color appears approximately 5 layers in from the hottest layer in this series, ductility is maximal.
F	Odd numbers, Layers 1-47	Mo foil	Both sides of layers are shiny, little if any MoO ₂ deposits can be detected. Ductility is excellent.

Notes: (1) See Figure 3 for location of the various end disc sets in the test package.

(2) Examination was performed at magnifications up to 30X.

TABLE II

Results of Visual Examination of Insulator Layers

From The Side of Test Package (Set I)

<u>Layer Number</u>	<u>Description</u>	<u>Observations</u>
No. 1	Zirconia Cloth	Hottest cloth, black, brittle, pulls apart easily.
No. 2	Mo foil	Shiny on both sides, reduced ductility relative to cooler layers, does not crack when bent, no evidence of recrystallization. Extensive thermal etching, wrinkled.
No. 3	Zirconia Cloth	Black, brittle, breaks when bent.
No. 4	Mo foil	Similar to No. 2, wrinkles are increased, small threads of zirconia are stuck on "Hot" side, thermally etched.
No. 5	Zirconia Cloth	Black on "Cold" side. Light gray with dark gray regions on "Hot" surface, fragile, breaks when bent, cloth was torn in various spots.
No. 6	Mo foil	Similar to No. 2, various areas contain pattern of weave from zirconia. Thermally etched, wrinkled, no signs of recrystallization.
No. 7	Zirconia Cloth	Similar to No. 5, slight increase in ductility, slightly stronger.
No. 8	Mo foil	Similar to No. 2. Slight increase in ductility. No signs of recrystallization.
No. 9	Zirconia Cloth	Black on "Cold" surface, light gray on "Hot" side. Brittle.
No. 10	Mo foil	Shiny on both sides, increased ductility wrinkling greatly reduced. Small fibers of zirconia adhering to both sides, thermally etched.
No. 11	Zirconia Cloth	Similar to No. 9, dark gray areas, cloth still pulls apart easily.

TABLE II

(Continued)

<u>Layer Number</u>	<u>Description</u>	<u>Observations</u>
No. 12	Mo foil	Similar to No. 10
No. 13	Zirconia Cloth	Black on "Cold" surface, black, gray and light gray on "Hot" surface, cloth appears to be in a better condition.
No. 14	Mo foil	Beginning of discoloration of "Hot" surface, "Cold" surface is shiny, small spot appears to be a possible reaction zone, creases when bent, thermally etched, wrinkled.
No. 15	Zirconia Cloth	Dark area on "Hot" surface with tiny hole matches spot on layer 14 which appeared to have reacted. Increased strength, black "Cold" surface appears lighter than Layer 12's "Cold" surface.
No. 16	Mo foil	"Hot" surface has slight dark tinge, "Cold" surface appears slightly more dull. Zirconia fibers stuck on surfaces. Thermally etched.
No. 17	Zirconia Cloth	Black on "Cold" surface, gray on "Hot" surface, cloth breaks when bent, cloth was torn across width of sample.
No. 18	Mo foil	"Hot" surface is slightly darker, has a small speck which appears dark on "Cold" surface, could be an area of a dark oxide, creases when bent, thermally etched.
No. 19	Zirconia Cloth	Light gray on "Hot" surface, very very dark gray on "Cold" surface; cloth appears to be stronger when pulled.
No. 20	Mo foil	"Cold" surface is shiny, "Hot" surface has dull violet appearance, Zirconia fibers adhering to "Hot" surface, thermally etched.
No. 21	Zirconia Cloth	Very dark gray on "Cold" surface, light gray on "Hot" side, breaks when bent.

TABLE II
(Continued)

<u>Layer Number</u>	<u>Description</u>	<u>Observations</u>
No. 22	Mo foil	"Cold" surface shiny, "Hot" surface has violet appearance - MoO ₂ . Ductility is fair, small hole in sheet.
No. 23	Zirconia Cloth	Similar to No. 21.
No. 24	Mo foil	Similar to No. 20. Tiny shiny spots can be seen on dull "Hot" surface.
No. 25	Zirconia Cloth	Very very dark gray on both sides. Breaks when bent.
No. 26	Mo foil	Darker violet color on "Hot" surface, "Cold" surface is shiny, a dark spot surrounded by a light shiny area can be found on the "Hot" side.
No. 27	Zirconia Cloth	Similar to No. 25.
No. 28	Mo foil	"Cold" surface is slightly less shiny, tiny shiny spots can be found on dull, violet "Hot" surface, creases when bent.
No. 29	Zirconia Cloth	Black on both sides, does not break when bent.
No. 30	Mo foil	Similar to No. 28.
No. 31	Zirconia Cloth	Similar to No. 29. tears when bent excessively.
No. 32	Mo foil	Similar to No. 30, slightly more dark on "Hot" surface.
No. 33	Zirconia Cloth	Black on both sides, brittle, breaks when bent.
No. 34	Mo foil	Similar to No. 32.
No. 35	Zirconia Cloth	Black on both sides, breaks when bent, slight increase in strength.
No. 36	Mo foil	Similar to No. 32.

TABLE II

(Continued)

<u>Layer Number</u>	<u>Description</u>	<u>Observations</u>
No. 37	Zirconia Cloth	Black on both sides, doesn't tear when pulled or bent.
No. 38	Mo foil	Similar to No. 32. Dark spots surrounded by light areas can be detected.
No. 39	Zirconia Cloth	Similar to No. 35.
No. 40	Mo foil	Similar to No. 32. Has soldered spots.
No. 41	Zirconia Cloth	Black on "Hot" side, slightly lighter on "Cold" side. Tears when pulled.
No. 42	Mo foil	Heavy oxide deposits on "Hot" surface, small spots which appear light can be found on "Hot" surface. "Cold" surface appears shiny but a violet cast can be detected at 30X. Fairly ductile.
No. 43	Zirconia Cloth	Black on both sides, appears slightly stronger, doesn't tear when bent.
No. 44	Mo foil	Similar to No. 42.
No. 45	Zirconia Cloth	Similar to No. 43.
No. 46	Mo foil	Similar to No. 42. A small dark blue spot can be found on "Cold" shiny surface, at 30X it appears that there is a tiny hole in the sheet.
No. 47	Zirconia Cloth	Black on both sides, creases when folded lightly.
No. 48	Mo foil	Similar to No. 46. The dark blue spot matches up with the spot on Layer 46.
No. 49	Zirconia Cloth	Similar to No. 47.
No. 50	Mo foil	"Hot" side is dark violet, shiny side has blotches of violet coloring, a dark blue spot also appears on the "Cold" surface.
No. 51	Zirconia Cloth	Similar to No. 47.

TABLE II

(Continued)

<u>Layer Number</u>	<u>Description</u>	<u>Observations</u>
No. 52	Mo foil	Similar to No. 50. A hole through the foil can be detected.
No. 53	Zirconia Cloth	Similar to No. 47.
No. 54	Mo foil	Similar to No. 50.
No. 55	Zirconia Cloth	Black on both sides, creases slightly when folded.
No. 56	Mo foil	"Hot" surface has heavy oxide deposits, "Cold" surface no longer appears shiny, light violet cast, many dark blue spots can be seen in a sort of pattern, ductility decreased slightly.
No. 57	Zirconia Cloth	Color appears to be a deeper and darker black, creases slightly when folded.
No. 58	Mo foil	"Cold" surface is a darker violet, small dark blue spots can be seen on "Cold" surface. Tiny microscopic holes were through the sheet, "Hot" surface is dark violet.
No. 59	Zirconia Cloth	Black on both sides, doesn't crease when folded.
No. 60	Mo foil	Dark violet on "Hot" surface, "Cold" side is darkening, number of small blue deposits is increasing, ductility decreased slightly.
No. 61	Zirconia Cloth	Similar to No. 59.
No. 62	Mo foil	"Cold" surface is still darker than layer 60, irregular shaped spots can be seen on "Hot" surface, different from any other spots previously found.
No. 63	Zirconia Cloth	Similar to No. 59.
No. 64	Mo foil	Both "Hot" and "Cold" sides are approximately the same violet color, irregular shaped areas can be seen on "Cold" surface, light spots can be seen on both surfaces, ductility is fair.

TABLE II
(Continued)

<u>Layer Number</u>	<u>Description</u>	<u>Observations</u>
No. 65	Zirconia Cloth	Black on both sides, a dark spot can be seen on both sides, doesn't crease when folded.
No. 66	Mo foil	No irregular shaped areas, color about the same.
No. 67	Zirconia Cloth	Similar to No. 59.
No. 68	Mo foil	"Cold" surface is a little shinier, "Hot" surface is unchanged, a array of dark blue elongated spots has appeared, shiny spots are increased in number.
No. 69	Zirconia Cloth	Black on both sides, doesn't crease when folded.
No. 70	Mo foil	Both sides are badly discolored, light spots are present on both sides, layer appears to be a little more brittle.
No. 71	Zirconia Cloth	Similar to No. 69.
No. 72	Mo foil	Similar to No. 70, irregular shaped lighter violet areas can be seen on "Hot" surface. Layer No. 71 was stuck to Layer 72 when package was being sectioned.
No. 73	Zirconia Cloth	Similar to No. 69.
No. 74	Mo foil	Similar to No. 70, a number of small light spots can be seen on the "Hot" side, they are probably a different form of oxide deposits.
No. 75	Zirconia Cloth	The spots which appear to be areas where this layer stuck to another can be seen on the "Cold" surface, black on both sides, doesn't crease when folded.
No. 76	Mo foil	"Cold" surface appears to have a blue color, light spots can be seen on "Cold" surface. A long narrow dark violet spot can be detected on "cold" surfaces, "Hot" surface is violet with evidence of many light specks. No noticeable change in ductility.

TABLE II

(Continued)

<u>Layer Number</u>	<u>Description</u>	<u>Observations</u>
No. 77	Zirconia Cloth	"Hot" side is dark gray, "Cold" surface is black, doesn't crease when bent.
No. 78	Mo foil	Long narrow light spot on "Hot" surface matches with spot on layer 76, many light specks can be detected on "Hot" surface, "cold" surface is shiny again.
No. 79	Zirconia Cloth	Similar to No. 77.
No. 80	Mo foil	"Cold" side is shiny, "Hot" surface is violet with many light specks, no noticeable change in ductility. Light spot can also be seen on cold side.
No. 81	Zirconia Cloth	Both surfaces black, creases when bent.
No. 82	Mo foil	Similar to No. 80, light spot on "Hot" surface matches with light spot on "Cold" surface of Layer 80.
No. 83	Zirconia Cloth	Both sides dark gray, doesn't crease when bent.
No. 84	Mo foil	"Cold" side is shinier, "Hot" surface is lighter violet, light spots still appear on "Hot" surface, slight increase in ductility.
No. 85	Zirconia Cloth	Similar to No. 83.
No. 86	Mo foil	"Hot" surface is a little lighter than that of layer 84, "Cold" surface is shiny. No noticeable change in ductility.
No. 87	Zirconia Cloth	Light gray on "Hot" side, medium gray on "Cold" doesn't crease when bent.
No. 88	Mo foil	"Hot" surface has violet cast, "Cold" surface is very shiny. Good ductility.
No. 89	Zirconia Cloth	Similar to No. 87.
No. 90	Mo foil	Similar to No. 88.

TABLE II

(Continued)

<u>Layer Number</u>	<u>Description</u>	<u>Observations</u>
No. 91	Zirconia Cloth	Very light gray on both sides. Doesn't crease when bent, good strength.
No. 92	Mo foil	Similar to No. 88.
No. 93	Zirconia Cloth	Lighter gray than Layer 91 on both sides, doesn't crease when bent.
No. 94	Mo foil	Similar to No. 92.
No. 95	Zirconia Cloth	Lighter gray than Layer 93 on both sides, good strength.
No. 96	Mo foil	Lighter violet cast on "Hot" surface, "Cold" surface is very shiny, good ductility.
No. 97	Zirconia Cloth	Lighter than Layer 95 on both sides, doesn't crease when folded.
No. 98	Mo foil	Slight violet cast on "Hot" surface, "Cold" surface is very shiny.
No. 99	Zirconia Cloth	Lighter than Layer 97.
No. 100	Mo foil	Shiny on both sides, good ductility.
No. 101	Zirconia Cloth	Almost white with some light gray spots present.
No. 102	Mo foil	Similar to No. 100, blotch of blue tint in one area.
No. 103	Zirconia Cloth	Lighter than No. 101.
No. 104	Mo foil	Very shiny on both sides, no spots, good ductility.

Notes: (1) See Figure 2a for location of samples in test package.

(2) Visual examination was performed at magnifications up to 30X.

TABLE III

Results of Visual Examination of Insulator Layers From

Side of Test Package (Set II)

<u>Layer Number</u>	<u>Description</u>	<u>Observations</u>
No. 1	Zirconia Cloth	Black on both sides, brittle, breaks when bent.
No. 2	Mo foil	Thermally etched, both sides are dull, brittle, creases when bent, small dark spot on "Hot" surface. No sign of recrystallization.
No. 3	Zirconia Cloth	Black on "Cold" side, gray with black areas on "Hot" surface. Brittle, hard to handle.
No. 4	Mo foil	Similar to No. 2, wrinkled, also has dark spot.
No. 5	Zirconia Cloth	Similar to No. 3. Torn.
No. 6	Mo foil	Wrinkled, thermally etched, no sign of recrystallization; brittle, creases when folded, both sides appear dull.
No. 7	Zirconia Cloth	Similar to No. 3.
No. 8	Mo foil	Similar to No. 6, many zirconia fibers stuck on "Hot" side, no sign of recrystallization.
No. 9	Zirconia Cloth	Similar to No. 3.
No. 10	Mo foil	Similar to No. 6.
No. 11	Zirconia Cloth	Similar to No. 3.
No. 12	Mo foil	Similar to No. 6.
No. 13	Zirconia Cloth	Similar to No. 3, breaks apart easier.
No. 14	Mo foil	Similar to No. 6, first appearance of shiny spot of "Hot" surface.
No. 15	Zirconia Cloth	Similar to No. 3, appears to be in better condition, not as fragile.

TABLE III

(Continued)

<u>Layer Number</u>	<u>Description</u>	<u>Observations</u>
No. 16	Mo foil	Similar to No. 6, zirconia fibers can be seen adhering to the surface, no sign of recrystallization.
No. 17	Zirconia Cloth	Similar to No. 3.
No. 18	Mo foil	"Cold" surface is beginning to shine, two dark spots can be seen where a hole was through the sheet, appears to be a slight increase in ductility.
No. 19	Zirconia Cloth	Similar to No. 3, slight increase in strength.
No. 20	Mo foil	"Hot" surface is discolored, a light violet cast can be detected, many shiny spots can be seen on "Hot" side, a few dark spots can also be observed, "Cold" surface shines more.
No. 21	Zirconia Cloth	Similar to No. 19.
No. 22	Mo foil	"Hot" surface is darker violet, many light spots exists, they appear to be locations which are a different form of oxide.
No. 23	Zirconia Cloth	"Cold" surface is black, inner surface is gray, in better condition, increased strength, doesn't break when folded.
No. 24	Mo foil	Similar to No. 22.
No. 25	Zirconia Cloth	Similar to No. 23.
No. 26	Mo foil	Many zirconia fibers adhering to the "Hot" surface, it appears that light spots originate from locations where zirconia fibers stick to Mo.
No. 27	Zirconia Cloth	Black on both sides, condition of zirconia cloth appears to be getting better.

TABLE III
(Continued)

<u>Layer Number</u>	<u>Description</u>	<u>Observations</u>
No. 28	Mo foil	Similar to No. 26, long zirconia fiber is stuck on Mo, area around fiber is very shiny.
No. 29	Zirconia Cloth	Similar to No. 27.
No. 30	Mo foil	"Cold" surface is shiny, "Hot" surface is violet color, a couple of very dark blue spots can be seen on the "Cold" side, no change in ductility.
No. 31	Zirconia Cloth	Similar to No. 27.
No. 32	Mo foil	Color on "Hot" surface appears slightly darker, only light spots can be found on the "Hot" surface but no sign can be found on the "Cold" shiny surface.
No. 33	Zirconia Cloth	Black on both sides, creases badly when folded.
No. 34	Mo foil	Similar to No. 32.
No. 35	Zirconia Cloth	Black on both sides, breaks when folded.
No. 36	Mo foil	Similar to No. 34, "Cold" side is more dull.
No. 37	Zirconia Cloth	Color appears to be slightly lighter, cloth tears when folded.
No. 38	Mo foil	Color on "Hot" surface is darker, "Cold" surface is similar to layer No. 32, no change in ductility, many light spots can be detected on "Hot" surface.
No. 39	Zirconia Cloth	Color of cloth appears slightly lighter, strength of cloth appears to be a little better.
No. 40	Mo foil	Color of "Hot" surface seems to be a little darker, "Cold" surface has 2 light spots and "Hot" surface has many light spots.

TABLE III

(Continued)

<u>Layer Number</u>	<u>Description</u>	<u>Observations</u>
No. 41	Zirconia Cloth	Both sides black, creases when folded, not as brittle as hotter layers, stronger.
No. 42	Mo foil	Similar to No. 40.
No. 43	Zirconia Cloth	Similar to No. 41.
No. 44	Mo foil	Similar to No. 40.
No. 45	Zirconia Cloth	Similar to No. 41.
No. 46	Mo foil	Similar to No. 40, "Cold" surface is duller.
No. 47	Zirconia Cloth	Cloth appears lighter in color, more ductile.
No. 48	Mo foil	A few very dark blue spots are on the "Cold" surface, layer is ductile; many light spots on "Hot" side. Condition is not as good as layers 40 - 46.
No. 49	Zirconia Cloth	Similar to No. 47.
No. 50	Mo foil	"Cold" side has a light blue cast, "Hot" surface has many light spots as well as "Cold" side.
No. 51	Zirconia Cloth	Color is lightening - dark gray, cloth is in satisfactory condition, creases when bent.
No. 52	Mo foil	"Hot" side is darker, many light spots on both sides.
No. 53	Zirconia Cloth	Similar to No. 51.
No. 54	Mo foil	Condition of "Cold" surface has become worse, many light spots can be found on "Cold" surface. "Cold" side has blue color, "Hot" surface is slightly worse.

TABLE III

(Continued)

<u>Layer Number</u>	<u>Description</u>	<u>Observations</u>
No. 55	Zirconia Cloth	Color has darkened somewhat, condition is similar to No. 51.
No. 56	Mo foil	"Cold" surface is discolored more than Layer 54. Light spots have increased in number, ductility has remained the same, "Hot" side is similar to No. 52 and No. 54.
No. 57	Zirconia Cloth	Color is slightly lighter, doesn't crease when folded.
No. 58	Mo foil	"Cold" side has discolored some more, color of "Cold" surface is almost as dark as the "Hot" side.
No. 59	Zirconia Cloth	Similar to No. 57.
No. 60	Mo foil	Similar to No. 58, many light spots can be seen on the "Cold" surface.
No. 61	Zirconia Cloth	Color is lighter than Layer 57, condition of cloth is satisfactory, doesn't crease when bent.
No. 62	Mo foil	"Cold" surface has pattern of dark spots similar to weave of zirconia cloth, color of "Cold" side is darker, no noticeable change in ductility.
No. 63	Zirconia Cloth	"Cold" side has more of a shine than previous cloths, doesn't crease when folded.
No. 64	Mo foil	"Cold" surface is darker, "Hot" surface remaining about the same color.
No. 65	Zirconia Cloth	Both sides appear to be dark gray, doesn't crease when folded, strength has increased, good ductility.
No. 66	Mo foil	Very badly reacted area, "Cold" surface is darker, similar to No. 64.
No. 67	Zirconia Cloth	Similar to No. 65.

TABLE III

(Continued)

<u>Layer Number</u>	<u>Description</u>	<u>Observations</u>
No. 68	Mo foil	A very badly reacted area on the "Hot" side of the foil matches spot on "Cold" surface of Layer 61, color of "Cold" surface similar to Layer 66.
No. 69	Zirconia Cloth	Similar to No. 65.
No. 70	Mo foil	Color is similar to No. 68, light spots aren't as severe, no noticeable change in ductility.
No. 71	Zirconia Cloth	Similar to No. 65.
No. 72	Mo foil	Discoloring has increased, similar to No. 70.
No. 73	Zirconia Cloth	Similar to No. 65.
No. 74	Mo foil	Similar to No. 72.
No. 75	Zirconia Cloth	Similar to No. 65, has an area which appears was stuck to a Mo layer.
No. 76	Mo foil	"Cold" surface is showing signs of a gloss, "Hot" surface appears to be lighter, adequate ductility.
No. 77	Zirconia Cloth	Similar to No. 65.
No. 78	Mo foil	Similar to No. 70.
No. 79	Zirconia Cloth	Cloth is in satisfactory condition, doesn't crease when bent.
No. 80	Mo foil	"Cold" surface is shiny with a light blue cast and also areas of dark blue, ductile, "Hot" surface is lighter.
No. 81	Zirconia Cloth	Lighter color - dark gray, good strength, and flexibility.
No. 82	Mo foil	Similar to No. 80, ductile.
No. 83	Zirconia Cloth	Similar to No. 81.
No 84	Mo foil	Similar to No. 80, ductile.

TABLE III
(Continued)

<u>Layer Number</u>	<u>Description</u>	<u>Observations</u>
No. 85	Zirconia Cloth	Color is lighter gray, cloth is in good condition.
No. 86	Mo foil	No sign of discoloration although "Cold" surface is somewhat dull, "Hot" surface is lighter, a long shiny spot can be found on the "Hot" side, ductile.
No. 87	Zirconia Cloth	Both sides have a medium gray color, good strength and flexibility.
No. 88	Mo foil	"Hot" surface is much darker than Layer 86, "Cold" surface is shiny, ductile.
No. 89	Zirconia Cloth	Similar to No. 87.
No. 90	Mo foil	Similar to No. 88.
No. 91	Zirconia Cloth	Color is a light gray, good condition.
No. 92	Mo foil	Similar to No. 88, "Cold" surface is possibly more shiny.
No. 93	Zirconia Cloth	Color is a lighter - very light gray.
No. 94	Mo foil	"Hot" side is very light violet, "Cold" surface is shiny.
No. 95	Zirconia Cloth	Color is lighter.
No. 96	Mo foil	Similar to No. 94.
No. 97	Zirconia Cloth	Color is lighter, a small dark particle is stuck on "Cold" surface.
No. 98	Mo foil	Similar to No. 94.
No. 99	Zirconia Cloth	Similar to No. 95.
No. 100	Mo foil	A reaction spot can be found on "Cold" side, ductile.

TABLE III
(Continued)

<u>Layer Number</u>	<u>Description</u>	<u>Observations</u>
No. 101	Zirconia Cloth	Off white color.
No. 102	Mo foil	Both sides shiny, dark spot can still be detected, ductile.
No. 103	Zirconia Cloth	Dirty white with darker spots, good condition.
No. 104	Mo foil	Similar to No. 102.

NOTES: (1) See Figure 2b for location of this set of samples in test package.

(2) Visual examination was performed at magnifications up to 30X.

TABLE IV

Results of X-ray Diffraction Analysis of Molybdenum Layers From End Disc Sets

<u>Set</u>	<u>Layer Number</u>	<u>Side</u>	<u>Result*</u>
B	No. 49	"Hot"	Mo strong; MoO ₂ Type - weak
B	No. 49	"Cold"	Mo strong
C	No. 3	"Hot"	MoO ₂ Type - Strong; Mo - weak
C	No. 3	"Cold"	Mo - strong

* MoO₂ indications were observed on sides of the sample discs which contained substantial films with colors ranging from blue to violet.

TABLE V

Results of X-Ray Diffraction Analysis of Zirconia Layers From End Disc Assembly

<u>Set</u>	<u>Layer Number</u>	<u>Results</u>	<u>Observations</u>
A	No. 2	Tetragonal ZrO ₂	
A	No. 14	Tetragonal ZrO ₂	
A	No. 44	Tetragonal ZrO ₂	
B	No. 4	Tetragonal ZrO ₂	c/a of the B4 and B10 samples appears to be the same and "more tetragonal" than B46 and C2.
B	No. 10	Tetragonal ZrO ₂	
B	No. 12	Tetragonal ZrO ₂	Slightly "less tetragonal" than layers B10 and B4 but definitely more than C2 and B46.
B	No. 46	Tetragonal ZrO ₂	c/a nearly equal to 1.
C	No. 2	Tetragonal ZrO ₂	c/a is nearly equal to 1, but closer to 1 than c/a for Sample B46.
D	No. 2	Cubic ZrO ₂	
E	No. 2	Cubic ZrO ₂	
F	No. 2	Cubic ZrO ₂	
Unused		Cubic ZrO ₂	

NOTES: (1) Results obtained from G. M. Faulring from Mining and Metals Division
of Union Carbide, Niagara Falls, New York.

TABLE VI

Results of Reflectance Measurements on Samples of
Mo Layers From End Disc Sets A & B

<u>Set</u>	<u>Layer Number</u>	<u>Side</u>	<u>Absorbance</u>	<u>Reflectance %</u>
A	No. 3	"Cold"	0	100%
A	No. 3	"Hot"	<0	100%
A	No. 5	"Cold"	<0	100%
A	No. 5	"Hot"	<0	100%
A	No. 7	"Cold"	0.04	91%
A	No. 7	"Hot"	0.04	91%
A	No. 9	"Cold"	<0	100%
A	No. 9	"Hot"	0.01	98%
A	No. 11	"Cold"	<0	100%
A	No. 11	"Hot"	0	100%
A	No. 13	"Cold"	<0	100%
A	No. 13	"Hot"	0	100%
A	No. 23	"Cold"	0.01	98%
A	No. 23	"Hot"	<0	100%
A	No. 25	"Cold"	<0	100%
A	No. 25	"Hot"	0.02	96%
A	No. 27	"Cold"	0	100%
A	No. 27	"Hot"	0.02	96%
A	No. 29	"Cold"	<0	100%
A	No. 29	"Hot"	0.07	86%
A	No. 39	"Cold"	<0	100%
A	No. 39	"Hot"	0.18	66%
A	No. 43	"Cold"	<0	100%
A	No. 43	"Hot"	0.17	67%

TABLE VI
(Continued)

<u>Set</u>	<u>Layer Number</u>	<u>Side</u>	<u>Absorbance</u>	<u>Reflectance %</u>
B	No. 11	"Cold"	0	100%
B	No. 11	"Hot"	0.20	63%
B	No. 39	"Cold"	0	100%
B	No. 39	"Hot"	0.23	58%

NOTES: (1) The samples were measured on a Lang 14 Spectrophotometer with Lang 1411 Reflectance attachment.

(2) Data:

IR source: tungsten lamp
IR detector: PbS cell
Wavelength: 1.2 microns (1200A)
Slit: 1.85 to 2.40 mm.

(3) Zero adjustment was made so that a unused sample of Mo foil versus a sample of unused Mo foil read zero. All other samples were measured against the unused Mo sample, as a reference. Therefore, all values tabulated in the Table are relative to an unused Mo foil, which was assumed to have adequate surface properties prior to thermal treatment.

FIGURE 1a

STABILITY TEST THERMAL CONDUCTIVITY DATA
CYLINDRICAL TESTING

**effect of temperature on
oxidation of unalloyed-
molybdenum samples (2 x 1
x 0.055 in.) exposed to
moving air for 30 minutes
at temperature.**

molten molybdic oxide (MoO_3)
observed on surface of specimens
at temperatures of 1500 F and
over. weight loss expressed as
percentage of original weight

Figure 1b(2)

Figure 2a. Shown at left is the test package which was thermally treated at 2000°F for 10,000 hours. Arrow #1 indicates the thermocouple leads. The arrows numbered 2 and 3 show the location of the end disc which will be shown in detail later in the report. The number 4 arrow indicates the location where the test package was sectioned to obtain samples for metallurgical examination. This first sectioning yielded samples designated as Set I. The white area at location 4 is the high purity alumina tube.

Mag: Approx. 1/10X

Figure 2b. This photograph shows the same test package which was described in Figure 2a. The arrow in the figure at left indicates the location of the second sectioning which yielded samples designated as Set II. The white region indicated by the arrow is the high purity alumina tube. This location is on the opposite side from the section labeled Set I in Figure 2a.

Mag: Approx. 1/10X

Figure 3

Insulation Test Cylinder Configuration

FIGURE 4

FIGURE 5

Figure 6. The above photomicrograph shows samples of the zirconia cloth after thermal treatment for 10,000 hours. These samples were obtained after sectioning of the test package at position 4 shown in Figure 2a. Appearance of the ZrO_2 cloth greatly changes as the layers become hotter.

Mag: 3/4X

Figure 7a. This photomicrograph shows the zirconia layer #6, side 1 from the end disc Set B. "Square" weave can be seen.

Mag. 50X

Figure 7b. The above photomicrograph shows the same zirconia cloth as in Figure 7A. The "long" weave of side 2 can be detected in this photograph.

Mag. 50X

Figure 7c. Shown above is layer #2, side 1, of the end disc Set E. The "square" weave of the zirconia cloth can be seen.

Mag. 50X

Figure 7d. This photomicrograph shows the same zirconia cloth as in Figure 7c, only the reverse side (side 2). Long weave can be seen.

Mag. 50X

Figure 8a. This photomicrograph shows the end disc assembly used in the test package shown in Figure 2a. A careful count will indicate that 6 sets of discs are present. The sets are stepped and each is 0.25" thick. The hottest set of discs is the smallest in diameter and is designated as end disc Set A. The remaining sets are lettered from B through F, with the end disc Set F being the coldest set and also having the largest diameter. This assembly was removed from position 3 in Figure 2a.

Mag: Approx. 7/8X

Figure 8b. The photomicrograph shown at left shows the end disc Set A. This set of discs is the hottest set of the end cap assembly shown in Figure 8a. The top Mo layer had reacted in various areas as indicated by the arrows in Figure 8b. The black areas detected in the section where the Mo layer had been missing are portions of the ZrO_2 cloth which was under the first Mo layer.

Mag: Approx. 8/10X

Figure 8c. Shown at left is the end disc Set B, the second hottest set of discs. Condition of the top Mo layer is much better than the top Mo layer of Set A (shown in Figure 8b). Arrow indicates Mo wire which was used to keep each set of end discs intact.

Mag: Approx. 8/10X

Figure 8d. The photomicrograph shown at right shows the end disc Set C. The Mo layer has been discolored by deposits of MoO_x which had been volatilized on hotter Mo layers and subsequently condensed on the cooler Mo layer shown at right.

Mag: Approx. 8/10X

set D

Figure 8e.

Mag: Approx. 8/10X

set E

Figure 8f

Mag: Approx. 8/10X

set F

Figure 8g

Mag: Approx. 8/10X

Shown above in Figures 8e, 8f, and 8g are the end disc Set D, Set E, Set F respectively. MoOx deposits can be seen on the top Mo layer of each set. A comparison of Figures 8b through 8g indicates that the MoOx deposits are greatest on the top Mo of sets D and E. This would indicate that the temperature range associated with the D and E sets provides optimal conditions for the condensation of the MoOx which had volatilized.

Figure 9a. Shown at left is the hottest layer from the end disc Set A. This Mo layer is the same layer shown in Figures 8a and 8b. Sections of the Mo foil were missing. Closer examination was later performed at a magnification of 500X in the areas numbered 1 through 4.

Mag: 1.6X

Figure 9b. This print shows the hottest layer of end disc Set A. Location #4, as indicated in Figure 9a, can be seen at left at a higher magnification. The Mo layer has deteriorated due to high temperature oxidation forming a volatile oxide. Consequently, large areas have reacted and are missing.

Mag: 10X

Figure 10a "Hot" Side Mag: 500X

Figure 10b "Cold" Side at Position #1 in Figure 9a. Mag: 500X

Figure 10c "Cold" Side at Position #2 in Figure 9a. Mag: 500X

Figure 10d. "Cold" Side at Position 3 in Figure 9a. Mag: 500X

Figure 10e "Cold" Side at Position #4 in Figure 9a. Mag: 500X

The photomicrographs shown on this page all show the hottest Mo layer of end disc Set A at various positions, as indicated in Figure 9a. These photographs show that the surface appearance of the Mo foil changes somewhat as a function of location. Evidence of thermal etching can be detected in each of the photomicrographs. Figure 10e shows the region adjacent to the portion of the foil which had been oxidized and volatilized.

Figure 11a. End Disc Set A, Mo, layer #5, "Hot" Side. Mag: 400X

Figure 11b. Same as 11a, "Cold" Side Mag: 400X

Figure 12a. Mo Layer #15 of End Disc Set A, "Hot" Side. Mag: 400X

Figure 12b. Same as 12a, "Cold" Side. Mag: 400X

Figure 13a. Mo Layer #45 of End Disc Set A, "Hot" Side. Mag: 400X

Figure 13b. Same as 13a, "Cold" Side Mag: 400X

Figure 14a. Mo Layer #7 from End Disc Set B, "Hot" Side. Mag: 500X

Figure 14b. Same as 14a, "Cold" Side Mag: 500X

Figure 15a. Mo Layer #47 from End Disc Set B, "Hot" Side. Mag: 500X

Figure 15b. Same as 15a "Cold" Side. Mag: 500X

Figure 16a. Mo Layer #3 from End Disc Set C, "Hot" Side. Mag: 500X

Figure 16b. Same as 16a, "Cold" Side. Mag: 500X

Figure 17a. Mo layer #3 of End Disc Set D, "Hot" Side. Darker color of surface indicates heavy oxide deposits. Area which appears white could possibly be another form of oxide, probably MoO_3 which has a white to yellow color.

Mag: 500X

Figure 17b. Same as Figure 12a, "Cold" Side. Mag: 500X

Figure 18a. Mo layer #3 from End Disc Set E, which is one of the colder end disc sets. This photomicrograph shows the "hot" side. Dark color indicates a heavy oxide deposit.

Mag: 500X

Figure 18b. Same as 18a, "Cold" Side.

Mag: 500X

Figure 19. Shown at left is Mo layer #3 from the end disc Set F. This set of discs was the coolest and most closely resembles the surface appearance of an unused Mo foil. This layer appears to be bright and the presence of an oxide deposit can not be detected as on hotter layers.

Mag: 500X

Figure 20. This photomicrograph shows an unused sample of the Mo foil typical of that used in fabrication of the test package. Surface appearance was bright and shiny.

Mag: 500X

Figure 21a

Mag: 500X

Figure 21b

Mag: 500X

Figure 21c

Mag: 500X

The above photomicrographs show the Mo layers 98, 34, and 2 in Figures 21a, 21b and 21c, respectively. These samples were obtained from the wall of the test package. Mo layers #98 and #2 shown in Figures 21a and 21c respectively were obtained from the location which is indicated in Figure 2b. The Mo layer #34 shown in Figure 21b was obtained after the test package was sectioned at position 4 shown in Figure 2a. The figures shown above clearly illustrate the degree of thermal etching as a function of increasing temperature. Layer #98 (Figure 21a) is an example of the typical appearance of one of the colder layers while layer 34 (Figure 21b) shows the initial effects of thermal etching on the surface appearance. Layer 2 (Figure 21c) is the hottest layer and clearly shows the difference in surface appearance.

Figure 22a: Mo layer 64 obtained from location 4 in Figure 2a. This photomicrograph shows a bright spot which was quite common in the samples which were examined. The color of the spot was yellow which would indicate that it is a MoO_3 deposit. The darker areas surrounding the bright spot are MoO_2 deposits. This photograph was taken on the "Cold" side of the layer.

Mag: 100X

Figure 22b: This photomicrograph shows Mo layer 26 sampled from the area indicated in Figure 2b. A zirconia fiber can be seen on the "Cold" side of the layer. The surrounding area had heavy oxide deposits.

Mag: 100X

Figure 22c: Shown above is a photomicrograph of Mo layer #46 obtained from location #4 in Figure #2a. It appears that a hole had been made through the Mo layer. The area which is pointed out by the arrows was yellow in color indicating the presence of MoO_3 . MoO_2 forms a low melting eutectic with MoO_3 which could explain the presence of a hole.

Mag: 100X

Figure 23a: Shown above is Mo layer #3 from end disc set E. A texture can be observed from the ZrO₂ cloth which was touching the Mo.

Mag: 26X

Figure 23b: Same as 23a only the opposite of the Mo layer is shown. This side was against the "long" weave of the zirconia. Texture can be observed in the above Figure.

Mag: 26X

Figure 23c: This photomicrograph shows the texture on the Mo layer #56 which was observed during examination of set II which was sectioned at the location indicated in Figure 2b. "Square" weave of the zirconia has given the Mo a similar texture.

Mag: 50X

Figure 24a: The photomicrograph at left shows many zirconia fibers which have stuck to the Mo foil. The layer is a sample of the end disc set A, layer #15. The photograph was taken on the "hot" side which had a fairly heavy oxide deposit.

Mag: 50X

Figure 24b: This photomicrograph shows the same Mo foil as described in Figure 24a, only at a higher magnification. The zirconia fibers appear to have a coating which may be a molybdenum deposit.

Mag: 400X

Figure 24c: Shown at left is Mo layer #7 from the end disc set B. A zirconia fiber can be seen adhering to the "Hot" side of the Mo layer. A light region can be observed surrounding the ZrO_2 fiber. This area is a different form of oxide deposit as opposed to the dark MoO_2 type deposits also shown in Figure 24c.

Mag: 500X

Figure 25a: Shown at left is a sample of the zirconia cloth which was used in end disc set B, layer #6. Small globules can be seen lodged between the fibers. These small deposits were identified as Mo deposits via an X-ray image.

Mag: 500X

Figure 25b: This photomicrograph shows the opposite side of the zirconia cloth described in Figure 25a. No deposits can be detected. Compare this photograph with Figure 25a, in which deposits are observed.

Mag: 500X

Figure 26a: This photomicrograph shows zirconia layer #14 from end disc set A. Deposits can be observed on the ZrO₂ fibers

Mag: 500X

Figure 26b: Shown above is an electron image of the same zirconia cloth described in Figure 26a. Small globules can be seen on the fibers as indicated by the arrows.

Mag: 800X

Figure 26c: Shown above is an X-ray image which indicates that there are Mo deposits on zirconia fibers. Sample is the same zirconia cloth which is described in Figure 26a.

Mag:

Figure 26d: This X-ray image indicates the presence of yttrium, an element which is used to stabilize the zirconia. The zirconia cloth contains approximately 5% yttria which is an oxide form of yttrium. The sample is the same sample described in Figure 26a.

Mag: 800X

APPENDIX A

TYPICAL ANALYSIS FOR ZIRCONIA CLOTH

SPECTROGRAPHIC ANALYSES OF TYPICAL ZIRCONIA CLOTH
(VOLATILE-SENSITIVE ARC PROCEDURE)

<u>ELEMENT</u>	<u>UCC, ZYW-5</u>
Aluminum	0.08
Boron	0.03
Barium	0.001
Calcium	0.1
Cobalt	0.0006
Chromium	0.003
Copper	0.004
Iron	0.2
Hafnium	2.-
Lanthanum	0.03
Potassium	0.008
Lithium	-
Magnesium	0.01
Manganese	0.004
Sodium	0.02
Nickel	0.004
Phosphorus	0.04
Lead	0.004
Scandium	0.003
Silicon	0.2
Titanium	0.02
Yttrium	M
Ytterbium	0.4
Zinc	0.02
Zirconium	M
<u>Miscellaneous</u>	
Antimony	0.002
Tin	

APPENDIX B

MOLYBDENUM FOIL CERTIFICATION

CERTIFICATE OF CHEMICAL ANALYSES AND PHYSICAL TESTS

HAMILTON PRECISION METALS

PHONE 717 — 394-7161
TWX 717 — 560-4417

A DIVISION OF THE HAMILTON WATCH CO.

TEST NO. 701015-04

CUSTOMER	UNION CARBIDE/LINDE DIV., TONAWANDA, N.Y.	COMPLETE	DATE JANUARY 13, 1971
SIZE:	.0005" ±10 x 12" x coil	QUANTITY SHIPPED:	198 ft.

CUSTOMER'S PURCHASE ORDER NO. 8-51-5643K	HAMILTON JOB NO. 6980	MATERIAL Molybdenum As Rolled	SPEC:

ITEM	HEAT	CHEMICAL ANALYSES															
		Al	Be	Cr	C	Co	Cu	Fe	Mn	Ni	Si	S	Ti	W	Mo	P	Sn
	0677	4		1			4	9	1	1	6			1-5			4
		Ca 2	Mg 1	K 15	N 7												

ITEM	HEAT	TEMPER	PHYSICAL TEST RESULTS					
			TENSILE #/SQ. IN.	YIELD #/SQ. IN.	% ELONG IN 2"	HARDNESS	GRAIN SIZE	BEND TEST

We hereby certify that the above material is Molybdenum in the As Rolled condition.

SUBSCRIBED AND SWORN TO BEFORE ME THIS 13th DAY
OF January 1971

NOTARY PUBLIC

My Commission expires

We hereby certify that the chemical analyses and physical or mechanical tests reported above are correct as contained in the records of the company.

HAMILTON PRECISION METALS

John P. Markert