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AEC RESEARCH AND DEVELOPMENT REPORT

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LOS ALAMOS SCIENTIFIC LABORATORY
OF THE UNIVERSITY OF CALIFORNIA • LOS ALAMOS NEW MEXICO

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QUARTERLY STATUS REPORT OF THE LASL
PLASMA THERMOCOUPLE DEVELOPMENT PROGRAM
FOR PERIOD ENDING APRIL 20, 1963
(Title Unclassified)

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All LAMS reports are informal documents, usually prepared for a special purpose. This LAMS report has been prepared, as the title indicates, to present the status of the LASL Plasma Thermocouple Development Program. It has not been reviewed or verified for accuracy in the interest of prompt distribution. All LAMS reports express the views of the authors as of the time they were written and do not necessarily reflect the opinions of the Los Alamos Scientific Laboratory or the final opinion of the authors on the subject.

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IN-PILE EXPERIMENTS

Metallized Alumina Insulation

The development of a tungsten coated alumina insulator brazed to niobium with Palco (Pd-Co) has made possible the design of a reactor cell with a niobium pin base which radiates away the heat conducted down the pin. With this design the necessity for water cooling of the pin base is removed and a more reliable construction is possible (Fig. 1). The first test demonstrated the suitability of the pin base design, but the niobium sleeve-nickel collector configuration resulted in too high a collector lip temperature. This was corrected, with the result that both ends of the insulator were in the temperature range of 950° to 1000°C when the cell was delivering 60 watts of electrical power.

Metal Pin Irradiation Test

The metal pin irradiation test cell was removed from the reactor when a leak developed in the closure section above the pin chamber. The pin was made from a Mo-UO₂ cermet coated with 0.5 mil of tungsten. At the time of removal from the reactor the pins had been irradiated for 319 h. Upon disassembly, it was apparent that considerable evaporation had occurred at the operating temperature 2100°K , so that the pin shrank by approximately 3% in diameter. The excessive evaporation, in the presence of several millimeters of argon, can be ascribed to the large pin to mockup collector separation distance. This presumably allowed free convection flow to be set up in the argon so that the presence of the gas did not significantly reduce the vacuum evaporation rate. Another pin of the same type shrank by approximately 1% during irradiation at about 1950°K . At the time of disassembly the presence of a tungsten layer could no longer be detected visually.

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Fig. 1. Plasma Thermocouple Cell with Metallized Alumina Insulation

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Bonding of Low-Density Pins

Several failures have occurred during irradiation tests in the vanadium bond used to attach low-density (80% of theoretical) pins to the niobium shoe. The bonds had been tested for stress prior to assembly and found to be satisfactory. The failures occurred in the pin just above the bond so that some carbide was left on the shoe after separation. This suggests that the failure arises from diffusion of vanadium into the porous carbide pin. It is not certain whether failure results from the formation of a very brittle zone (such as occurs for zirconium bond of carbide to niobium) or from stresses caused by liquid phase sintering of the carbide-vanadium quaternary or from some unsuspected mechanism.

Porous Pin Tests

In view of the observed swelling on irradiation of UC-ZrC fuel pins of high density, efforts have been directed toward producing pins with 15 to 20% porosity connected to the surface. To date, two of these pins have been irradiated to about 0.03 a/o burnup and one to about 0.09 a/o. Although this is a very limited sample, the in-pile results are not too encouraging. Swelling was at least as great as with high-density pins (approximately 97% of theoretical density). Metallographic examination of these pins may reveal the nature of the problem and this is being undertaken. Additional tests will be made, including some with a $(\text{UC})_{0.18}(\text{ZrC})_{0.82}$ pin which may be considerably harder at high temperature and hence may show less swelling.

Drop-In Assemblies

In-pile irradiation testing is continuing using one and two pin drop-in assemblies. These are periodically withdrawn from the OWR, radiographed, and if no signs of damage are detectable, they are re-inserted in the reactor. This technique appears to be quite successful and should speed the accumulation of data relating to radiation damage.

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For the most part, the tests are being made on pins produced over the last year from UC-ZrC powders prepared in several ways. Some of the pins have been "solution treated" by heating in vacuum at high temperatures for 20, 40, and 80 h in an attempt to remove undesirable second phase material indicated by metallographic examination. Such solution treatment may improve the quality of the pins as determined by their ability to withstand liquid cesium immersion for 24 h at 500°C and to survive radiation damage. It has been determined that arc-melted powder has the smallest proportion of the second phase and a 500-g lot of UC-ZrC powder prepared from 25 g arc-melted buttons has been in process for several months. Pins produced from this powder should become available shortly for cesium and in-pile evaluation. In the meantime, tests of less reliable pins will continue for the development of experimental techniques, both for in-pile exposure and subsequent handling and examination.

Reactor Flux Monitoring

A continuing problem has existed in determination of the neutron flux in the Omega West Reactor at the points where plasma thermocouple cells are located in the core. Two fission chambers, manufactured by the General Electric Company, have been used recently to monitor this flux. After some amplifier troubles were overcome, the results have shown good agreement with calculations and with radiochemistry sampling. The monitor outputs follow variations caused by control rod withdrawal to compensate for poison buildup over the week-long operating cycle. Variations in the flux of about 20 to 25% have been measured. With these monitors, a more accurate knowledge of the power generated in the pin during tests appears to be possible.

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VARIABLE SPACING CELL

Effect of Cesium Fluoride

Coverage of tungsten thermionic emitters by cesium fluoride is expected to increase the surface work function from 4.6 to more than 5 eV. However, the direct introduction of CsF into the cell volume failed to produce any significant change in the effective work function of the emitter. Since it was suspected that contaminants in the cell were interfering with the action of CsF on the tungsten emitter, the system was dismantled, cleaned, and reassembled with an improved pumping system. After bakeout, vacuum electron emission measurements were made and then CsF was introduced directly into the cell body. Measurement of the work function indicated a slight increase (< 0.1 eV) relative to the bare W system. Cesium was then introduced and current-voltage curves taken at cesium temperature of 150°C and above. There was no appreciable difference in these characteristics over the Cs-W system. Contaminants may still be influencing the operation, but further improvement in the vacuum attainable in this cell does not appear to be feasible at present.

Since CsF proved to be ineffective in changing the emitter work function, fluorine gas was introduced into the system. Initially, a fill of approximately 1 torr was introduced for 1 min after which the system was pumped down. This flush of gas was repeated three times. Then, the emitter temperature was raised to 1840°K and the change in electron emission observed as a function of time. From the data, an initial maximum effective work function of 5.1 eV was determined. The work function gradually decreased with time as the fluorine coverage of the emitter surface decreased. Subsequent measurements were taken after repeated flushings of the system with fluorine gas. Effective work functions of the order of 5.0 eV were observed if the pressure after flushing was more than about 2×10^{-6} torr. At lower pressures, the higher work functions were not observed presumably because of removal of fluorine from the emitter.

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Work Function of Uranium Sulfide

In the variable spacing cell, the emitter temperature is determined by means of a blackbody hole in the emitter button. It is not necessary to know the emissivity of the surface in question. Consequently, the variable spacing cell provides a convenient means for measuring vacuum electron emission currents and determining effective work functions of uranium sulfide (US) deposited on tantalum. X-ray scans of the emitter surface indicated that it was indeed US. After a suitable bakeout period, vacuum electron emission measurements were made and the results indicated that the effective work function was 4.82 ± 0.06 eV, with the Richardson $A = 120 \text{ A/cm}^2\text{-}^\circ\text{K}^2$, in the range from 1700 to 1825 $^\circ\text{K}$. Slight evaporation occurs at 1900 $^\circ\text{K}$ and excessive evaporation at 2100 $^\circ\text{K}$ in vacuum, so that the measurements could not be extended to higher temperature. The addition of cesium vapor into the cell caused complete separation of the US layer from the tantalum base.

As an independent check of this high value for the work function of US, a Langmuir type tube was constructed; US was deposited by electrophoresis on 0.020 in. W and on Ta filaments and the cell was baked out. Although the emissivity of US is not known, it is possible to assume that it is a blackbody, and determine a lower limit to the effective work function. The result obtained was about 4.6 eV, in agreement with the value given above.

CESIUM PLASMA STUDIES

Window Cell

After a series of window failures, the window cell (LAMS-2852, p. 4) is now operating successfully. The first objective will be to determine the temperature distribution in a plane diode with radiation shields. An important parameter in this study is the heat received by the collector. Operation to date indicates that measurement of the collector power can be made with sufficient accuracy to evaluate the effect of radiation shields.

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Isothermal Plasma Cell

Preliminary operation of the isothermal plasma (IAMS-2796, p. 6; IAMS-2852, p. 4) cell showed that the background light from double (or more) scattering was too high and necessitated redesign of the end pieces of the cell. The rebuilt cell has operated briefly and showed qualitative improvement but a commercial ceramic-to-metal seal failure at the operating temperature of 2000°C prevented quantitative measurement. The resulting damage from water will require rebuilding of the cell.

MATERIALS AND FABRICATION DEVELOPMENT

UC-ZrC Powder Preparation

The preparation of solid solution UC-ZrC powders is now reasonably well defined. The elemental materials U, Zr, and C are arc-melted to yield 25-g buttons. These are heated in vacuum at 2000°C for 24 h to homogenize the structure; they are then crushed to provide -200 mesh powder. This process is followed for both Oy UC-ZrC and D-38 (i.e., depleted) UC-ZrC.

It may be possible to secure homogeneity in a shorter heating time by treating the powder rather than the button, since the particle size of the powder favors a more rapid diffusion in the cast structure. To test this possibility, the cast buttons will be crushed to powder and heat treated.

Some success has been achieved in the spheroidization of UC-ZrC powders by passing the powder through a plasma arc. Close particle size control in feed material and a non-reactive atmosphere seem to be required. The greatest loss of material appears to accompany the use of powders containing a large portion of -400 mesh fines. The carbide spheres produced have been on the order of -235 mesh. The yield was low, with evidence of vaporization of the carbide. The quantity of usable product should increase with improved experience in the control of the variables.

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Pin Fabrication

Experiments have been planned to use powders of controlled particle size to form a differential density in the D-38 part of the fuel pin. High density is desirable at the D-38-Nb collector interface to prevent or minimize the migration of the Vd braze metal into the carbide. The low-density end of the D-38 section should match the density of the Oy UC-ZrC fuel section of the pin. The density match is desired to reduce thermal problems which may be introduced by variable density at the D-38:Oy interface.

The Oy UC-ZrC portion of the pin should possess some degree of porosity to allow the escape of gaseous fission products; otherwise pressure may build up and fracture the pin. Escape of gases is best provided by a limited open porosity with control of the pore size and distribution. Experiments to secure controlled porosity are underway. From limited data, it appears that open porosity and pore size are reduced with time at temperature (20 to 80 h in vacuum at 2000°C). Possibly the condition can be stabilized with the proper regulation of void volume in the cold pressed pin which on sintering acquires a reasonably permanent pore structure.

Thermal treatment of uncoated fuel pins under vacuum at 2000°C for 80 h results in a tendency for vaporization losses to become stabilized. The losses during the fourth 24-h heating cycle were on the order of 20% of the first cycle. With continued heating it might be expected that losses would continue to diminish.

Bonding of Fuel Pins to Metal Components

Cesium vapor testing of the fuel pin-collector braze has been concluded after 1 yr exposure. The fuel pin was brazed to the Nb collector using a 1-mil foil of Vd as the braze metal. The fuel pin temperature was 700°C and the Cs vapor was at 400°C. There appeared to be no deterioration nor attack by Cs at the braze joint.

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Metallographic examination of the fuel pin-collector braze joint has shown diffusion of the Vd braze metal into the carbide of the fuel pin. Fracture in the carbide has been evident near the front of the diffused area. Probably the density (and therefore porosity) of the carbide affects the rate at which diffusion occurs. It is planned to make time-temperature studies of the diffusion rate as a function of the density of the carbide at the braze junction.

Ceramic-to-Metal Seals

One method of metallizing the Al_2O_3 insulator which separates adjacent plasma cell collectors has been by reduction of a WO_3 coat in H_2 . During the firing in H_2 some ceramics have formed a glass which migrated to the insulator surface where it seriously affected the continuity of the W coat produced in the reduction. The resulting braze between the Nb collector and Al_2O_3 insulator was not leak-tight.

Present practice is to form a W coat by spraying the metal onto the Al_2O_3 . After firing, there appears to be no glass phase on the surface and subsequent brazes of the ceramic to the collector are leak-tight. This result may indicate that the WO_3 combines with the ceramic to form a glass although there is no proof of reaction.

In the braze operation, Palco (Pd-Co) alloy in 1 mil thickness has been used as the braze metal. This foil has presented some problems in assembly and surety of a leak-tight joint. Electrodeposition of alternate layers of Co and Pd to give a composite 1 mil thick has improved the situation. Braze joints using the plated alloy with a slight interference fit have proved to be leak-tight.

Tensile tests have shown that Al-13 ceramic, W metallized and brazed with Ni-Au alloy, possesses strengths on the order of 7700-9000 psi. The W was applied to the ceramic in metallic form and fired at 1600° , 1650° , and $1700^\circ C$. The higher tensile strengths were obtained from the higher firing temperatures. Most of the tensile breaks came

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in the shoulder of the ceramic test pieces which would indicate that the braze joints had higher tensile values than those given.

Coating Development

Tungsten coating of UC-ZrC pins and carbide coating of W pins have been tried. The W coat was coarse and low in density. The carbide coat appeared to be oxidized, and some volatilization occurred during arc spraying. Both coats were adherent, so that further work will be done, particularly on the adjustment of process variables. Either of the procedures should improve the structural integrity of the pin. The W coat can decrease carbide loss and provide a strong "can," whereas the W-pin would give a strong core upon which to build a carbide fuel element.

To insulate electrically the collector assembly from the outer Nb sheath, the collectors are coated with an arc-sprayed Al_2O_3 . This coat has proved to be porous and therefore susceptible to shorting between the collectors and sheath. As a means of sealing the coat, a $\text{CaO}\cdot\text{MgO}\cdot\text{Al}_2\text{O}_3$ eutectic (CMA) has been arc-sprayed onto the Al_2O_3 . It was hoped that the low melting CMA would flow when fired into the pores of the Al_2O_3 and seal the coat. A smooth, glassy coat was formed by the CMA; however, it was difficult to control the thickness of the glazed coat and there was an excess or deficiency of the eutectic on the surface.

Further tests were made in which various mixtures of Al_2O_3 and CMA were arc-sprayed on Nb-Zr rods and fired. There was evidence of considerable attack on the Nb-Zr by the CMA, the extent increasing with increase in the CMA/ Al_2O_3 ratio and the firing temperature. The tests will be repeated at a lower firing temperature.

Magnetic Swaging

Plasma thermocouple cells in series are insulated from each other by a ceramic and joined end-to-end to form an assembly. The assembled cells are to be coated with Al_2O_3 to insulate them electrically from an outer Nb sheath. One method of forming the sheath has been by

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magnetically swaging a thin-wall Nb tube onto the coated cell assembly, but the results have not been satisfactory. In an alternative technique, a Nb sheath will be either spray-coated, thermally deposited, stretched, or hydrostatically pressed over the Al_2O_3 . Any of these processes should provide the mechanical contact between sheath and Al_2O_3 insulation required to conduct heat from the plasma cell to the coolant.

Tungsten Cladding Techniques

Conditions have been established which permit the deposition of W metal, either from $\text{W}(\text{CO})_6$ or WF_6 , onto small W cylinders (0.2 in. diam x 1.5 in. long). It is anticipated that W from WF_6 may be less brittle than that from $\text{W}(\text{CO})_6$. However, preliminary coating from $\text{W}(\text{CO})_6$ may be required where the surface to be coated will react with WF_6 .

Coating from $\text{W}(\text{CO})_6$ was performed by passing 1.3 l/min of H_2 gas over solid $\text{W}(\text{CO})_6$ at 200°C and then onto the W cylinder heated at 300°C . The coating rate was 0.2 mil/min. In the other procedure, a mixture of 0.16 l/min of WF_6 and 1.5 l/min of H_2 was used at a coating temperature of 580°C ; the coating rate was 0.17 mil/min.

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