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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 OCTOBER 20, 1963
(Title Unclassified)

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

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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 TESTING

Mo-UO₂ Pins

In-pile testing has been directed toward the design of a triple pin assembly (three thermionic cells stacked in series) suitable for extended operation. As a part of this effort a single pin test unit was assembled and tested in the OWR. Distinguishing features were the provision for cooling the collector by conduction through a thin He blanket and a new Cs reservoir configuration. The fuel pin was fabricated with a Mo-20 v/o UO₂ cermet and was clad with a 0.010-in. thick layer of vapor-deposited W. The test of this assembly confirmed the design calculations for the helium cooled collector. However, the data obtained on the cesium reservoir temperature distribution were somewhat ambiguous and so the reservoir has been re-designed.

Another long term irradiation test unit was designed to test two Mo-40 v/o UO₂ cermet pins made with 9.3% enriched uranium. These pins have a 0.015-in. W cladding put on by a reactive vapor deposition method by San Fernando Laboratory. The pins are supported by tacks, one of Cb and one of Mo-Re, brazed to the cermet with a Cb-V alloy as shown in Fig. 1. A high-temperature thermocouple, made with 0.014-in. diam W and W-25% Re wires, is located in the top pin. With the OWR at full power this thermocouple indicated a pin temperature which dropped from an initial value of 2120°K at the start to a value of 2010°K at the end of the week. Failure of the thermocouple was observed to have occurred when the reactor was brought up to power the following week. The initial pin temperature indicated by the high-temperature thermocouple was within 10°K of that calculated for this assembly.

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Fig. 1. Irradiation test PTC assembly for cermet pins

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UC-ZrC Pins

A discrepancy between calculated and observed temperature was found for NOM-1, an irradiation unit containing UC-ZrC fuel pins with W sleeves. It is probable that this test ran for 900 h at pin temperatures at least 200°K lower than those indicated by the thermocouple in the top pin. As a result only 0.024% of the total fuel atoms in the top pin were burned up. When NOM-1 was removed from the reactor and radiographed the only apparent change in its appearance was a small amount of extrusion of the top of one pin out of the W sleeve in which it was encased. The fact that the sleeves were intact indicates that little, if any, diametral swelling took place. The change in length of the pin indicated a volume increase of 2%, roughly that expected for an unclad carbide pin at this burnup level.

To obtain additional data, the cell was converted to a drop-in unit and replaced in the OWR. A radiograph taken after 1440 h of irradiation showed a slight amount of increase in length of the $(\text{UC})_{0.18}(\text{ZrC})_{0.82}$ pin; however, the $(\text{UC})_{0.30}(\text{ZrC})_{0.7}$ pin appeared unchanged in appearance. Total atomic burnup of the pins in this assembly at the time of radiograph was approximately 0.05%. At this burnup an unclad pin would have been expected to have increased in volume by 7%. The estimated volume increase occurring for the sleeved $(\text{UC})_{0.18}(\text{ZrC})_{0.82}$ pin is 2%.

Three-Cell Assembly

Figure 2 shows the configuration of a three-pin cell using Mo-40 v/o UO_2 pins coated with a 0.015-in. layer of vapor-deposited W. The U in these pins is 9.7% enriched. The design of the series stack is such that each cell can be built as a subassembly and quality checked before it is joined to the other cells by electron beam welding. The cooling of the collectors of the triple cell assembly is accomplished through a 0.031-in. thick blanket of He at a pressure of 100 torr. In the region surrounding the Cs reservoir there is a vacuum chamber into which gaseous fission products which escape from the pins are vented.

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Fig. 2. Three-cell PTC assembly

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A preliminary test of this cell in the OWR was terminated after 1 week's irradiation. The power output was much lower than expected, apparently because entry of helium into the vacuum chamber resulted in a cesium reservoir temperature of only 180°C.

The effect of intentional variations in Cs pressure in an assembly with a W-coated fuel pin was investigated with a cell similar to that in Fig. 2, except that only one emitter-collector assembly was used. The Cs reservoir temperature was varied by changing the pressure of He in the space surrounding the reservoir. The maximum power output of this cell was 2 watts occurring at an indicated cesium pressure of 1.6 mm and an emitter temperature of 2070°K. The values of open circuit voltage and power output are not in good agreement with data from electrically heated cells and the discrepancies are being investigated.

VARIABLE SPACING CELL

For the past three months, the variable spacing cell (IAMS-2951, p. 4) has been used to obtain electron temperatures and ion densities across the emitter-collector gap for a variety of cell operating conditions. After a number of hours running time, the UC emitter (with sprayed W surface) was removed from the cell and an x-ray scan of the surface was taken; only W was evident in the spectrum. Most of the UC apparently evaporated to the guard ring and collector. Since the time of the x-ray scan, the emitter has operated for more than 130 h at temperatures of 2015°K or above. It has been exposed to air at room temperature on several occasions, but the surface work function, as determined from the current at zero applied voltage, is still approximately 3.4 V.

Electron temperatures obtained from the radiation recombination continuum of the Cs-spectrum have been determined for a collector-emitter gap of 0.070 in. in the current range of zero applied voltage. Emitter temperatures varied from 2000° to 2250°K and Cs reservoir temperatures from 250° to 315°C. Under certain operating conditions an electron temperature

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minimum appeared in the gap, but the reason for this is not known. Ion density measurements may lead to an explanation of the phenomenon.

Spectroscopic grade He was introduced into the operating cell in order to observe the resulting changes in cell operation. At Cs reservoir temperatures of 275°C and 200°C, a cell spacing of 0.6 mm, and an emitter temperature of 1750°C, there was no noticeable change in cell operation when 6, 12, and 24 torr of He were added. Open circuit voltages and other electrical characteristics remained unchanged. An attempt made to extend the measurements to lower emitter and cesium reservoir temperatures and for different spacings was terminated by a He leak.

ISOTHERMAL PLASMA CELL (2000° CELL)

Minor changes made in the Isothermal Plasma Cell (IAMS-2852, p. 4) have resulted in satisfactory performance for all parts of the device at the rather severe design conditions. An optical system has been assembled to permit the study of the light emitted from the hot plasma region. Quantitative measurements show that scattered light from the incandescent container, which was one of several earlier difficulties, has now been reduced to a level that will permit measurement of all the essential features of the emission spectrum.

CESIUM VAPOR TUBE

The cesium vapor tube (IAMS-2951, p. 6) has been operated extensively and several hundred individual scans have been made involving 15 Cs resonance lines. The lines broadened by Ne, Ar, Kr, or Xe were studied in absorption and data were taken over a range in Cs pressure from 10^{-3} torr to 10 torr. The resultant line shapes are due to three main effects: (1) pressure broadening (impact) which leads to a symmetrical dispersion shape, (2) resonance broadening due to coupling between Cs atoms, and (3) line shifts due to perturbation interactions (static) between the Cs and the rare gas atoms.

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The last two of these lead to asymmetrical lines. In the data obtained so far all shifts and broadening effects and their pressure dependence are observed to occur in accordance with qualitative predictions.

Cesium vapor is so optically thick for the resonance lines that their quantitative study is quite difficult. However, by carefully adjusting the concentration of inert gas it is possible to broaden the lines to the point where the Cs vapor is optically thin, and meaningful measurements can be obtained. Preliminary determinations of oscillator strengths have been made for a number of states and the results compared with theory and the most reliable published experimental data.

CESIUM VISCOSITY EXPERIMENT

An apparatus has been constructed for measuring the viscosity of cesium vapor at temperatures from 800° to 2400°C . It is an automatic balance for determining the rate of distillation of cesium from one leg of a symmetrical retort through a radiation-heated capillary to the other leg. The legs of the retort are immersed in electrically heated, heavy-walled copper pots containing a liquid metal maintained at constant temperature.

As the cesium moves from one side of the balance to the other, an electrical sensing system automatically and continuously adjusts the balance chain to compensate for the transfer of mass, thus keeping the retort in very nearly a fixed position. The continuous adjustment of the chain is recorded and provides a measure of the rate of transfer of cesium through the capillary. From this rate, the pressure difference across the capillary, the temperature, and the geometry of the capillary, the viscosity can be calculated.

FISSION PRODUCT RETENTION

A study of fission product activity retention in a variety of UC-ZrC pins, which were lightly irradiated and subsequently heated, has yielded a rough value of the diffusion rate vs pin porosity. A strong dependence on

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density indicates the advantage of high porosity for fission product release. A corresponding study of strength and creep rate vs porosity is necessary before any conclusion can be made as to the effectiveness of porosity in preventing pin swelling.

MATERIALS AND FABRICATION

UC-ZrC Preparation

Batches of $(\text{UC})_{0.18}(\text{ZrC})_{0.82}$ powders have been made using either U^{238} or U^{235} . Following the usual procedure, the elements were arc melted to form buttons which were subsequently crushed to powder then homogenized by heating at 2000°C in vacuum for 24 h. Both metallographic and x-ray diffraction studies indicate the powders to be essentially single phase, solid solution UC-ZrC.

UC-ZrC solid solution is a brittle, hard material which possesses little ductility when fabricated into a fuel pin. The pin has a tendency to chip and fracture quite readily. To secure a stronger, more ductile matrix, the addition of 10 w/o of either W, Mo, or Nb to the powder mix was suggested. Hot pressing runs were made with each of these metals as a constituent. The material containing W did not press at 1800°C . Products using Mo and Nb have been pressed into slugs from which experimental pins are being machined. Further tests with W will await results from Mo and Nb.

Several arc melting runs have been made to produce buttons of $(\text{UC})_{0.90}(\text{ZrC})_{0.10}$ from the elemental materials. Metallographic examination of an arc melted sample indicated several phases in contradiction to the x-ray diffraction data. Since the etchant used may have confused the appearance of the structure, a number of etchants were prepared and tried. Best results were obtained with a solution of 20 ml H_2SO_4 , 10 ml H_2O_2 , and 2 ml HF, which gave a clean, single phase structure in agreement with the x-ray data.

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The feasibility is being tested of producing solid solution $(\text{UC})_{0.90}(\text{ZrC})_{0.10}$ by adding Zr metal powder to a charge comprising U and C to form $\text{UC}_{1.1}$. It is hoped the stoichiometric Zr addition will combine with the excess C (beyond UC) to form the mixed carbide in the ratio desired.

Preparation of UC powder by crushing arc-melted buttons to secure -140 +325 mesh particle size remains a problem. Mechanical processes, such as ball milling, result in a large quantity of fines which must be separated. The fines contribute to a severe material loss if present in UC powder that is arc sprayed. Hand crushing to -100 mesh seems to proceed satisfactorily, but reduction below that size produces considerable fines. Apparently, beyond a certain mesh the powder fragments into quite small particles possibly caused by cleavage planes in a brittle material.

Pin Fabrication

The most economical process for making PTC fuel pins, either of UC-ZrC or Mo- UO_2 , is to hot press a slug from which cylinders somewhat larger than the fuel pin diameter are elox machined. The carbide pins are ground and metal-oxide pins machined to the present 0.250 in. pin diameter. Where an axial hole is required for thermocouple insertion, the hole is drilled by eloxing. Slugs are 1.5 in. in diam from which it has been possible to elox eleven pins. This procedure yields pins possessing more uniform properties than the single-pin technique. There is also less material loss in the slug process.

Processing of fully enriched Mo- UO_2 pins has been slowed due to the requirement for pins having low enrichment. These latter pins are composed of Mo-40 v/o UO_2 (10% U^{235} + 90% U^{238}).

Bonding of Fuel Pins to Metal Components

Fuel pins are joined to collectors by means of a metal tack, which is inserted in an axial hole in the pin and brazed. One problem has been to maintain the desired alignment between pin and tack. When the alignment

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deviates too much from the desired 3 mils T.I.R., the fuel pin is shifted from its axial position in relation to the collector. Too great a misalignment could result in contact between the pin top and the collector shorting the cell. To improve alignment, jigs and fixtures were redesigned. Pin-tack brazes made with the new fixtures have given better results (10 mils T.I.R.) but not as good as desired.

Pin tacks are presently being made from Nb and Mo-40% Re. Although the thermal conductivity for Mo-40% Re is not yet available, the alloy should have a lower value than pure Nb. On this basis, and the higher melting point, Mo-Re would be a better tack material than Nb. As the availability of the Mo-Re improves, it will probably be adopted in preference to Nb.

Exploratory pressings are being made to form the pin and tack as an integral unit. From the Mo-40 v/o UO_2 pin composition, two intermediate compositions of Mo-25 v/o UO_2 and Mo-10 v/o UO_2 grade the tack length to the Mo-Re terminal. A properly designed integral unit will possess advantage as compared to the individual brazed tack. However, the variable composition in the tack portion poses the problem of compatibility in thermal expansion of the various sections. Preliminary investigation of thermal expansions indicates a possible requirement of smooth transitions in composition from the pin to the tack end, rather than sharp boundaries between selected compositions.

Ceramic-to-Metal Seals

Brazing of W-metallized Al-300 appears to be influenced by the brazing conditions. In vacuum above 1400°C, a W oxide evidently forms on the W which permits wetting and flow of ceramic constituents from the Al-300 to the metallized surface. The presence of the "glass" phase prevents joining of the ceramic to the metal collector by the braze metal. This phenomenon is not observed in H_2 firing since the W oxide is not formed.

W-metallized surfaces of Y_2O_3 and 3 $Y_2O_3 \cdot Al_2O_3$ were examined using the microprobe. The darkened region between the W and Y_2O_3 was found to be

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depleted in Y_2O_3 and to contain Al and Si. Sources of the Al and Si have not been fixed although two possibilities exist, namely, the metallizing mix and/or the furnace refractories.

The compound $3 Y_2O_3 \cdot 5 Al_2O_3$ is of particular interest as it is the grain boundary phase in Al-13 and Al-14, ceramic materials currently in use for seals. W coatings were fired at 1500° , and 1600° , and $1700^\circ C$ and examined with the microprobe. Possible enrichment of Y at the W-ceramic interface with diffusion of Y into W was indicated. Thus the Y appears to act as a bonding agent between the ceramic and the W.

Arc sprayed Ni-plated W powders have an improved density and lower open porosity as compared with arc-sprayed W powders for all firing temperatures. At a firing temperature of $1650^\circ C$, the Ni-plated W powders had a density of 93% and open porosity of 0.5%. This temperature will be used in the first trial firing of arc-sprayed W-2% Ni coated insulators to secure a thicker W layer on the metallized surface for protection against Pd braze metal attack.

The plating of W-metallized insulators with a thin Pd layer (0.5 mil) improved the subsequent braze of the insulator-collector using Pd, as indicated by leak tightness tests. Other materials as plates on the metallized surface will be tried, e.g., a Rh-plate on W metallized surfaces followed by a V braze.

Coating Development

Both carbide and metal-oxide pins require W coating to prevent U loss during cell operation. W coats have been placed on pins by arc spraying W powder, vapor deposition from $W(CO)_6$, and vapor deposition from WF_6 . Of these three procedures, the WF_6 process seems to be best. At present, pins are being coated at San Fernando Laboratories (SFL) using the WF_6 method. Apparatus has been constructed at IASL to coat pins using WF_6 . Several test runs have been made to overcome process difficulties. Results indicate that the unit will soon be ready for production coating.

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Mo-40 v/o UO_2 pins coated by SFL with 12 mils of W from WF_6 have shown a tendency for the W coat to expand away from the pin and split when the coated pin was heated at 1800°C overnight. It is not known why cracking occurred; however, two possible conditions may influence the results. The pin surface prior to coating may be contaminated through contact with the atmosphere or by handling, or the surface may require activation by thermal treatment before coating. In several instances where the pin was heated at 1650°C for 1 h prior to coating, the W coat (by SFL) retained its adherence to the pin on subsequent heating at 1800°C . Further tests are planned to determine the effect of prior thermal treatment as it influences the stability of the W coat.

The emissivity of the W coat placed on UC-ZrC fuel pins can be improved by overcoating with UC. For this purpose the UC must possess a high degree of purity without extraneous phases which may contaminate the Cs plasma during cell operation. To secure the desired purity, two approaches are being tried. In one case the UC is formed with excess U; the product is then heated in vacuum to volatilize the excess U. In the second procedure, excess C is added with subsequent heating of the carbide in H_2 to remove excess C.

Arc-spray procedures are logical for placing an overcoat of UC on W-coated pins. The spraying should be done in an inert atmosphere, but the facilities will not be available for several weeks. In the interim, it is hoped that high quality UC powder can be produced.

Cladding Development

Several stretch-formed, Nb-clad thermal conductivity samples have been examined. They were prepared by stretch-forming Nb tubing over a mockup of the Al_2O_3 -coated collector. In several cases a Nb spray coat was placed on the Al_2O_3 for the purpose of achieving better mechanical contact with the outer Nb sheath. Good contact is desired to enhance the thermal conductivity. Stretch forming is accomplished by tensile elongation of a tube causing it to contract and grip the sprayed collector

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assembly. Hot forming seems required to avoid the springback that would normally accompany cold forming.

The irregularity and hardness of the Nb arc-sprayed layer prevented intimate contact over a wide area with the stretch-formed Nb tube. A softer Nb spray coat may be needed which will deform to provide the desired amount of contact between it and the outer Nb sheath. Spraying in an inert atmosphere to prevent contamination of the Nb metal spray may yield the ductility desired.

The Al_2O_3 coat, arc sprayed on the inner mockup collector, seemed to be free of cracks, so that it apparently survived the stretch-forming operation. Any cracks in the Al_2O_3 would reduce its value as an electrical insulator between the cell collector and the outer Nb sheath.

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