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LAMS-3042

AEC RESEARCH AND DEVELOPMENT REPORT

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 JANUARY 20, 1964
(Title Unclassified)

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LAMS-3042
C-93b, ADVANCED CONCEPTS
FOR FUTURE APPLICATION-
CONVERSION DEVICES
M-3679 (33rd Ed.)

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

REPORT COMPILED: February 1964

REPORT DISTRIBUTED: February 25, 1964

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Exempt from CCRP Re-review Requirements
(per 7/22/82 Duff/Caudle memorandum)
NK 3/17/05

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Contract W-7405-ENG. 36 with the U. S. Atomic Energy Commission

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IN-PILE TESTING

UC-ZrC Pins

The assembly NOM-1, described in LAMS-3000, p. 4, was removed from the reactor after 2013 h irradiation. Radiography then revealed that the W sleeve on the $(\text{UC})_{0.3}(\text{ZrC})_{0.7}$ pin (burnup 0.065 a/o) had cracked badly, although after 1440 h there had been no pin damage. Visual inspection after disassembly showed that the coating had cracked longitudinally and had peeled away from the carbide pin. The volume of the active portion had increased by 7.7%. The coating on the $(\text{UC})_{0.18}(\text{ZrC})_{0.82}$ pin (burnup 0.075 a/o) had a 360° circumferential crack; the volume of the active portion had increased by 6.8%.

It is apparent that a 0.012-in. thick vapor-deposited W sleeve was not sufficiently strong to appreciably influence the rate of swelling of the UC-ZrC pins.

Mo-UO₂ Pins

An irradiation test cell, NOM-2, was made up with two W-coated Mo-40 v/o UO₂ pins having 10% enriched uranium. Radiography after 1700 h indicated no deterioration of either the pins or the W cladding. The calculated burnup is 0.074 a/o. The cell has been replaced in the Omega West Reactor for further irradiation.

A triple assembly unit, designated Tass 3, consisted of three stacked W-coated Mo-40 v/o UO₂ pins and Nb collectors. The cell output declined from 30 to 8.5 watts in the first 400 hours of irradiation. This was followed by a slow decrease to 3.4 watts during the next 165 hours, and a sharp drop to 0.5 watt in the final 48 hours of irradiation.

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After 613 hours exposure, the assembly was removed from the OWR for inspection. Radiography indicated that the claddings had deteriorated in all three pins and visual examination after disassembly confirmed that this was the case. The pins had been made from very early batches which varied considerably from batch to batch in the bond between the W cladding and the Mo-UO₂ pin body. For two of the pins, replacement of the tacks after the W cladding was applied seemed to have a very deleterious effect on the cladding. It should be noted that these claddings were not representative of the quality of cladding which can now be produced and similar poor performance is not expected in future tests.

Four test units made with W-coated Mo-40 v/o UO₂ fully enriched pins were sent to the University of Virginia for irradiation in the University's 1-MW (max) pool reactor (UVAR). The purpose was to determine if the UVAR would be suitable for long-term testing of thermionic cells of the present design. The irradiations have been completed, but all the data have not been analyzed. The main conclusion, however, is that by using the present pins of Mo 40 v/o UO₂ fully enriched uranium, the neutron flux is sufficient for the intended long-term tests. The maximum gamma heating rate is lower than expected and may necessitate some modification in the design of the Cs reservoir.

VARIABLE SPACING CELL

As reported in IAMS-3000, p. 6, the variable spacing cell has been operating with arc-sprayed W on a backup of Ta emitter on which a layer of UC was electrodeposited and melted in place. The thickness of UC was below the level of detection by x-ray diffraction scans (~ 5%) with W lines solely in evidence. Despite this, the work function based on emission measurements has repeatedly coincided with that of UC. After about 200 h of operation with repeated cycling and exposure to air at room temperature, a failure of an ion gage during startup of operation exposed the surface to air when the emitter was at 400°C. After this exposure, the UC type

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emission was no longer in evidence. The vacuum emission data gave an effective work function of 4.9 V. Baking the emitter at 2000°C for 1 h did not improve the emission.

Subsequently, the cell has been operated with an emitter fabricated by brazing a Ni foil to a standard Ta button emitter. Data were obtained in the driven arc mode (the collector and guard ring were 2 V positive with respect to the emitter) for a variety of cell conditions. The emitter was maintained at 800°C to 1000°C (preignition temperature), Cs reservoir temperature varied from 200° to 295°C, and cell spacings ranged from 0.4 to 2.5 mm. Current voltage characteristics, current densities, electron temperatures, and ion densities have been obtained. The data are being reduced and will be reported when the reduction is complete.

The cell has now been disassembled, cleaned, baked out to 600°C, and reassembled with a W emitter. It is intended to run some experiments at high Cs pressure (> 500°C).

WINDOW CELL

A succession of leaks has led to the complete reconstruction of the triode window cell. The new cell is similar to the earlier one but incorporates a number of minor changes and refinements. The emitter, the triode connection, and both windows are all accessible through metal O-rings or Conoseal fittings, rather than welds. The Cs pod design and the collector cooling arrangement have been improved. Radiation shields will be placed in the cell and measurements will be made of cell efficiency and electron temperatures.

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EFFECT OF HELIUM ON THERMIONIC CONVERTER PERFORMANCE

A thermionic converter was operated with a partial pressure of helium in the interelectrode spacing for the purpose of measuring both converter performance and thermal conduction with helium present. The converter used for the experiment was of cylindrical geometry with liquid metal cooling on the collector. The emitter was fabricated from W bar and coated with UC which was then melted to form the emitting surface. The collector was nickel. Emitter dimensions were 0.625 in. (1.59 cm) inside diameter with a length of 1.125 in. (2.86 cm). The collector was 0.3125 in. (0.795 cm) in diameter. This resulted in a spacing of 0.156 in. (0.396 cm). Partial pressures of helium from 0 to 40 torr were introduced into the cell at emitter temperatures of 1900°K and 2100°K with Cs pressures of 10^{-3} and 1.0 torr.

For specified emitter temperature and Cs pressure, increasing the He pressure increases the thermal conductivity, decreases the current at a given voltage, and produces a small decrease in the open-circuit voltage.

MATERIALS AND FABRICATION

Powder Preparation and Processing

Preparation of various powders required in the PTC program has continued. These powders were primarily UC to be arc-sprayed onto W for emissivity studies; Mo-40 v/o UO_2 to supply material for pin fabrication; and UC-ZrC for use in establishing an optimum crushing and grinding procedure. Powders containing carbides were prepared by vacuum arc-melting the elemental constituents. Mo and UO_2 powders were obtained from local or outside sources.

It has been difficult to secure a high quality UC free from second phases; frequently UC_2 has been detected. An attack on the problem was made by arc-melting U and C to form the carbide with a deficiency or

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an excess of C. The product was then heated in vacuum to remove excess U in the case of low C, and in H_2 to reduce UC_2 to UC in the case of high C. In both cases the excess constituent was reduced with the composition approaching UC. Best success was experienced in the case of excess C in that no second phase was observed in the final structure.

It has been determined that the optimum particle size of UC powder for arc-spray work should be -140 +325 mesh. It has proved difficult to acquire a good yield of powder within this range when the arc-melted material was crushed and ground. There was a pronounced tendency for the UC to fragment into a high percentage of fines when taken beyond -100 mesh. Screens introduced into ball mills to make a separation while grinding offered no advantage. It may be necessary to recycle fines through a compacting stage to prevent material loss.

The sintering of cold pressed Mo- UO_2 proceeds considerably better when a porous UO_2 powder is used in making the powder blend. Porous UO_2 on the order of 100 μ diameter has been made by the coalescence of 1 μ powder (G.E.). This UO_2 tends to sinter and shrink along with the Mo matrix producing high density in the final product. Where high-density UO_2 powder is used in the blend, it appears to block shrinkage of the Mo and the composite has a lower density.

The present design of a PTC unit involves the joining of a series of single cells by brazing and welding of several different materials. Since the probability of a joint failure should correspond to the number of joints, a reduction in the total would be an advantage. To this end, some consideration has been given to using larger pins, ~ 6 in. long by 0.75 in. diam, for a single cell. With the larger pin, the number of single cells to be joined in series could be reduced thus improving the mechanics involved in the assembly.

Two methods are available to form a rod of uniform density which has a large length-to-diameter ratio, namely, isostatic pressing and extrusion. Both methods have been investigated in the fabrication of Mo and Mo- UO_2 rods. Each process is a cold compacting procedure which

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relies upon sintering to achieve particle coalescence and improved density. Pins of the above dimensions are not readily formed by hot pressing to uniform density. Die-wall friction restricts movement of the powder and tends to cause hang-up.

The addition of Mo or W in the range of 10 to 40 w/o to UC-ZrC was proposed. The metal addition was primarily to improve strength and reduce brittleness in the compact. An addition of 10 w/o Mo was made to $(\text{UC})_{0.18}(\text{ZrC})_{0.82}$. The powders were blended and hot pressed into pins which were treated for various times at 1800° or 2000°C in vacuum. Metallographic examination of the heat treated structures showed consolidation of UC-ZrC into grains; however, a boundary second phase became evident which seemed focused at Mo locations. From the structural appearance it seems that Mo additions will not enhance mechanical properties of UC-ZrC. The effect of W addition will be studied.

Pin Fabrication

To meet the needs of various developmental programs, Mo-40 v/o UO_2 powder blends were hot pressed into 1.5-in. diam slugs. Two U enrichments were used: D-38 UO_2 and U^{235}O_2 . Three Mo-oxide compositions were prepared: D-38 UO_2 primarily for experiments in W coating using vapor deposition from the reaction between WF_6 and H_2 ; 10% U^{235}O_2 + 90% U^{238}O_2 for low enrichment pins; and 100% U^{235}O_2 for high enrichment pins.

Each hot-pressed slug usually yields 11 to 14 pins by the Elox cutting process. The Elox pins are somewhat oversize and are reduced to the desired 0.250 in. diam by machining. When required, an axial hole is drilled in the pins to the desired depth by Eloxing.

Fabrication of experimental pins in Mo and Mo- UO_2 by extrusion of the lubricated powders has received attention. The extruded shape requires careful heating and handling to remove the lubricant (binder) and sinter the remaining powder. There is a tendency for the material to be quite friable during the period when the binder has been driven off and sintering has not yet started.

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Extruded tubes of Mo, 0.42 in. in o.d. and 0.144 in. i.d., were heated at 1300°C in H₂ for 1 h and at 1730°C in H₂ for 5 h. Densities of the sintered pieces were 87-89% of theoretical. Similar extrusions made of Mo-40 v/o UO₂ were sintered in the same manner. The sintered tubes showed slight deviations from straightness. It is felt that straightness can be achieved by suitable fixtures to hold the extruded piece during heating.

Mo has also been isostatically pressed about a tapered W rod. Removal of the rod was facilitated by the taper. The pressing was sintered to give a piece about 1 in. o.d. and 7 in. long. The surface was quite irregular. The piece would require machining after sintering to secure a uniform o.d. for further operations.

Hot swaging has been considered as a means for consolidating sintered tubes to achieve higher density. The process may be tried when tooling becomes available.

Bonding of Fuel Pins to Metal Components

A supply of Mo-50% Re alloy has been received. This material will furnish tacks for joining the fuel pin to the collector. The Mo-Re alloy is presumed to be better than Nb because of a lower thermal conductivity; hence it does not drain heat from the pin as fast as Nb.

The Mo-50 Re tack is joined to the Mo-40 v/o UO₂ pin by a braze using Nb-23% V (m.p. 2040°C) as the brazing metal. The axial hole in the pin is enlarged somewhat to a depth of 0.250 in. to accommodate the tack. Two Nb-23 V preforms of 10-mil foil, 0.125 in. i.d. by 0.188 in. o.d., are slid over the tack and butted against the pin bottom. The braze is made at ~ 2060°C using inductive heating.

Alignment of pin and tack has presented a problem. Improved fixturing has reduced the T.I.R. for the brazed assembly to an average of 5 mils. Variation in alignment influences the gap between the pin and collector and in extreme cases may short the cell. A uniform gap of some 20 mils about the pin is desirable and considerable attention has been given to maintaining this requirement.

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A 0.20-in. diam slug consisting of two sections, one Mo-40 v/o UO_2 1.2 in. long and the other Mo-40% Re 0.7 in. long, was cold pressed to form an integral unit. A similar piece was pressed isostatically. These pressings were sintered for 3 h in H_2 at $1700^\circ C$ and in vacuum for 6 h at $2000^\circ C$. The sintered pieces were sound.

A hot-pressed piece of the same compositions was sintered at the higher temperature only. It swelled in the Mo-Re region presumably due to diffusion of the two metals involving a Kirkendall effect. The pieces will be examined metallographically for structure.

Ceramic-to-Metal Seals

The formation of a nonconductive layer similar to a glass has occurred on the W-metal deposit on several Al-14 (0.5 Y_2O_3 in Al_2O_3) ceramic insulators. X-ray diffraction studies of the metallized surface indicated the presence of Y_2O_3 and Al_2O_3 . The nonmetallic phase is considered to result from an eutectic formation between yttrium garnet ($3Y_2O_3 \cdot 5Al_2O_3$) and Al_2O_3 which is forced or squeezed from the grain boundaries of the ceramic to the surface during vacuum firing.

Density and porosimetry measurements of air-fired Al-14 show $\sim 3.5\%$ closed porosity. These closed pores would be expected to contain air. In subsequent vacuum firing, as occurs during brazing, the air enclosed in the pores would create pressure and thus force the viscous eutectic (Y_2O_3 - Al_2O_3) from the grain boundaries to the surface where the eutectic could form a nonconducting layer in the W-metal deposit.

In other experiments with air-fired Al-14 ceramic, heating at $1700^\circ C$ for 10 min in 10^{-5} torr resulted in a change of density from 96.5 to 92.3% of theoretical. There was also generated $\sim 1.6\%$ open porosity. These data indicate that any Al_2O_3 ceramic containing Y_2O_3 will tend to lose leak-tightness when heated in vacuum at temperatures where the yttrium garnet- Al_2O_3 eutectic becomes plastic and can migrate.

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It was thought that H_2 might behave differently than air in subsequent vacuum firing. Because of the H_2 size factor, it might diffuse through the ceramic lattice and not force out the eutectic. To test the idea, Al-14 was fired in wet H_2 at $1700^\circ C$ for 17 h. Density of the fired piece was 95.3% of theoretical. This specimen was refired in vacuum at $1700^\circ C$ for 10 min, when the density measured 95.46% of theoretical. There was a slight volume increase of 0.4% but no apparent "squeeze-out" or eutectic. The experiment seemed to confirm the theoretical expectations.

Since the Y_2O_3 appears necessary to bond the W metal to Al_2O_3 , then some other path must be taken than remove the Y_2O_3 from the ceramic to avoid the eutectic phase. From the above it appears that the Al-14 can be fired in H_2 and so avoid later difficulty in vacuum firing. Other possibilities may be to reduce the amount of Y_2O_3 in the Al_2O_3 , or to use a lower temperature during vacuum brazing by choosing a different brazing material. Experiments in which the Y_2O_3 is decreased are under way.

Further tensile testing of Al_2O_3 ceramics containing various proportions of Y_2O_3 was completed. Ceramic specimens W-metallized at $1500^\circ C$ and brazed with Nicro gave a tensile strength of 7800 psi for 2 w/o Y_2O_3 and 6530 psi for 0.5% Y_2O_3 . These results indicate a possibility of securing adequate strength with lower metallizing temperatures than used previously.

Coating Development

A number of Mo-40 v/o UO_2 pins coated with W by the $WF_6 + H_2$ vapor process were examined metallographically. Where there had been no thermal pre-treatment of the pin, the W coat did not evidence a bond with the pin material. Heat treatment (20 h at $1800^\circ C$ in vacuum) subsequent to coating did not promote bonding. Photomicrographs show a distinct narrow void between the coat and pin body.

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With thermal pre-treatment, the W coat shows good bonding to the pin. Pre-heat treated pins which were heat treated subsequent to coating indicate that the bond retains its good adherence to the pin.

As an experiment, consecutive W coats were placed on pre-heat-treated pins. Two pins had two coats (~ 5 mils total); two pins had four coats (~ 8 mils total). The consecutive coats were placed without removing the pin from the apparatus. Metallography showed a line of demarcation which delineated the interface between consecutive coats. After the coated pins had been heat treated at 2000°C for 20 h, the coats showed considerable grain growth across the interfaces of coat layers. There was no evidence of the previous layered formation in either the two-coat or four-coat specimens.

Occasionally, and at random locations, small nodules tend to build up with the coating process. These may extend 1-2 mils above the normal coating face. The cause of the nodules and the reason for their specific locations are not understood. As a general rule, the coating thickness is quite uniform on the pin lateral surface. This is not so true on the pin ends.

Cladding Development

Work in the cladding development program concerned with arc-spraying Al_2O_3 on Nb tubing has been delayed so that the new inert atmosphere box, which is now available, could be used. With access to the new equipment and subsequent to operational test runs, ceramic coating of Nb to mockup similar processing for the Nb-1Zr collector body will begin.

The Union Carbide Corporation has developed a method for electroplating refractory metals from a molten fluoride bath. This process has interest in PTC work since it is planned to clad the ceramic-coated series of cell assemblies in a Nb sheath. In the

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experimental work so far performed in trying to clad Al_2O_3 -coated Nb with this outer sheath, two methods have been examined: arc spraying Nb onto the Al_2O_3 , and collapsing a Nb tube by stretch-forming. A third procedure, vapor deposition of Nb, has received some attention.

Of the methods considered, vapor deposition and arc spraying have produced porous coats; stretch-forming a tube did not provide the required physical contact with the Al_2O_3 . Since the Nb sheath will act as a thermal conductor, it must have intimate contact with the Al_2O_3 .

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