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STUDIES OF THERMIONIC MATERIALS FOR SPACE POWER APPLICATIONS

Informal Monthly Report for the Period
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Thermionic Direct Conversion Group

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The work carried out under Contract NAS 3-4165 during September, 1963 is summarized as follows:

1. Fabrication Development

1.1 UC-ZrC Fuels

The developmental work during this period on the control of UC-ZrC characteristics has been directed to two approaches. (1) In order to control uniformity of UC-ZrC specimens, work has been started on the development of a suitable technique for isostatic cold pressing; and (2) In order to reduce fission gas retention by having the maximum number of interconnected pores, the effect of particle size on the pore structures of cold-pressed and sintered specimens is being studied.

Isostatic cold pressing is being done in a conventional steel die using reversible vinyl chloride gels as the isostatic medium. The three media tried to date are "R. T. V." made by General Electric and two grades of "Chemosol" (35 and 50 durometer) made by Plaschem. The R. T. V. was not strong when cured. It contained some cracks and extruded rather easily so that little pressure could be applied. The "chemosol" gels, however, were quite strong and the normal amount of pressure ~ 60,000 psi could be applied provided the split die was held in its shoe properly. The hold-downs were not strong enough and a new stronger ones are currently being made. A solid die is also being fitted with punches and will be used in future work. Several compacts of 30 UC - 70 ZrC and 10 UC - 90 ZrC were made. The results showed that compacts of uniform density can be made by this technique; as indicated by the fact that different sections of individual pressings showed no more than 1-1/2 percent variation in density. Measurements of the densities after sintering showed that the density was not pressure dependent beyond ~ 35,000 psi. One of the 30 UC - ZrC pieces pressed at 60,000 psi which was annealed overnight at 1800°C had a density of 85.2% of T. D. after the anneal. Sections cut from the piece have been submitted to Metallography to check the uniformity of pore distribution. All of the powders used for the above were of -325 mesh size. In general cold-pressed densities of ~ 70% T. D. could be obtained isostatically which is 3 to 5% higher than that obtained for this material by the conventional method previously used. The study will be continued during the coming month.

Three compacts of 30 mol-% UC - 70 mol-% ZrC were cold pressed using -100/+150 mesh, -150/+220 mesh, and -220/+325 mesh fraction. The powder was made from a compact which had been homogenized overnight at 1800°C. After sintering and annealing at 2000°C overnight the resulting densities in the pieces were 75 to 77% of theoretical. Because of these low densities future work with 30 UC - 70 ZrC will be made by using powder fractions of finer particle size and mixtures of powder fractions which will be amenable to obtaining higher densities. However, since UC-ZrC specimens of high UC concentrations usually sinter to higher densities, the above powder fraction sizes will be used during the coming month to control pore size of 90 mol-% UC - 10 mol-% ZrC.

Preparation of UC-ZrC by Gas Reaction

A batch of 100 grams of 30 mol-% U - 70 mol-% Zr alloy was hydrided at 760°C and tumbled in the shaker furnace to break up the hydride. The hydrided material broke into small pieces but only a small fraction turned into fine powder. The material was then reacted with CH_4 at 1000°C for 4 hrs. and shaken to prevent sintering during reaction. Chemical analysis showed the fine powder portion contained 6.7% C and the larger particles contained considerably less carbon in varying amounts. The shaking of the furnace did prevent the sintering (clumping) previously encountered. The material has been ground to -325 mesh and will be reacted again with CH_4 in an attempt to bring the carbon content to stoichiometry (8.12%C).

1.2 Vapor Deposited Tungsten

Two paralleling efforts have been initiated to study the techniques of cladding tungsten on fuels. A subcontract is under negotiation with San Fernando Laboratories (SFL) to utilize their knowledge and facilities to develop greater understanding of the optimum fuel plating conditions, protection afforded by the seal coating process, and the stability of the tungsten coatings upon thermal cycling to high temperatures. A comparable vapor deposition apparatus is under construction in our laboratory. With this apparatus, it is planned to first reproduce the quality of tungsten produced by SFL, and then, under well controlled conditions, to establish the limits of flow rates, gas purities, deposition temperatures, gas mixtures, fluid dynamics, mandrel preparation, and materials used in chamber construction in order to achieve claddings of reproducible properties and structures.

2. Measurements of High-temperature Properties of Thermionic Materials.

2.1 Rate of vaporization as a function of pore structures of UC-ZrC.

The purpose of the study is to try to correlate the high temperature Langmuir rates of vaporization of UC-ZrC samples of various compositions with their surface roughness factors (defined as $\frac{\text{true surface area}}{\text{geometrical surface area}}$) and pore size distribution. The true surface area is to be determined by the Braunner-Emmett-Teller (BET) method involving the physical absorption of an inert gas (e.g. Kr) at low pressures (<1 torr). The pore size distribution is to be determined by mercury porosimetry. Samples from the same carbide cylinder will be used in 2.2 and 2.3 for the studies of their fission product release and fission product diffusion (through W clad) properties.

The first sample for such a series of studies has been prepared. It is a hot-pressed 30 UC-70 ZrC sample A_1 of high density ($\sim 96\%$). Sample A_1 has been cavitroned into four circular pieces of 3/8 in. diameter. The first piece A_1-1 is 1/8 in. thick and will be used for the study of rate of vaporization, BET surface area, microstructures and pore size distribution. The other three pieces A_1-2, A_1-3 and A_1-4, each 0.06 in. thick, will be used for the study of fission product release and fission product diffusion through W clad. These samples are now being outgassed in vacuum at 1900°C. The measurement of the Langmuir rate of vaporization of A_1-1 in the temperature range 1800°C - 2100°C and the full characterization of the pore structures of the sample are planned for October.

2.2 Fission product release from UC-ZrC.

The purpose of the study is to characterize the rate of release of fission products from UC-ZrC fuels of various compositions with their surface roughness factors and pore size distribution in the temperature range 1600°C - 2000°C. The results should help to guide the selection of fuel materials and their fabrication techniques for the irradiation studies and in-pile cesium cell applications. The method used is the post-irradiation annealing type where the fuel samples are irradiated in the TRIGA reactor at ambient temperatures to a known number of fissions. After a suitable period to allow shorter-lived activities to decay, a sample is quickly brought to the temperature planned, and the release of the fission products Xe-133, Ba-140, Te-132 and I-131 are determined as a function of annealing time. These particular nuclides are picked for the study because they are of adequate yield and of convenient half life for post-irradiation experiments. Also, they represent three important classes of fission products: Xe, a noble gas; Ba, an electropositive metallic element; and Te and I, electronegative nonmetallic elements. The rates of release of volatile fission products (especially Kr and Xe) are of particular interest, since they are closely related to the fuel swelling problem.

Sample A_1-2 which is a hot-pressed 30 UC - 70 ZrC of high density (~96%) (see Section 2.1) will be studied at 1800°C during October after thermally stabilized at 1900°C.

2.3 Fission product diffusion through W-clad.

The purpose of the study is to determine the rates of diffusion of various fission products from uranium-containing fuels through W-clad in the temperature range 1600°C to 2000°C as a function of the structures of the W-clad. The experiment will be performed in an experimental arrangement similar to the diffusion-emission cell. The fission gases diffusing through the clad will be caught in a liquid nitrogen cooled charcoal trap and monitored in situ. The other fission products diffusing through the clad will be condensed on a water-cooled copper surface coated with carbon.

The carbon coating is used to facilitate the capture of strong carbide-forming fission products. During the experiment, the vacuum emission of the W surface will be monitored for any change. The results should indicate how clean the W surface and the cesium plasma can be kept during the operation of a W-clad emitter in a reactor. The correlation of the rates of diffusion with structures of the W-clad should serve as a guide for the selection of optimum fabrication methods.

The fabrication of two cells suited for such studies is in progress. Sample A_1-3 which is a hot-pressed 30 UC - 70 ZrC of about 96% theoretical density (see Section 2.1) will be clad with vapor-deposited tungsten as the first sample. It is expected that during October the fabrication of the cells will be completed and the order of the counting equipment will be made.

2.4 Fuel-clad gross diffusion studies.

Previous gross diffusion studies have placed heavy emphasis on the interaction between uranium-containing fuels, (e.g. UC, UC_2, UC-ZrC, and UO_2) and various refractory metals and alloys (e.g. W, Ta, Mo, Nb, Ir, Re, W-26Re, and W-2Mo) at 1800°C. W was shown to be the most suitable cladding for use with the above mentioned fuels at such a high temperature. This year, the study will be broadened to include a wider temperature range 1400-2000°C for periods of time up to 1000 hrs. in order to gain a thorough understanding of how the interaction is affected by temperature. Since the stoichiometry of fuel bodies may be one of the important factors affecting the interaction, each fuel sample will be studied at both stoichiometric and slightly hyperstoichiometric compositions.

In view of the large number of fuel-metal combinations and temperatures to be included in the study, it is planned to start the investigation with UC-ZrC of low uranium contents, e.g. 30 UC - 70 ZrC to establish the maximum temperatures T under which various refractory metals are compatible with such fuels. The results should help to eliminate the testings of the same metals with UC-ZrC of higher uranium-contents at temperatures higher than T. Thus the portion of the fuel composition-temperature spectrum to be studied can be considerably reduced.

Because of the large number of specimens required to cover the temperature composition range to be studied, an additional diffusion furnace capable of holding more than one specimen holder is being procurred. Ta, Nb, Mo, W, Re, Ir and W-26Re needed for the studies have been ordered. The UC, 80 UC - 20 ZrC, 50 UC - 50 ZrC, 30 UC - 70 ZrC samples, both stoichiometric and hyperstoichiometric in carbon contents, are being prepared. It is planned to start the experiments in October.

2.5 Fuel-clad diffusion-emission studies.

This is a continuation of the work under Contract NAS 3-2532. The first case to be examined is Re clad stoichiometric UC at 1800°C. The UC wafer will be contained in a recess of a cast W-base and will be covered with a Re disc of about 20 mil thick. The Re will be bonded to the W-base in a vacuum hot-press. Fabrication of such a sample is in progress.

2.6 Refractory metal interdiffusion.

The purpose of the study is twofold, to gather information for the diffusion bonding of refractory metals to W, and to test the feasibility of duplex emitters in which a layer of better emitting materials, such as Re and Ir is separated from the uranium-containing fuel by a layer of W. The diffusion between W and Ta, Mo and Nb will be studied in the temperature range 1200-2000°C, while the diffusion between W and Re (vapor deposited) and Ir (vapor-deposited or electroplated) will be studied in the temperature range 1400-2000°C. The refractory metals needed have been ordered. It is planned to start the experiments in October.

2.7 Refractory metals diffusion-emission studies.

The cases of Re and Ir layers over W are to be studied. The purpose is to find out the feasibility of the concept of duplex-type emitters in which the W provides a barrier between the carbide fuel and the emission contributing materials such as Re and Ir. Fabrication of the diffusion-emission cell for such a purpose is in progress.

2.8 Mechanical properties of UC-ZrC.

During the last contract year, measurements of the mechanical properties of UZrC fuels were initiated to derive strength and elasticity data for use in predicting the thermal shock resistance and swelling behavior of various UC to ZrC ratio fuels. During this effort, test equipment was developed, and measurements made on 10 UC - 90 ZrC, 80 UC - 20 ZrC and UC in the temperature region 1600° to 1800°C.

This year, the work will be extended to include a wider range of composition, temperature and strain rate with controlled variations in porosity and microstructure.

Current work involves a modification to the test equipment. During the last contract year, the molybdenum support pedestal was found to have distorted because of severe side loading. This occurred when the uranium carbide specimens being tested crept to a bow shape before fracturing during testing at a low strain rate. The sample support pedestal is currently the subject of revisions to develop more side load resistance.

When the mechanical difficulties mentioned are corrected, measurements of modulus of rupture will proceed with UC, 50 UC - 50 ZrC and 30 UC - 70 ZrC samples.

2.9 Emission-microscopy of W-(uranium-containing carbide) cermets.

It is believed that although uranium-containing carbides are excellent electron emitters in vacuum, their performance in cesium vapor is ion-generation limited. The purpose of this study is to explore the possibility of improving their performance by incorporating high work function patches on the carbide surfaces. Uranium-containing carbide-W cermets offer such a possibility. However, in order to achieve such a goal, the W patches on the cermet surface would have to be able to maintain their high work function in the presence of uranium-containing materials. Study of the electron emission patterns of these cermets at high temperatures as a function of time would indicate whether this will happen. The first sample to be studied will be a 30 UC - 70 ZrC emitter containing 10 wt-% W.

The sample is being fabricated. Examination of the emission patterns of this sample in the temperature range 1600°C to 1800°C in an electron emission microscope will be made during October.

3. Life-testing of Cesium Thermionic Cells.

A re-evaluation of the thermionic cells for life testing of candidate fuel emitters was made on the basis of the requirements to operate these cells to 10,000 hours. This places particular emphasis on the thermionic cell components which have to last 10,000 hours in order to fully evaluate each emitter. For this primary reason, the following major refinements are being made:

(1.) The operation of the cell will be in an evacuated chamber.

(2.) The sample emitter holder and fueled emitter will be incorporated into one unit and made of vapor-deposited tungsten in the high temperature regions.

(3.) The collector-guard ring assembly will be replaced by a collector assembly.

A program schedule will be established as soon as the cell fabrication group can evaluate complete drawings to estimated parts needed and time of assembly.

4. Irradiation Studies.

The feasibility of using the Plum Brook reactor for the irradiation studies is being examined under Project 306.35 which represents an amendment to Contract NAS 3-2532. Calculations of the neutron flux distribution in the V-tube as a function of position (both radially and axially) are being made. The design of the cooling system and the radial movement mechanism for the capsule is being carried out. The details have been reported in the monthly informal report for Project 306.35. No irradiation work will be carried out under the present contract until the termination of Project 306.35 by October 13, 1963.