FOURTH QUARTER REPORT
of
RESEARCH AND DEVELOPMENT PROGRAM
of
THERMIONIC CONVERSION OF HEAT TO ELECTRICITY

June 29, 1965

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Program Manager:	Dr. J. E. VanHoomissen 215-862-2211, Ext. 480
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I. INTRODUCTION

This is the Fourth Quarterly Letter Report describing progress on work performed from March 30, 1964, to June 29, 1965 under contract NObs-90496, "Research and Development Program of Thermionic Conversion of Heat to Electricity, June 30, 1964." The work performed under this contract is based upon and is a continuation of work initiated under contract NObs-88578. Both contracts were issed by the U. S. Navy, Bureau of Ships, and supported by the Advanced Research Projects Agency.

The objective of this program is the development of a nuclear thermionic electrical generating system for the Department of the Navy. Work under this contract is being performed to develop the materials capabilities which are essential for this nuclear thermionic system. This work consists of three major tasks. They are:

Task A - UO_2- Refractory Metal Reaction Kinetics

Task B - Insulator Materials Development

Task C - Ceramic-to-Metal Seal Development

The overall project responsibility for contract NObs-90496 at the General Electric Company is held by Dr. John E. VanHoomissen, Manager, Project SPR, Special Purpose Nuclear Systems Operation. The individual technical contributors with primary responsibility for individual tasks are:

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II. TECHNICAL PROGRESS

TASK A - UO_2-Refractory Metal Reaction Kinetics
Sub-Task A-1 - UO_2 Diffusion Studies

Objectives - The purpose of the task is to continue studies of diffusion of uranium, from urania, through tungsten and to initiate similar studies for molybdenum. The temperature range for tungsten is primarily 1800 - 2200 C and for molybdenum it is primarily 1600 - 1700 C.

Progress During the Fourth Quarter - The initial tests of vapor deposited tungsten at 1800°C and all the molybdenum tests were completed and discussed in the Third Quarter. During the Fourth Quarter, contined tests of UO_2-W (vapor deposited) were completed at 1800 and 2000°C. The specimen tested at 1800°C was on test for 1270 hours with an an average uranium flux rate of 6.33×10^{-9} gm/cm^2 hr. The specimen tested at 2000°C was on test for 1565 hours with an average uranium flux rate of $< 2 \times 10^{-10}$ gm/cm^2 hr.

The results of the tests at 1800°C showed a gradual decrease in the uranium flux rate from 10^{-8} gm/cm^2 hr at the initiation of the test, to a much lower value of about 3×10^{-10} gm/cm^2 hr at the end of the test. The diffusion rate at 2000°C was 0.8×10^{-10} gm/cm^2 hr for the first 200 hours, followed by a steady average flux of about 3×10^{-10} gm/cm^2 hr for the remaining 1365 hours of test.

A specimen of hyperstoichiometric UO_2 encapsulated in vapor deposited tungsten has been run for 300 hours at 1800°C. Initial flux rates of 8×10^{-10} gm/cm^2 hr were observed. Additional test results are not available at this time. These initial rates are consistant with previously observed enhancement of diffusion rates with hyperstoichiometric urania clad in molybdenum.

Sub-Task A-2 - Oxygen Diffusion Studies

Objective - The chemical compatibility of UO_2 with its metal clad in thermionic fuel element, particularly under thermal cycling conditions, depends on the rate of diffusion of oxygen through the clad. The objective of this task is to evaluate the diffusivity of oxygen in molybdenum in the range 1500 to 1800°C.

Progress During the Fourth Quarter

Results of tests to determine C_o, the saturation concentration of oxygen in molybdenum in a given partial pressure of oxygen, at 1500°C are shown in Table I. The approximate value of D, as described in the Third Quarter, corresponding to saturation for a give time at 1500°C is also given in Table I. Tests were conducted in a partial pressure of oxygen of 7.6×10^{-7} torr. The results of tests up to and including the 190 hour test indicate that saturation may still not have been reached after 190 hours. The results do show, however, that D is probably less than 10^{-7}. To define C_o more accurately and to investigate the possibility of using the saturation treatments as a means of determining D, additional samples (designated numbers 32, 33, 37, and 38) were tested at 1500°C.

TABLE I
Oxygen Concentration vs Time for Determining C_o at 1500°

Sample Number	Time (hr)	D for Saturation (cm^2sec^{-1})	Oxygen Concentration (ppm)
8	0 (vacuum anneal only)		7.7
9	0 (vacuum anneal only)		3.7
10	0 (vacuum anneal only)		4.6
11	0 (vacuum anneal only)		3.7
1	2 min.	10^{-4}	8.8
2	12 min.	10^{-5}	11.0
3	2 min.	10^{-6}	14
4	20	10^{-7}	21
23	190	10^{-8}	25
32	152		41
33	114		51
37	50		15
38	100		76

The oxygen concentrations of samples 32, 33, and 38 are quite high compared to earlier samples and that of sample 37 is low. A new tank of argon-oxygen gas mixture was used for these tests. Because of the irregular results, the oxygen concentration of the gas mixture was analyzed with a Beckman oxygen trace analyzer (accuracy ± 5%) and was found to be a factor of 2 higher than that reported by vendor analysis. Some evidence of external oxidation was also found on the samples having high values. The high oxygen partial pressures and evidence of some external oxidation make the oxygen concentration of samples 32, 33, 37, and 38 unreliable and unsuitable for comparison with previous results at 1500°C.

The tests to determine C_o at 1800°C were initiated during this period and the results are tabulated, again with approximate value of D, in Table II.

In advertent shutdown of the experimental apparatus during treatment of samples 27 and 28 make these results somewhat questionable and they should be checked. As was the case for the 1500°C tests, D again appears to be less than 10^{-7}.

TABLE II
Oxygen Concentration vs Time
for Determining C_o at 1800°C

Sample Number	Time (hr)	D for Saturation ($cm^2 sec^{-1}$)	Oxygen Concentration (ppm)
24	2 min.	10^{-4}	8.3
25	16	10^{-5}	10
26	2-1/2	10^{-6}	13
27	27	10^{-7}	21
28	52	10^{-7}	32
34	100	10^{-7}	25

Consistent achievement of a temperature of 1800°C in the 5 kw induction heater with 1/16" diameter samples has proven to be very difficult; it has required the full power output of the unit. Any disturbance of the power supply producing a temporary overload situation has caused shutdown of the equipment. To permit dependable attainment of 1800°C, 1/8" diameter molybdenum rod has been ordered and will be used exclusively for the remaining 1800°C tests. The larger diameter rod will improve the coupling between the high frequency generator and the sample and permit operation at 1800°C without requiring full output power. Reduction of the power required for tests will have the added benefit of minimizing inadvertent shutdowns by diminishing the sensitivity of the induction unit to power transients.

TASK B - Insulator Materials Development

Objective - Identify quantitatively the equilibrium gaseous species which exist when high purity alumina is heated in the presence of niobium metal in the temperature range 800-1800 C. The kinetics of Al_2O_3-Nb reactions yielding gaseous products will be partly elucidated by determination of diffusion constants for oxygen in niobium.

Progress During the Fourth Quarter - Experimentation on the Al_2O_3-Nb reaction has been completed. The reaction proceeds as follows (for low oxygen pressures):

$$Al_2O_3 + 3\ Nb = 2\ Al(g) + 3\ NbO$$

The weight loss rate due to the above reaction is about 50 times the weight loss rate due to dissociation of alumina at all temperatures examined (1550-1900°C).

TASK C - Ceramic-to-Metal Seals

Objective - The objective of this task is the development of high temperature tolerant, cesium resistant ceramic-to-metal seals. Under this task, investigations are being performed in the following areas:

(1) Development of alumina-based cermet fabrication techniques leading to hollow cylindrical shapes for emitter-collector seal insulators.

(2) Effort to improve high-temperature stability of the interstitial and interfacial phases which form when metal metal-oxide mixtures are sintered in contact with alumina.

(3) Evaluation and/or development of methods of bonding the metallic surface of insulators to structural metal members.

(4) Long-time testing of materials and seals at high temperature in both vacuum and cesium vapor environment.

Progress During the Fourth Quarter

Cesium Resistant Metallizing - Significant differences have been observed in many developmental metallizing coatings applied to two pure, polycrystalline alumina ceramic; Lucalox* and body A-976. A difference exists in the amount of oxide retained in the interstices of the sintered metal coating and results from a difference in purity of the substrate materials. Several metallizing compositions have, however, been demonstrated to yield satisfactory seals to both materials.

Graded Cermets - A group of graded cermet cylinders, including grades from a 10 v/o molybdenum core to 100 v/o molybdenum surface layers, were subjected to thermal cycling and 1250°C vacuum life testing. Cylinders which contained an adequately thick central region (those layers with compositions from 10 v/o up to 25 v/o metal) withstood nine cycles to 900°C followed by 327 hours at 1250°C. No weight loss was detected.

Metal-to-Metal Bonding - Electron beam welds were attempted between 25 v/o alumina, 75 v/o molybdenum cermet discs and similar diameter

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* General Electric trade mark for a high-purity alumina ceramic

molybdenum cylinders. None of the three units welded were leak tight; however, failure was not attributed to the welds but to cracking of the recrystallized molybdenum cylinder adjacent to the weld. No attempts were made to minimize the thermal stresses to prevent this cracking. Although islands of alumina ceramic formed within and on the weld surface, bonding appeared excellent with negligible porosity in the weld. Bonding of a similar cermet to a molybdenum ring by nickel braze-diffusion-bond was quite successful with negligible change occurring in the bond as a result of exposure to 1500°C for 400 hours in vacuum.

Cesium and Vacuum Life Testing - Testing at 1200°C in both cesium and vacuum caused negligible change in the "as brazed" bond structures of various types of seals. Thirty-four out of thirty-five metal-to-ceramic seals made with nickel braze-diffusion-bonding, flow braze No. V (50 Nb - 30 Pd - 20 Ni) and flow braze No. VII (67 Nb - 33 Fe) remained leak tight. Some of these seals were tested a total of 800 hours. At 1500°C some changes in the bond structures occur; however, various metal-to-ceramic seals bonded with flow braze No. VII, and tested at 1500°C during the last reporting period, remained leak tight. Joints between niobium, tantalum, and molybdenum discs and molybdenum rings, formed with flow braze No. VII, showed a marked improvement as a result testing at 1500°C, with the thin braze layer being almost completely replaced by a direct bond between the refractory metals.