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GENERAL ATOMIC

DIVISION OF GENERAL DYNAMICS

GA-3562 (Rev.)

HIGH-TEMPERATURE VAPOR-FILLED THERMIONIC CONVERTER

QUARTERLY TECHNICAL PROGRESS REPORT

FOR THE PERIOD

JULY 1 THROUGH SEPTEMBER 30, 1962

Contract AF 33(657)-8563
Project No. 8173, Task No. 817305-5

Aeronautical Systems Division
Air Force Systems Command
U. S. Air Force
Wright-Patterson Air Force Base, Ohio

November 10, 1962

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FOREWARD

The work covered by this report was accomplished under Air Force Contract AF 33(657)-8563, but this report is being published and distributed prior to Air Force review. The publication of this report, therefore, does not constitute approval by the Air Force of the findings or conclusions contained herein. It is published for the exchange and stimulation of ideas.

INTRODUCTION

The program to investigate high-temperature vapor-filled thermionic converters under Contract AF33(657)-8563 has progressed to the point where detailed data are available on the post-test analysis of Cell E. Ultra-clean cell technology continues to be a major area of study and development. Construction of Cells F and G continue.

SUMMARY

PRESENT STUDIES

The post-test analysis of Cell E has been completed with the exception of the microprobe analysis of the emitter structure.

Interpretation of the data from the above analysis indicates the necessity of improving the cleanliness of future cell assemblies and especially the need for techniques to determine the emitter condition throughout final assembly.

A 10 UC - 90 ZrC emitter is installed in Cell F. Thermocouple installation and calibration and high-temperature vacuum emission tests are being conducted prior to the final closure of the cell. A second cell structure, Cell G, is on hand and an emitter will be installed pending the results of surface preparation.

Recent vacuum emission studies carried out under other contracts* on three UC compositions--10 UC - 90 ZrC, 30 UC - 70 ZrC, and 90 UC - 10 ZrC--demonstrate that emission behavior is essentially independent of bulk uranium content. The presence of some uranium on the emitting surface is of the utmost importance. Intentional "poisoning" of the surface of sample emitters has been produced by exposure to air at room temperature. These findings have been substantiated on the Mark V-E and V-F emitters. It has been concluded, therefore, that the emitter surface must be activated in addition to providing a clean cell environment during operation.

SIGNIFICANT ACCOMPLISHMENTS

1. Detailed post-test analysis of Cell E is complete (with one exception).
2. Practices and techniques designed to improve cell performance through the ultra-clean cell technology have been developed and tested.

PRESENT ACTIVITIES

Clean Cell Technology

Clean cell conditions are mandatory for desirable performance

*Office of Naval Research Contract Nonr-3193(00) and NASA Contract NAS5-1253.

characteristics. Consequently, the following cell modifications have been provided for Cell F:

1. Addition of a titanium getter.
2. Cesium transfer to the ampoule under high vacuum.
3. Use of a metal cesium ampoule.
4. Capability of higher cesium pressures.
5. Use of a larger Vac-ion pump for higher ultimate vacuum.
6. Employment of higher bakeout temperatures.
7. Replacement of the high-vacuum valve by the tube pinchoff.
8. Activation of the emitter surface.
9. Addition of a facility for vacuum emission measurements over the full operating temperature range.

It is believed that these changes in cell hardware and in cell preparation, coupled with the vacuum emission equipment, will materially improve the performance of Cell F and future cells.

DEVELOPMENT OF UC EMITTERS

Emitters with high uranium content appear attractive for thermionic cells; the larger bulk uranium supply aids in maintaining the required surface concentration even though bonding of the higher UC to metal support tubes required for bench testing presents a difficult technical problem. With observation of low emission in Cell E, a secondary effort has been placed on investigating 30 UC - 70 ZrC emitters. The first test 30 UC - 70 ZrC emitter showed severe cracking during thermal cycling and was examined to determine composition and possible materials reactions. The original carbide powder used in the fabrication was found to be slightly metal-rich. Tantalum carbide had formed at the UC-ZrC and tantalum interface. A liquid uranium phase was detected which was caused by the loss of carbon from the UC-ZrC.

A second 30 UC - 70 ZrC emitter, prepared at higher pressing temperatures, is now undergoing thermal cycling. After 10 cycles between room temperature and 1900°K , the hair-line cracks originally present had not opened up.

The recent vacuum emission data mentioned above have justified the continued use of 10 UC - 90 ZrC emitter for the Mark V program.

Three standard 10 UC - 90 ZrC emitters have been fabricated on tantalum support tubes according to procedures developed earlier in the program. One of these has been installed in Cell F and is now undergoing test.

FUTURE PROGRAM

The program for the balance of the contractual period will be devoted to operating Cells F and G and establishing that the high current emission observed from carbide emitters in the Mark V type cell can be obtained. A continuing effort will be devoted to clean-cell technology as dictated by experience and experimental observations. Concurrent operation of Cells F and G will proceed as rapidly as possible in order to achieve the goal of 3000 hours operation at high temperature.

DISCUSSION

POST-OPERATION ANALYSIS OF CELL F

Post-operation examinations have been made of the collector, the emitter, the high-vacuum valve, and the insulator as outlined in previous transmittals. In summary, the following facts were revealed during post-operation test:

1. The emitter surface was oxidized.
2. A section of the emitter showed high power output on the vacuum emission stand after removal from the cell. This result is under investigation at this time.
3. During the operation of this cell, a tantalum-carbon or tantalum-uranium reaction occurred.
4. A uranium deposit was found on the collector.
5. No evidence of cesium corrosion was observed on the insulator or ceramic.

Collector

A black, hard, crusty deposit was found on the collector. The deposit was not uniform longitudinally nor radially with the emitter. The collector was sectioned longitudinally and one-half was subjected to metallographic examination, while the deposit removed from the other half was chemically analyzed. The lack of adhesion observed between the deposit and the nickel substrate in certain sections indicated that it formed on top of the collector, rather than by diffusion into and interaction with the nickel. Metallographic examination showed that the deposit consisted of two distinct regions lying on a nickel substrate. (See Fig. 1.) Micro-hardness measurements indicate high hardness values characteristic of carbides or intermetallics in both regions. However, this deposit did not alter the collector work function.

The deposit was removed mechanically and by leaching with a solution of HNO_3 , HF , and HCl . Chemical analysis gave the following results (since the nickel substrate was also partially dissolved, it is not listed):

<u>Element</u>	<u>Wt-%</u>	<u>Mol-%</u>
Uranium	94.1	68.6
Zirconium	3.19	6.04
Iron	1.27	4.66
Carbon	1.44	20.7

It is apparent that the bulk of the deposit is uranium. The total weight of the material (excluding the nickel) removed from the one-half of the collector was 0.0627 gm. If a density of 10 gm/cm^3 is assumed for the emitter material (UC is 12 gm/cm^3), the weight of the deposit corresponds to a loss of approximately 0.001 cm (0.0004 in.) from the surface of the emitter. This is in agreement with vapor-loss studies of carbide materials conducted at General Atomic. The source of the iron is undetermined. It may have been introduced in part by the saw used to section the collector, or it may be due to the iron impurities in the carbide, or both.

Emitter

The emitter was examined to determine the following properties:

1. Surface uranium concentration by electron diffraction techniques.
2. Vacuum-electron emission.
3. Microstructure.
4. Composition of carbide.
5. Interdiffusion of the carbide and the tantalum support by electron-microprobe techniques.

All of these examinations have been completed except (5), which is now in progress.

1. Surface Uranium Concentration

An electron diffraction pattern was obtained from the surface of the emitter. A strong pattern of ZrO_2 and a weak pattern of UO_2 were observed. No indication of a carbide pattern was obtained. X-ray diffraction studies, which probe the surface more deeply than electron diffraction studies, showed a strong pattern of 10 UC - 90 ZrC (determined from lattice parameter measurements) with only slight traces of UO_2 and ZrO_2 .

Electron-diffraction techniques were employed because they observe material only near the surface (~ 1000 Å deep). This is important because the electron-emission characteristics are dependent primarily upon surface conditions. These results indicate that while carbide was maintained in the substrate, the surface was strongly oxidized.

2. Vacuum-Electron Emission from the Surface

A general study is being made at General Atomic, supported by NASA and ONR*, to determine the factors affecting the emission properties of carbide emitters.

Measurements of vacuum emission have been made on samples of the following compositions: 10 mol-% UC - 90 mol-% ZrC, 30 mol-% UC - 70 mol-% ZrC, and 90 mol-% UC - 10 mol-% ZrC. It was determined that the vacuum emission of these samples was not related to the bulk uranium concentration; and, in fact, they were behaving as dispenser-type cathodes whose emission is dependent upon maintenance of a layer of uranium metal at the specimen surface. Removal of this uranium layer degrades the emission; and such processes as poisoning by exposure to air, volatilization at high temperatures, or mechanical abrasion will effectively remove it. If the layer is removed by such processes, the high emission values characteristic of uranium-bearing carbides can be restored by annealing treatments (e.g., 2 hours at 2000°K in a pressure of 10^{-5} torr) which re-establish the surface uranium layer.

The above discussion is not to be construed as meaning that bulk uranium concentration can be disregarded. As the surface uranium layer tends to be removed by poisoning or volatilization, it can be replenished by uranium diffusion from the bulk material. The uranium diffusion is dependent on the bulk uranium concentration, which infers that maintenance of the surface uranium layer should be easier with carbides of high-UC content.

In order to obtain directly comparable data, a sample of the emitter from Cell E was installed in the same equipment used for the parametric vacuum emission study. In Fig. 3, the solid lines

*Office of Naval Research Contract Nonr-3193(00) and NASA Contract NAS5-1253.

are indicative of the emission currents obtained on representative 10 UC - 90 ZrC, 30 UC - 70 ZrC, and 90 UC - 10 ZrC specimens. The circled data points are the measurements made on the emitter sample from Cell E in an "as received" condition. The squared data points were taken after the emitter sample was exposed to air for 4 hours during a collector-cleaning operation. Subsequently, the emitter was held at 1945° for 20 hours while making intermittent emission measurement. Only a slight increase in emission was noted after this treatment. Next, the emitter was removed from the apparatus and the surface cleaned using an air abrasive tool. Another set of measurements were taken and the results, plotted as crosses, show an increase in emission by about a factor of two. Increasing the temperature to 1945°K for about an hour resulted in a slight decrease in emission.

3. Microstructure

The emitter was sectioned longitudinally and examined by metallographic techniques. Fig. 2(a) and 2(b) show the structure at the carbide-tantalum interface. Features which are apparent from these figures are:

- a. The tantalum shows carbide formation which was caused by removal of carbon from the carbide.
- b. A very-low-density structure exists in the regions between the tantalum teeth and immediately adjacent to the tops of the teeth. Micro-examination of similarly prepared emitters prior to extended thermal treatments have not shown this low-density structure; it is hypothesized that the structure was caused by components of the carbide, e.g., carbon or uranium, reacting with the tantalum and being removed from these regions. If not all of the components of the carbide reacted uniformly with the tantalum, one would then expect a skeleton structure, composed mainly of the less reactive component, to be left behind. Such a skeleton structure is illustrated in Fig. 2(b). Microprobe examination will be required to

determine if this structure is indeed rich in one of the components. From chemical data discussed below, it is expected that the structure would be mostly ZrC.

- c. Fig. 2(b) illustrates that the surface of the tantalum does not exhibit carbide formation, i.e., it has a very "clear" appearance. It is possible that diffusion of metallic components from the carbide into the tantalum are responsible for this. Microprobe examination will assist in clarifying this point.

4. Carbide Composition

A piece of the UZrC mixture was chipped from the tantalum substrate after completion of the 1000-hour operation and submitted for analysis. Results are tabulated below, together with the composition of this carbide prior to cell operation.

	<u>Concentration (Wt-%)</u>				
	<u>C</u>	<u>U</u>	<u>Zr</u>	<u>W</u>	<u>Ta</u>
Before Operation	10.20	19.67	67.02	4.16	-
After Operation	9.06	8.5	77.1	3.8	0.6

These concentrations represent a 98.6 mol-% monocarbide whose composition is 8.7 mol-% UC - 91.3 mol-% ZrC plus 1.4 mol-% UC₂ before operation and a composition of 2.2 mol-% U - 51.7 mol-% Zr - 46 mol-% C after operation. The latter is metal-rich but, in accordance with the ternary phase diagram,⁽¹⁾ is still a single-phase structure.

The decrease in carbon content is in agreement with the metallographic observation of tantalum-carbide formation. The decrease in uranium would be in correspondence with previously reported results⁽²⁾ determined for a similar system in which electron-microprobe analyses illustrated that uranium will progress long distances into the tantalum in relatively short times.

Insulator

The insulator was sectioned and metallographically examined. No evidence of cesium corrosion on the ceramic or the braze-alloy was observed.

VACUUM EMISSION STUDIES IN CELL F

A 10 UC - 90 ZrC emitter of Mark V geometry was placed in Cell F to study its low-temperature vacuum emission characteristics. The first run was made at temperatures between 1300° and 1700°K with the emitter in an "as received" condition. Subsequent measurements were made after surface cleaning and after a high-temperature annealing treatment. It can be seen (Fig. 4) that the combination of mechanical abrasion, in which the surface layer is removed, and the annealing procedure, which provided a new surface layer of uranium, produced significant changes. The emission data taken at the conclusion of these treatments showed the high values characteristic of uranium-bearing carbides and were in agreement with an extrapolated curve from high-temperature data. Fig. 4 summarizes the results from the four runs.

It should be noted that the final run performed after the emitter had been exposed to air for 7 hours did not evidence the severe poisoning previously discussed. This behavior is not completely understood at this time.

During these runs, the temperature over which saturated emission data could be taken was limited to the range of 1300° to 1700°K by the power supply available. A pulsed power supply capable of covering the temperature range of interest on carbide emitters of 12 to 13 cm² will be delivered the first week in October. No carbide cell will be operated with cesium present unless it first shows acceptable vacuum emission values prior to final closure of the cell.

ULTRA-CLEAN CELL TECHNOLOGY

From the results obtained in the post-test analysis of Cell E and in vacuum emission tests, several concepts of how to produce and maintain ultra-clean cells have evolved. These concepts are listed below. In some cases, employment of these concepts has resulted in minor design changes to the cell. However, the majority of the modifications affected the cell plumbing only, so that cell parts on hand could still be used effectively.

1. Addition of a titanium getter--Since the emitter from Cell E showed a strong electron diffraction pattern of ZrO₂ and UO₂, the need for a getter was established. The titanium getter for Cell F is mounted on the tantalum support tube and will be heated

primarily by radiation from the emitter to a temperature of 600° to 900°C.

2. Cesium transfer to the ampoule under high vacuum--This technique is employed to ensure a clean, gas-free cesium supply to the cell. The cesium is refluxed under a vacuum of 10^{-6} before admission to the ampoule.
3. The use of a metal cesium ampoule--To provide the capability of operating at higher cesium pressures, the ampoule material must be inert to cesium attack over the temperature range of interest. Glass ampoules are known to react with cesium above 250°C.
4. Capability of higher cesium pressures--A pot that has heating and cooling provisions will be cast on the cesium reservoir after the cesium ampoule has been crushed. Thermocouples embedded in the casting material (1602 braze) will very accurately determine and control the cesium temperature. The cooling capability is provided so that the effect of cesium pressure from room temperature to 400°C may be studied.
5. A larger Vac-ion pump for higher ultimate vacuum--This pump is to be located outside the bell jar and will have sufficient capacity to reduce the pressure to 10^{-8} torr during cell bakeout.
6. Capability of higher bakeout temperatures--More heater capacity has been provided to bring all portions of the cell to at least operating temperatures. In most locations, a temperature 100°C above operating range will prevail during bakeout.
7. Removal of the high-vacuum valve in favor of a pinchoff--The high-vacuum valve in Cell E proved to be a weak point. Since pinchoffs have been employed reliably for years in other applications, this technique will be adopted to seal off the cell. To provide added assurance of the integrity of the pinchoff, it will be encased in 1602 braze.
8. Emitter surface activation--It has been pointed out in the discussion of vacuum emission results that a clean emitter surface is necessary to obtain good cell performance. Consequently, it is planned to mechanically remove a surface layer from the emitter in Cell F

just prior to welding the collector in place. A short time at 1950° to 2000°K should then activate the emitter surface to the degree that has been observed on other carbide emitters.

9. Facility for vacuum emission measurements over the full operating temperature range--This tool will be used to detect changes in the emitter surface during the final assembly.

The techniques involved in the modifications listed above, with the exception of (1) and (9), have been checked out thoroughly on dummy assemblies to be certain that they may be successfully incorporated into Cell F. No deleterious effects are foreseen from the inclusion of the titanium getter; in fact, all the evidence points to a net gain in performance. Since the vacuum emission equipment is an investigative tool external to the cell, no operating difficulties can arise from its use.

EMITTER FABRICATION

The effort in this area has been concentrated on 30 UC - 70 ZrC fabrication problems which are common to all higher UC emitters. The requirements for the emitter structure are unique to bench testing; that is, the emitter must be a hollow leak-tight cylinder to accommodate filament heating. In the 10 UC - 90 ZrC fabrication, an overlay of UC-ZrC was hot-pressed on an emitter head of tantalum. This procedure was quite successful due to the ductility of the tantalum at the pressing temperatures. However, this method is not directly applicable to 30 UC - 70 ZrC or higher UC emitters since there is evidence that a reaction would occur at the carbide-tantalum interface.

One 30 UC - 70 ZrC emitter was fabricated according to this procedure and was thermally cycled. Small hair-line cracks originally present opened up severely, and uranium metal was evaporated from the emitter surface. Metallographic examination of the emitter indicated that both U (liquid) and UC phases were present (Fig. 5). Analysis of the carbide powder used in preparing the emitter showed that it was indeed slightly metal-rich. Examination of the tantalum-UZrC interface revealed the formation of tantalum carbide. This metal carbide formation increased the metal-to-carbon ratio in the UZrC, making it even more metal-rich. Thus, liquid uranium formed

and then boiled off, leaving numerous voids. An unexplained diffusion layer was also noted.

The density of the carbide on the surface of the emitter was quite low. During the thermal cycling and heat treatment, it is possible that the lower density material tended to densify by further sintering. As the volume of the carbide decreased, more cracks were observed. These subsequently grew larger.

Two changes in procedure have been employed to overcome these problems:

1. Using a carbon-rich carbide powder which allows a tantalum carbide layer to form at the metal-UZrC interface and prevent further interaction. The excess carbon is held to a minimum so that it will not promote liquid uranium formulation.
2. Employing a higher pressing temperature (1850°C). At this temperature the tantalum flows more readily and consequently will transmit more pressure to the radial surfaces of the die wall, thus increasing the density of the carbide.

A 30 UC - 70 ZrC emitter was produced using these techniques and is presently undergoing heat treatment and thermal cycling. After 10 cycles between room temperature and 1900°K , the hair-line cracks originally present had not opened up and there was no noticeable deposit on the bell jar. Further testing of this emitter is continuing.

The use of tungsten as a barrier layer over tantalum, or as the support tube itself, has been studied as a means of producing high-UC emitters. In one experiment, a 5-mil foil was placed between the carbide and the tantalum. At a pressing temperature of 1750°C there was no bonding between the carbide and the tungsten. In another test, the carbide was pressed on the tungsten at 2000°C . Examination of this bond will be performed prior to additional attempts at using the tungsten barrier concept.

As previously reported, a tungsten tube has been fabricated by a vapor deposition process. The tube was found to be leak-tight. Using the same technique, ZrC pellets have been coated to determine the effects of processing variables. These pellets are to be evaluated during October. Cups of 30 UC - 70 ZrC material have been prepared with a fluted internal surface to promote adherence. The first cup has just been delivered to the vendor.

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- (1) Benesowsky, F. and E. Rudy, Planseeberichte fur Pulvermetallurgie, Vol. 9, 1962, p. 6.
- (2) Weinberg, A. F. et. al., Investigations of Carbides as Cathodes for Thermionic Space Reactors, Quarterly Progress Report for the Period Ending February 28, 1962, General Atomic Report 3007.

300X

Fig. 1--Interior surface of collector

50X

- (a) Over-all view. Note carburization of tantalum and low-density around the teeth.

200X

- (b) Enlargement showing "clear" appearance of tantalum surface. The dark area is the center section jutting between the two teeth shown in (a).

Fig. 2--Carbide tantalum interface

Fig. 3--Vacuum saturated emission of Mark V Cell "E" after 1034 hr.

Fig. 4--Vacuum saturated emission of Mark V Cell F

Unetched

50X

- (a) Region of carbide-Ta interface showing extensive reaction and formation of voids in what was previously Ta. The voids were probably due to Ta displacing U in the carbide and the U subsequently boiling off.

Emitter sectioned as illustrated above. Top portion examined.

Etched

50X

- (b) Same as (a) but etched to more clearly delineate the diffusion layer.

Diffusion layer more clearly defined

Fig. 5 --Emitter after thermal cycling