GENERAL ATOMIC

Division of General Dynamics Corporation

John Jay Hopkins Laboratory

for Pure and Applied Science

GAMD-4220

Copy No. 46

TUNGSTEN CLADDING OF URANIUM-ZIRCONIUM CARBIDES BY VAPOR DEPOSITION

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National Aeronautics and Space Administration
Project No. 306.300
Contract No. NAS 3-2532

March 8, 1963

ABSTRACT

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Tungsten cladding of UC-ZrC specimens of compositions varying from pure UC to 30 a/o UC-70 a/o ZrC has been successfully accomplished. The carbides were found to be extremely reactive in the vapor deposition atmosphere; this required that the gases introduced must be of high purity, and the temperature of initial plating must be kept as low as is practicable to minimize damage to carbides and produce a seal coat. The temperature may then be raised for encapsulation in order to increase the coating rate and enhance the gap bridging capability of the deposition process.

TUNGSTEN CLADDING OF URANIUM-ZIRCONIUM CARBIDES BY VAPOR DEPOSITION

Introduction

Compatibility studies at General Atomic and elsewhere have indicated that pure tungsten is to date the material most suitable for use as a direct cladding material (cladding utilizing barriers excepted) for UC-ZrC compositions under consideration as candidate nuclear fuels for thermionic generators to be operated at temperatures up to 1800°C. Tungsten is a fairly difficult material to fabricate, using conventional techniques. Thus it was apparent that vapor deposition was a logical choice as a method for cladding such emitters for the GETR irradiation testing, included under General Atomic project No. 306.

Preliminary Investigation of Feasibility of Tungsten Vapor Coating UC-ZrC Specimens

As a preliminary investigation into feasibility of the method, tungsten vapor deposition had been done on steel mandrels and other metals by San Fernando Laboratories for some time with resulting deposits (in the form of tubes or coatings) of a relatively high quality. Several carbides of the GETR type 90 UC - 10 ZrC were sent to San Fernando Laboratories and were coated using a design shown in Fig. 1. The parts were outgassed at ~ 1800°C and were sectioned and found to be intact with no evidence of significant damage as a result of the vapor deposition coating process. It was then assumed that the ordinary vapor deposition techniques were applicable to coating the carbides to be used in GETR Irradiation Test of tungsten clad emitters.

Initial Attempts to Clad GETR UC-ZrC Irradiation Test Specimens by Tungsten at San Fernando Laboratories

A slight change in design suggested by San Fernando Laboratories was made to make the cladding process appear more economical (see Fig. 2).

When actual cladding of the carbides to be used in the GETR test was begun, a sequence of unanticipated difficulties in the coating process were encountered. Every carbide reacted in some degree (from slight attack to such severe attack that the carbide turned to powder) either during heating to the plating temperature or during plating. After a number of carbides had been ruined in these attempts to clad (using standard vapor deposition techniques) it became painfully apparent that the process would have to be changed or no satisfactory tungsten coated carbide specimens would be made. It was also apparent that the successful coating of the carbides during the preliminary investigation was due partly to the design (which prevented trapping of corrosive gases inside tungsten preform) and perhaps partly to circumstances in that the plating atmosphere was cleaner than is usual during ordinary tungsten vapor deposition from WF_6.

Changes Made in Equipment at San Fernando Laboratories to Minimize Contamination of Carbide Specimens During Coating

A two week program to develop a suitable method for coating the carbides was started. The first part of the study was to eliminate, as far as was possible, all sources of contamination in the plating atmosphere. The UC-ZrC compositions are all attacked rapidly in moist atmospheres and the attack is accelerated by raising the temperature.

Oxygen also attacks the carbides at even moderate temperatures.

Thus the sources of attack in the plating attempts were suspected to be HF*, WF_6, H_2O, and O_2 and perhaps a combination thereof.

The first step was to minimize contamination of the impure gases H_2, He, WF_6 and eliminate leaks in the plating system (equipment) itself. A liquid N_2 cooled activated charcoal trap was placed in H_2 line. The purest available He was introduced for the purge. Leaks were eliminated (as far as could be determined) in the WF_6 input side and the system itself. The system was rearranged so that the plating chamber and all imput gas lines could be evacuated by a mechanical vacuum pump and that the exhaust lines would be evacuated by the water ejector exhaust ordinarily used for evacuation of the system during plating. This insured that the system would be pumped down to the low micron range before plating and could be purged with the input gases before opening the water ejector valve. The system was also backfilled at least six times with He to dilute any residual contaminants before starting to plate.

Research Done to Develop Satisfactory Method for Tungsten Coating of UC-ZrC Specimens

Tests made showed that the carbides were attacked very rapidly in a HF atmosphere. HF is a product of the deposition process, i.e., $WF_6 + 3H_2 \longrightarrow W + 6HF$. A test was also made holding a 90 UC-10 ZrC specimen in pure WF_6 for 1/2 hour at 650/700°C with no significant attack - some plating occurred (possibly by displacement of carbon) and some discoloration but no serious attack. The above indicated that the entrapment of HF was probably causing the attack. It was decided to introduce some helium to help sweep away the reaction products (i.e. HF).

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*HF is a product of the vapor deposition reaction - $WF_6 + 3H_2 \longrightarrow W + 6HF$.

It was believed that if plating was done at 380°C and HF attack did occur, the resultant product would be volatile UF_6 rather than the powdery UF_4 formed at higher temperatures; and if some attack did occur, it would not impede further plating. X-ray diffraction had shown that at least part of the reaction product in the carbides attacked during plating at 650/700°C was UF_4. It was decided the most logical way to approach the problem was to develop a method for sealing the carbides at as low a temperature as practical with a coating which would prevent attack of the carbide during final encapsulation.

To quickly find a suitable seal coating method (though not necessarily the best possible, although this was preferable) it was decided to try some different gas mixtures and several coating temperatures from 250°C to 650°C. The objective was to determine what conditions would provide: (1) minimal attack on the carbide, (2) a practical deposition rate, and (3) when (1) and (2) were determined the thickness of seal coat required to prevent attack during subsequent encapsulation at higher temperatures.

The specimens, temperatures, gas mixtures, and results are listed in Table I. The specimens were evaluated by metallographic examination of the tungsten-carbide interfaces. Photomicrograph showing attack is No. 3275-1-1 and photomicrographs evidencing no significant attack are Nos. 3273-1-1, 3288-1-1, 3288-1-2, 3274-1-1, and 3289-1-1. The photomicrograph No. 3274-1-1 also show deposition over particles of dust showing surfaces prepared for coating must be dust free.

The above results (Table I) indicated that coating could be done at ~ 350°C to 400°C with no attack on the carbide. Heating of carbides coated at this temperature range (temperature measurement with T.C. in contact with carbide in later tests - first tests with T.C. in contact with graphite holder), with coating thickness of 1-1/2 to 5 mils HF for 1/2 hour at $\sim 700^{o}C$ showed that a .003 mil coating provided adequate protection that the coating had no holes (such as are due to points of contact where carbide rests during plating). Even thicker coatings with breaks in coating were obviously not satisfactory when examined metallographically. The results listed in Table I also indicated that a sufficient flow velocity of gas was required to minimize stay time of the corrosive gases on the carbides to prevent attack. Note that when the Helium was not used to keep incoming gas velocity high, attack on the carbide specimen occurred. Another source of difficulties can be the water ejector pump used to maintain the system at a partial atmosphere during plating. Should the pump pulsating or surging occur during plating - moisture may back up into the plating chamber and the carbide will be destroyed. Should this occur, plating must be stopped immediately.

<u>Procedure Established for Tungsten Vapor Deposition</u>

<u>Cladding of UC-ZrC Emitter Specimens</u>

The procedure established for seal coating the GETR capsules is as follows:

1. Evacuate the system (except for exhaust lines used during plating) with mechanical vacuum pump and leak check.
2. If no evidence of leaks back-fill chamber with helium at least six times to dilute residual atmosphere.
3. Evacuate once more. Check water ejector pump pressure, if all right, then fill to 1/2 atmosphere helium, open water ejector exhaust valve and maintain Helium purge flow of 4 to 5, l/min.
4. Open H_2 inlet valve and let in 2.4, l/min., of H_2.
5. Turn on $WF_6 \sim .3$, l/min.

6. Turn on power, heat to 350/400°C as indicated by thermocouples (simplytrol) and hold at temperature for $\sim$ 45 minutes to produce .003 to .004" thick coat.

7. Shut off power, and WF_6.

8. Allow to cool in H_2 and He stream.

9. Shut off H_2, allow to evacuate, close water ejector exhaust valve, allow to back-fill with Helium and remove part.

The arrangement for seal coating is shown in Fig. 3.

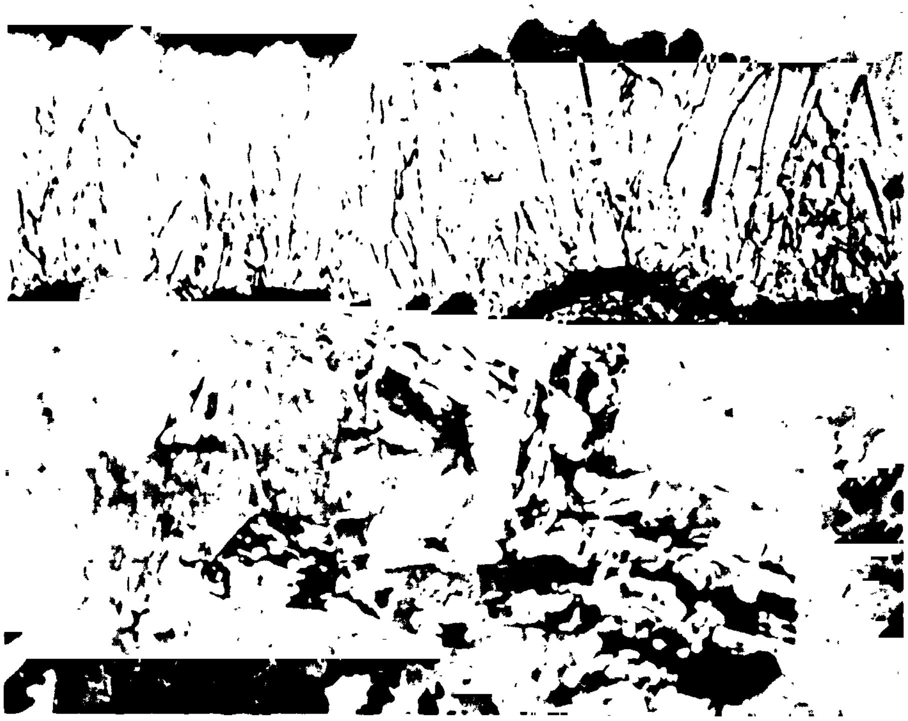
Encapsulation is done at 700°C with other conditions similar as for seal coating except that coating rates at 700°C are approximately 10 times as high as at 350/400°C for sealing. Also a higher H_2 flow rate is used, but no helium purge is used.

The part is always sealed with the grooved end up (see Fig. 3) and encapsulated with the opposite end up (see Fig. 4). This is done so that the thin spots (at parts of contact on holder for plating) are first coated during the encapsulations at 700°C.

A final precaution taken to maximize reliability of the water ejector exhaust system is to flush out the exhaust lines at least once a day to prevent plugging up by fluoride.

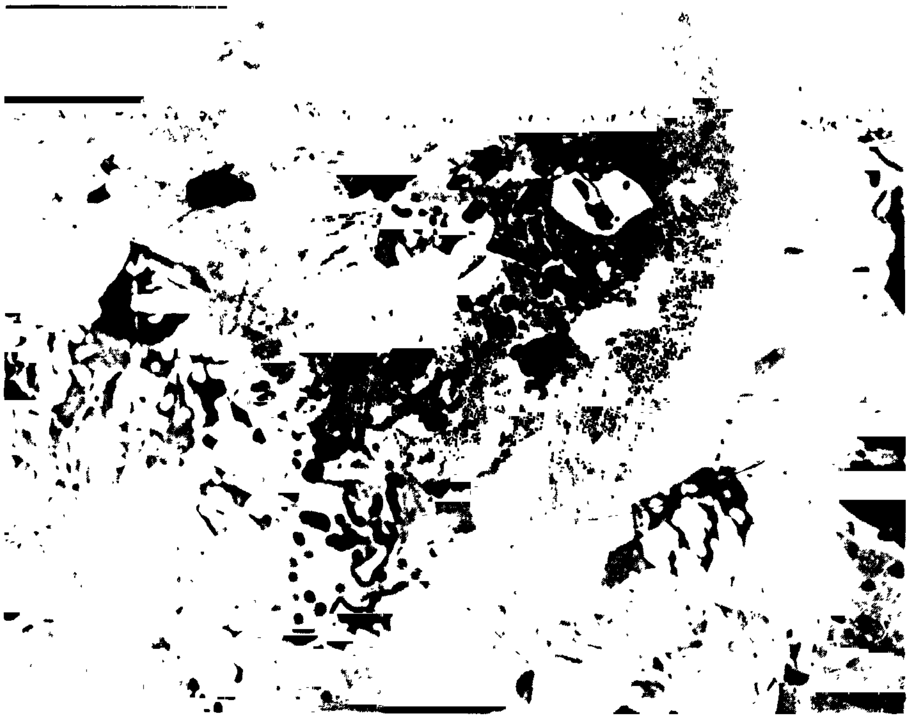
A total of thirty-two specimens were sealed and encapsulated, using the method described above. Most were encapsulated three at a time.

A cross sectional view of a finished tungsten coated specimen is shown in photograph No. M-3749-1-2 and an exterior view of a similar specimen is shown on photographs Nos. M-3757-1-1 and M-3757-1-2.



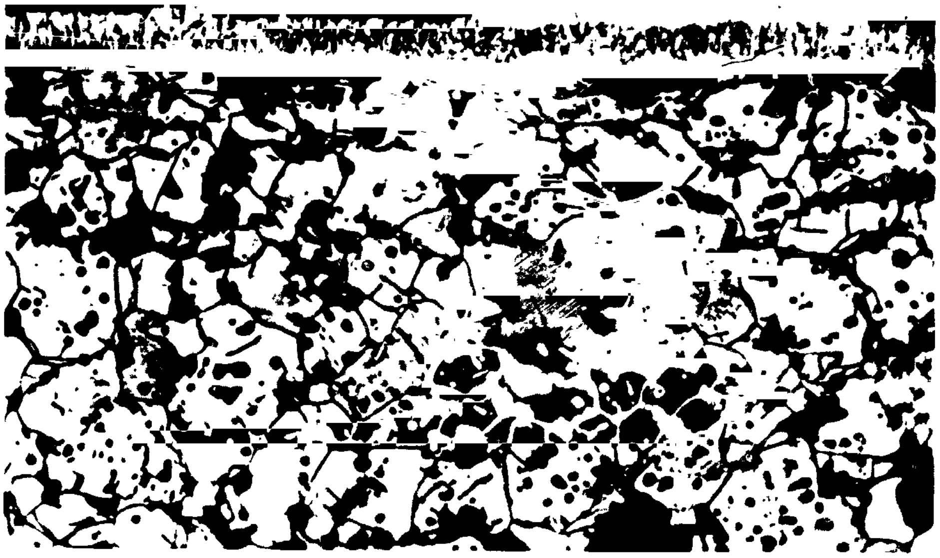
3288-1-2 500X No. 169

90 a/o UC - 10 a/o ZrC Tungsten vapor coated 30 min at 375/415°C, 4.85 l/min He, 1.2 l/min H_2, .3 l/min WF_6. Coating .002 inch thick.



3289-1-1 500X No. 173

90 a/o UC - 10 a/o ZrC Tungsten vapor coated 33 min at 250/260°C, 1.2 l/min H_2, .3 l/min WF_6, no He. Coating .00075 inch thick.

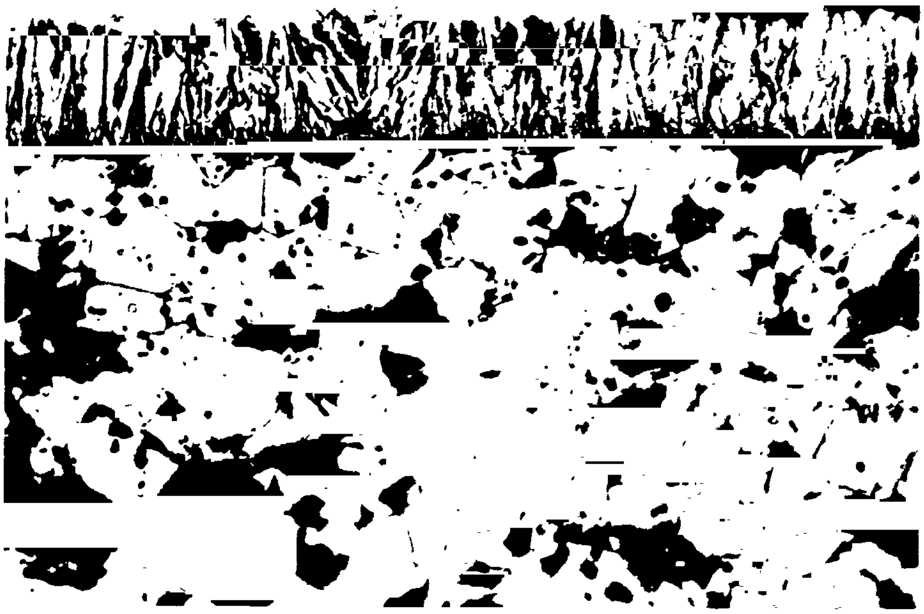


3273-1-1 250X No. 124

90 a/o UC - 10 a/o ZrC Tungsten vapor coated 41 min at 300/375°C, 1.2 l/min H_2, .3 l/min WF_6 , no He. Coating .00125 inch thick.

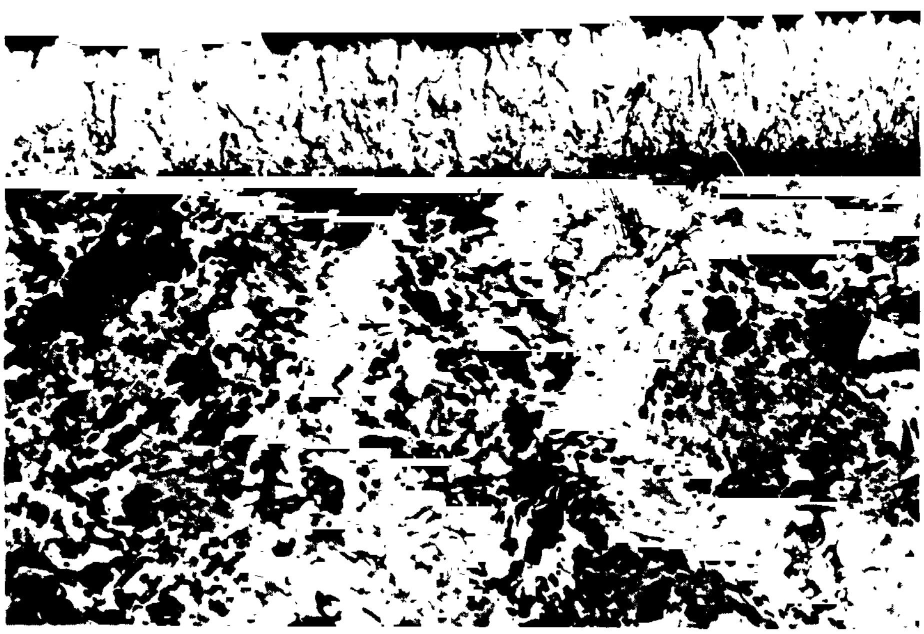
3274-1-1 250X No. 169-A

90 a/o UC - 10 a/o ZrC Tungsten vapor coated 23 min at 435°C, 4.8/5 l/min He, 1.2 l/min H_2, .3 l/min WF_6. Coating .0015 inch thick. Note coating over loose particles on surface of carbide.



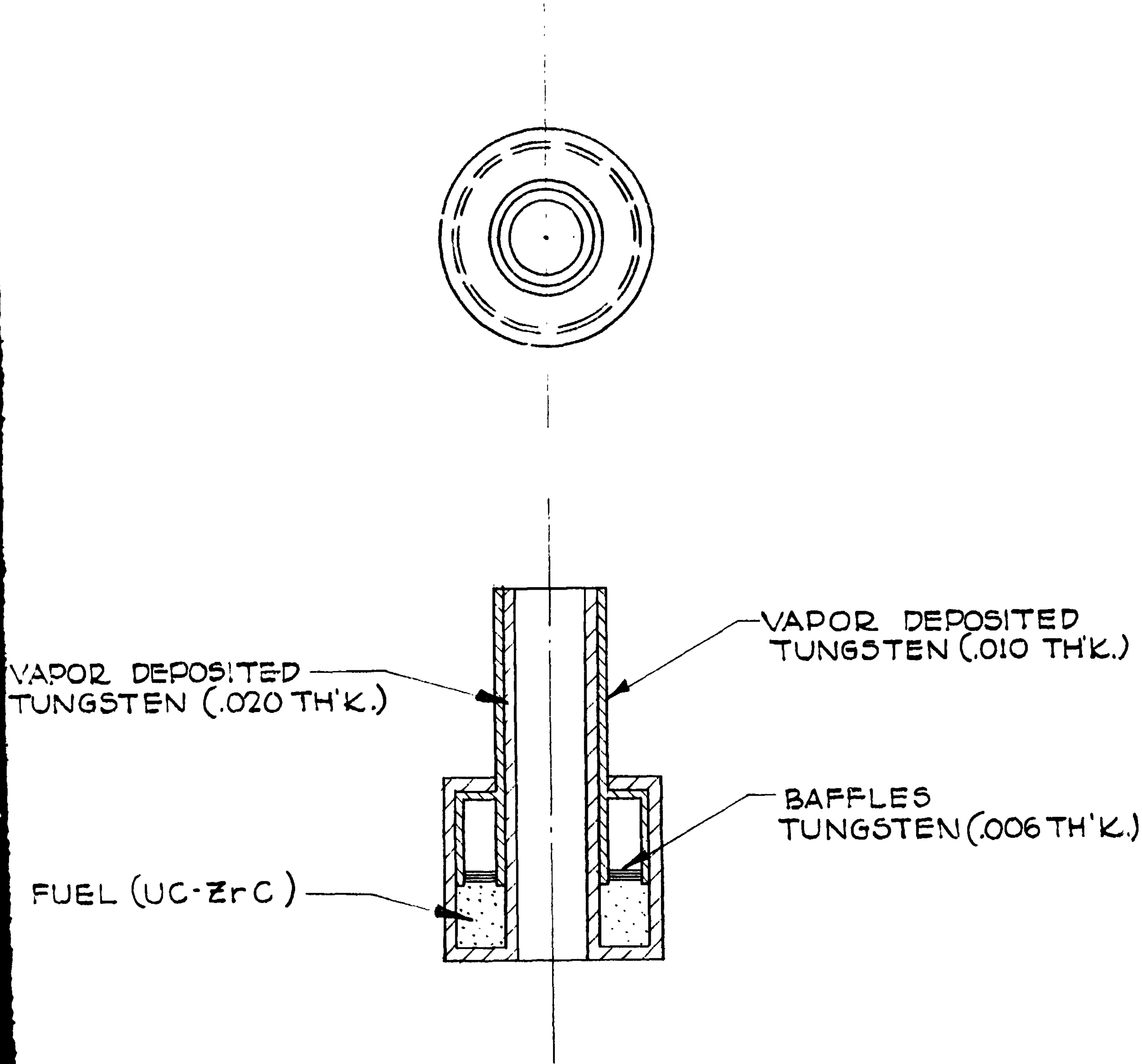
3275-1-1 250X No. 169-B

90 a/o UC - 10 a/o ZrC Tungsten vapor coated 15 min. at 500/625°C, 4.8/5 l/min He, 1.2 l/min H_2, .3 l/min WF_6. Coating .003 inch thick. Note attack of carbide near interface.



3288-1-1 250X No. 169

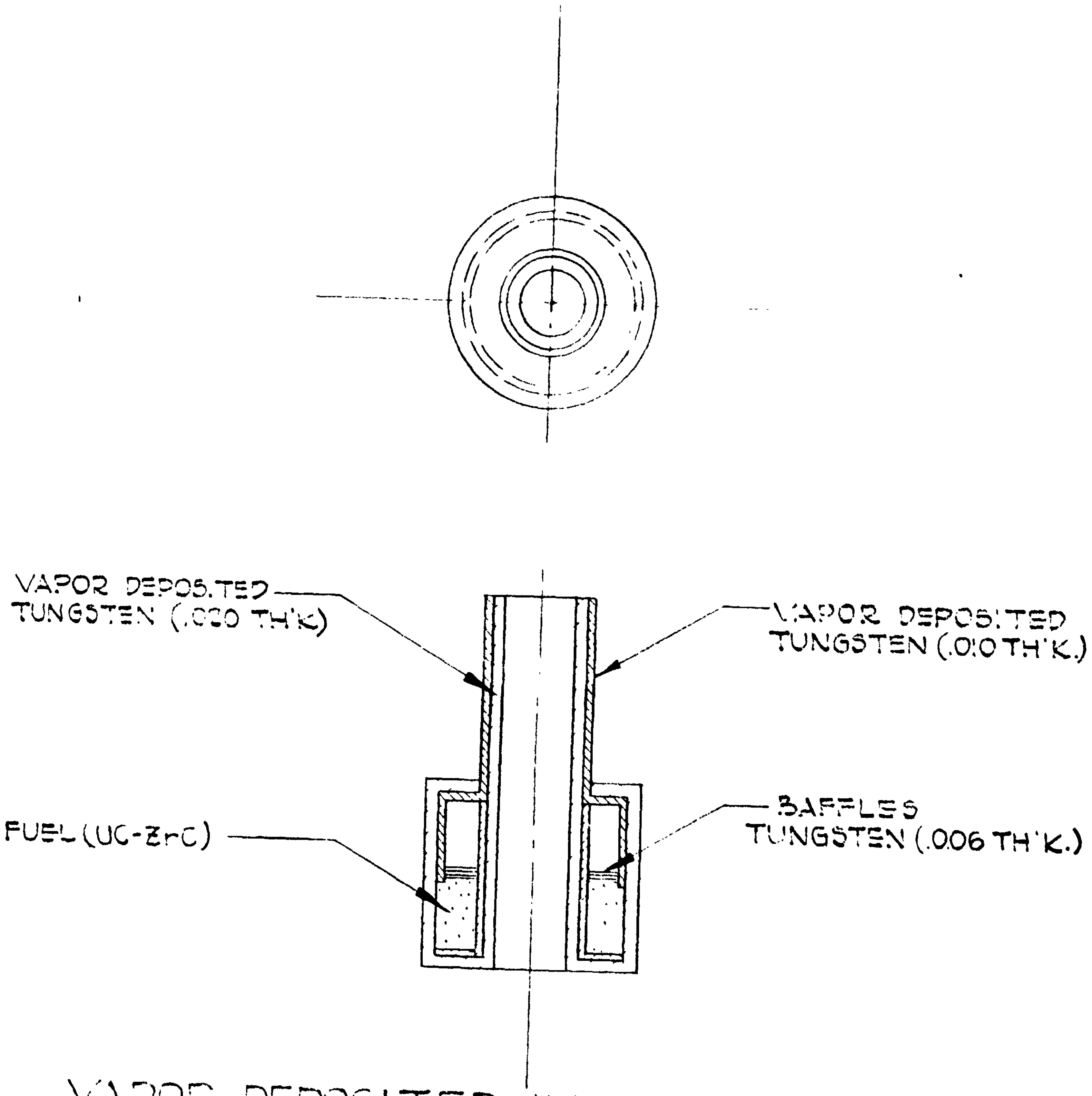
90 a/o UC - 10 a/o ZrC Tungsten vapor coated 30 min at 375/415°C, 4.8/5 l min He, 1.2 l/min H_2, .3 l/min WF_6. Coating .002 inch thick.



VAPOR DEPOSITED W EMITTER

SCALE 4 × 1 APPROX.

Figure 1



VAPOR DEPOSITED W EMITTER

SCALE 4 × 1 APPROX.

Figure 2

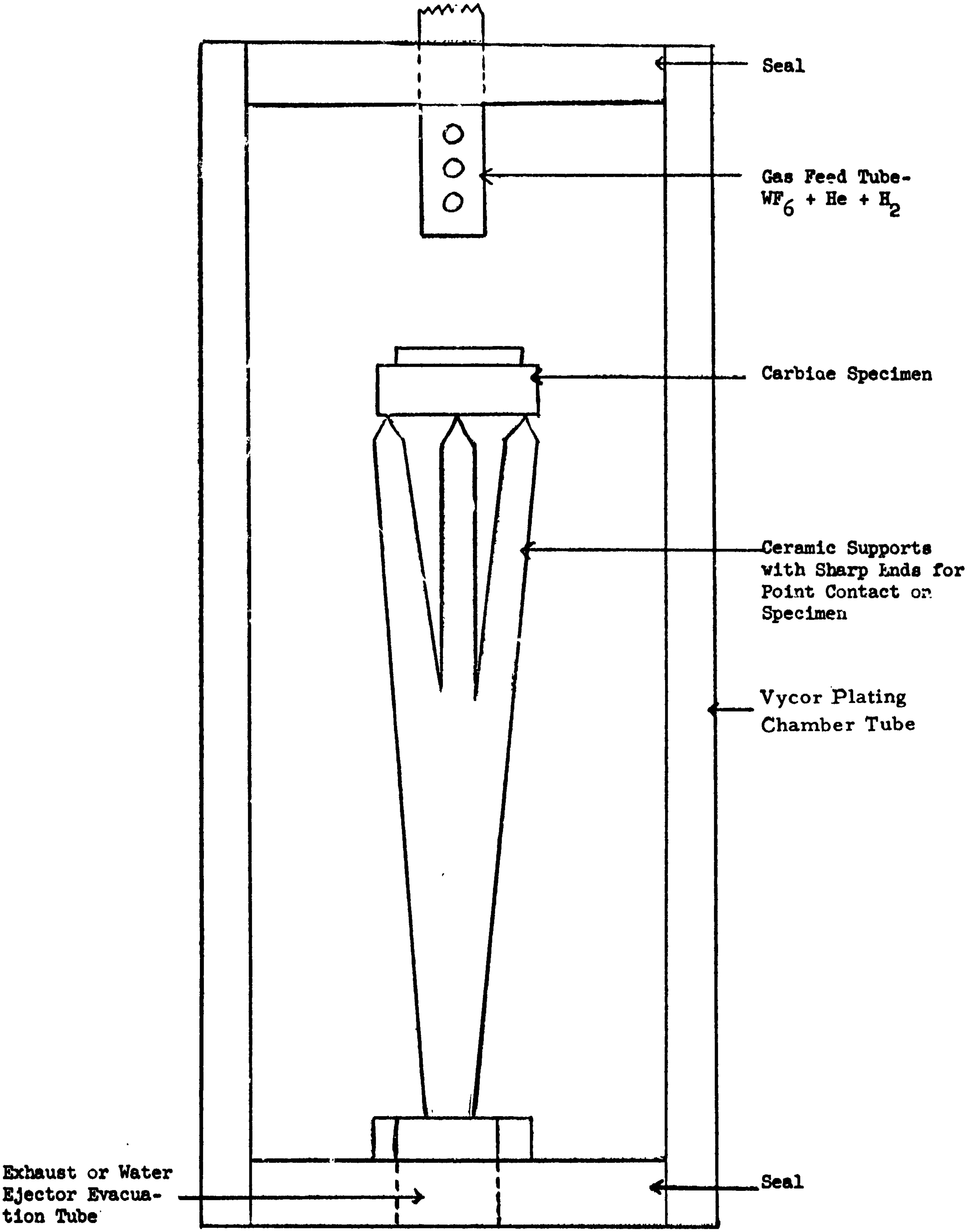


Figure 3 - Arrangement for Seal Coating (Schematics)

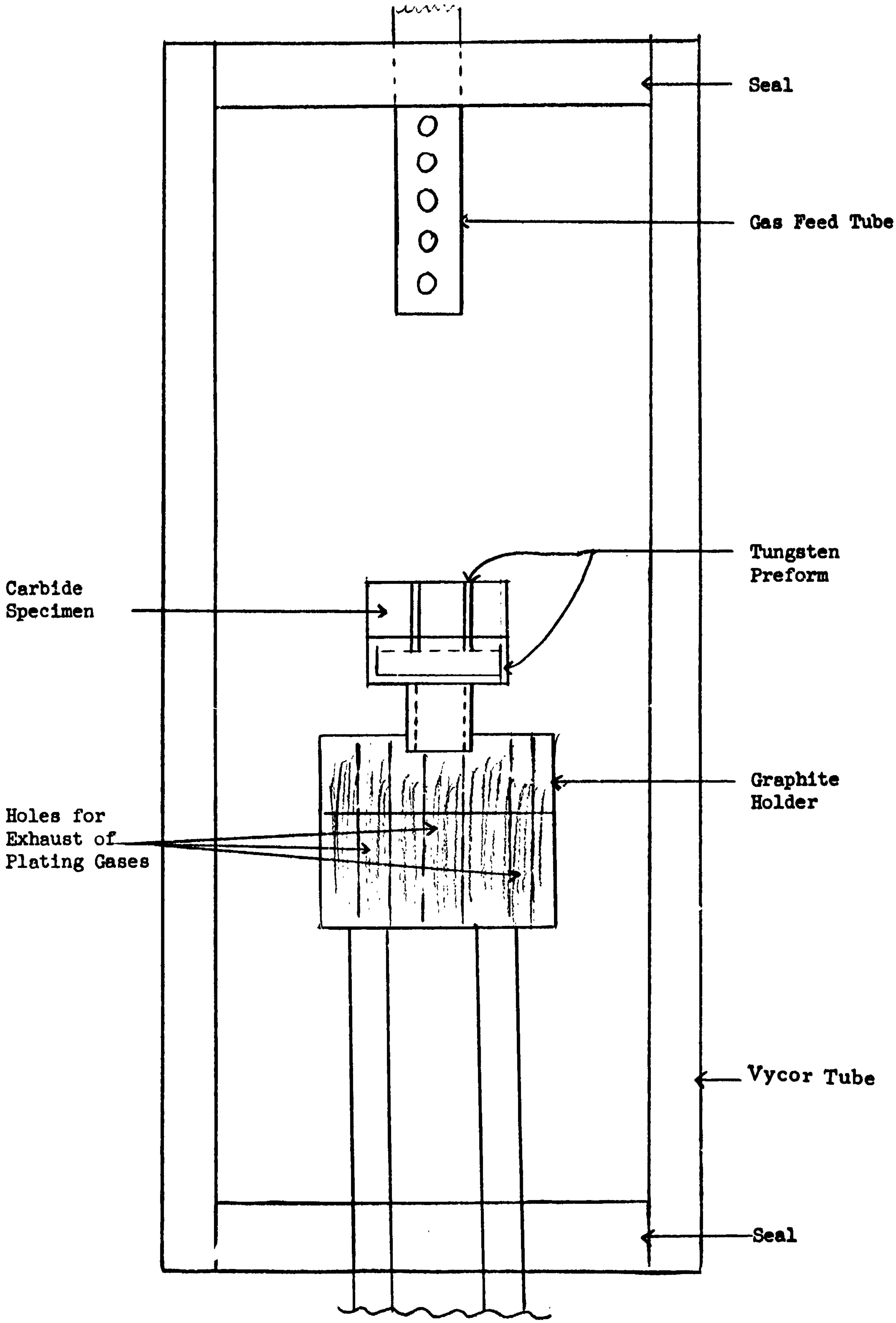


Figure 4 - Arrangement for Encapsulation (Schematics)

TABLE I

Specimen Type	Specimen or Capsule No.	H_2 Rate l/min	He Rate l/min	WF_6 Rate l/min	O. D. Before Plating	O. D. After Plating	Apparent Temp. °C As Indicated T. C.	Plating Time	Increase of Coating Thickness	Photomicrograph	Visual Appearance of Coating After Plating	Remarks and Results of Metallographic Examination
90/10 a/o UC-ZrC	124	1.2	none	.3	.329	.3315 / .332	300/375	41 min	.00125	3273-1-1	O.K.	No significant attack found.
90/10 a/o UC-ZrC	155	1.2	none	.3	.330	-	360/400	14 min	-	-	Specimen was attacked - stopped plating.	
90/10 a/o UC-ZrC	173	1.2	none	.3	.330	.3315	250/260	33 min	.00075	3289-1-1	O.K.	No significant attack found.
90/10 a/o UC-ZrC	132	.2	none	.3	.3303	.333	250	30 min	.0015	-	O.K.	
90/10 a/o UC-ZrC	58	1.2	none	.3	.329	-	-	-	-	-	Water ejector exhaust pump failed, moisture backed up into system part was attacked and disintegrated.	
90/10 a/o UC-ZrC	159	1.2	4.8/5	.3	.330	.338	375/415	30 min	.002	3288-1-1,2	O.K.	No significant attack found.
90/10 a/o UC-ZrC	159A	1.2	4.8/5	.3	.330	.333	435	23 min	.0015	3274-1-1	O.K.	No significant attack found.
90/10 a/o UC-ZrC	159B	1.2	4.8/5	.3	.1375	.1435	500/~625	15 min	.003	3275-1-1	O.K.	Carbide attacked near interface, see photomicrograph
90/10 a/o UC-ZrC	261	1.2	4.8/5	.3	.330	.334	420/475	5 min	.002		Attacked on side sitting flat on graphite holder - point contact needed to prevent gases from being trapped under specimen.	
90/10 a/o UC-ZrC	260	1.2	4.8/5	.3	.330	.333	400	15 min	.0015		O.K.	Subjected to HF at 700°C - fell apart in [illegible]
90/10 a/o UC-ZrC	255	1.2	4.8/5	.3	.330	.334	400	18 min	.002		O.K.	
90/10 a/o UC-ZrC	265	1.2	4.8/5	.3	.330	.336	380/425	28 min	.003		O.K.	Little or no attack (subjected to HF at 700°C for 1/2 hour).
90/10 a/o UC-ZrC	262	1.2	4.8/5	.3	.330	.338	400/405	34 min	.004		O.K.	
UC	268A	1.2	4.8/5	.3	.329	.3395	400/410	40 min	.005		O.K.	Badly attacked - subjected to HF at 700°C for 1 1/2 hour so attack may not have been due to plating.
UC	268B	1.2	4.8/5	.3	.3284	.338	400/420	47 min	.005		O.K.	Flat surface affected less than sides - although attack on sides very slight.
UC	158A	1.2*	4.8/5	.3	.275/.277	.282/.283	300/375	45 min	.003		O.K.	
UC	158B	1.2*	4.8/5	.3	.275/.277	.281/.283	300/375	45 min	.003		O.K.	
UC	FDC A	1.2	4.8/5	.3	.349 .053 thick	.060 thick	300/375	47 min	.0035		Some spots sticking out after plating, otherwise appeared to be O.K.	
UC	FDC B	1.2	4.8/5	.3	.350 .052 thick	.056/.057 thick	300/375	47 min	.0025		O.K.	

* No H_2 purge initially let in WF_6 and allowed to coat 5 min by displacement - surface light and dark, then let in H_2 and dark spots were covered up in several minutes.