

AD-A075 066

FULMER RESEARCH INST LTD STOKE POGES (ENGLAND)

F/6 9/1

FIELD EMISSION COLD CATHODE DEVICES BASED ON EUTECTIC SYSTEMS.(U)

JUL 79 D STEWART , P D WILSON , V G RIVLIN

AFOSR-77-3292

UNCLASSIFIED R744/2

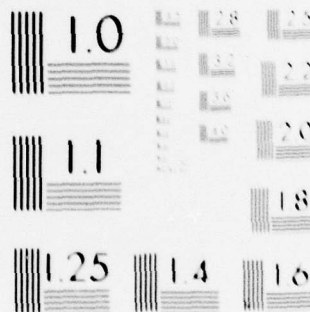
RADC-TR-79-170

NL

| OF |
AD
A075066



END
DATE
FILMED
3-80
DDC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AD A075066

RADC-TR-79-170

Interim Report

July 1979



FIELD EMISSION COLD CATHODE DEVICES BASED ON EUTECTIC SYSTEMS

Fulmer Research Limited

Duncan Stewart
Paul D. Wilson
Vivian G. Rivlin

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED

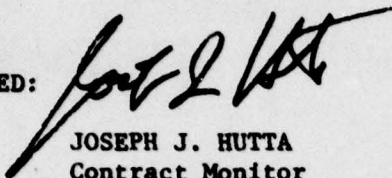
**ROME AIR DEVELOPMENT CENTER
Air Force Systems Command
Griffiss Air Force Base, New York 13441**

79 10 12 005

This report has been reviewed by the RADC Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be releasable to the general public, including foreign nations.

RADC-TR-79-170 has been reviewed and is approved for publication.

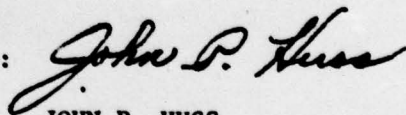
APPROVED:


JOSEPH J. HUTTA
Contract Monitor

APPROVED:


ROBERT M. BARRETT
Director
Solid State Sciences Division

FOR THE COMMANDER:


JOHN P. HUSS
Acting Chief, Plans Office

If your address has changed or if you wish to be removed from the RADC mailing list, or if the addressee is no longer employed by your organization, please notify RADC (ESM), Hanscom AFB MA 01731. This will assist us in maintaining a current mailing list.

Do not return this copy. Retain or destroy.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER RADC-TR-79-170	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) FIELD EMISSION COLD CATHODE DEVICES BASED ON EUTECTIC SYSTEMS	5. TYPE OF REPORT & PERIOD COVERED Interim Report 1 May 77 - 30 April 78	
	6. PERFORMING ORG. REPORT NUMBER R744/2	
7. AUTHOR(s) Duncan Stewart Paul D. Wilson Vivian G. Rivlin	8. CONTRACT OR GRANT NUMBER(s) AFOSR-77-3292	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Fulmer Research Institute Limited Hollybush Hill Stoke Poges Slough SL2 4QD	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 62702F 46001722	
11. CONTROLLING OFFICE NAME AND ADDRESS Deputy for Electronic Technology (RADC/ESM) Hanscom AFB MA 01731	12. REPORT DATE July 1979	
	13. NUMBER OF PAGES 32	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Same	15. SECURITY CLASS. (of this report) UNCLASSIFIED	
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE N/A	
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) Same		
18. SUPPLEMENTARY NOTES RADC Project Engineer: Joseph J. Hutta (ESM)		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Whisker composites, eutectic systems directional solidification pseudo-binary eutectic systems cold cathodes Fowler-Nordheim functions refractory compounds field emission thermodynamic stabilities		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A survey has been made of the performance as field emission cold cathodes of selected refractory materials fabricated as needle arrays by unidirectional solidification. Specially designed apparatus was used to observe the operating lifetimes and Fowler-Nordheim functions of needle arrays of niobium carbide, tantalum carbide in a nichrome matrix and of a $\gamma/\gamma' - \alpha$ eutectic in the Ni Mo Ta Al system. The results are co-related with SEM observations. Thermodynamic stabilities under the operating conditions are discussed.		

DD FORM 1 JAN 73 1473

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

TABLE OF CONTENTS

	Page
1. INTRODUCTION	5
1.1. Cold Cathodes: previous work	6
1.2. Present Position	8
1.3. Selection of Materials	9
2. EXPERIMENTAL METHODS	11
2.1. Cathode Fabrication	11
2.2. Test Chamber	12
2.3. Materials	12
3. RESULTS	13
3.1. Fowler-Nordheim Equation	14
3.2. γ/γ' - α Materials (A77-205)	14
3.3. Tantalum Carbide	15
3.4. Niobium Carbide	16
4. DISCUSSION	16
4.1. Thermodynamic Stabilities	16
4.1.1. Carbides	17
4.1.2. Borides	19
4.1.3. Nitrides	20
4.2. Emitter Geometry	21
4.3. Sputtering Damage - ion bombardment	21
4.4. Comparison of Materials	21
REFERENCES	23,24
FIGURES 4 - 15	

LIST OF FIGURES

1. TaC eutectic cathode in test diode.
2. Stainless steel chamber used for evaluating cathodes.
3. Cathode assembly in stainless steel vacuum chamber.
4. A-77-205 x 900
5. A-77-205 x 10K
6. A-77-205 x 10K
7. A-77-205 x 2K
8. Fowler-Nordheim plots with materials A77-205 as the cathode and at the anode-to-cathode separations shown.
9. TaC cathode x 500
10. Fowler-Nordheim plots with TaC as the cathode and at the anode-to-cathode separations shown.
11. TaC before testing x 2K
12. TaC before testing x 10K
13. TaC after testing x 5.5K
14. NbC cathode before testing x 730
15. NbC cathode before testing x 2.9K
16. Fowler-Nordheim plots with NbC as the cathode and at the anode-to-cathode separation shown.

PRECEDING PAGE BLANK - NOT FILMED

LIST OF TABLES

		PAGE NO.
TABLE 1	METAL REACTION PRESSURES OF CARBIDES, ACCORDING TO REACTION 4.	17
TABLE 2	METAL REACTION PRESSURES OF SELECTED CARBIDES, ACCORDING TO REACTION 4.	18
TABLE 3	CARBON REACTION PRESSURES OF CARBIDES OF Ta AND W, ACCORDING TO REACTION 5.	18
TABLE 4	METAL REACTION PRESSURES OF BORIDES, ACCORDING TO REACTION 6.	19
TABLE 5	BORON REACTION PRESSURES OF BORIDES, ACCORDING TO REACTION 7.	19
TABLE 6	NITROGEN REACTION PRESSURES OF NITRIDES, ACCORDING TO REACTION 8.	20

PREFACE

This report describes the experimental work carried out upon refractory materials mainly chosen according to the criteria set out in the previous report (R744/1). It was decided to concentrate efforts upon the carbides of niobium and tantalum and, further, to carry out some experiments on a complex eutectic system (Nb-Mo-Ta-Al). All samples were provided by other laboratories. The needle array format for testing was obtained by etching back chemically the matrix supporting the refractory fibres. The fibres were then etched further to obtain points.

All samples were tested in a stainless steel chamber to ascertain Fowler-Nordheim functions. Life tests at low operating currents are being carried out for up to 1000 hours but are not yet complete. After testing, little damage was found to the carbide which could be attributed to operating conditions.

The results are reviewed in terms of field emitter geometry and thermodynamic stabilities of the refractory compounds.

1. INTRODUCTION

Previous work at Fulmer has given results for tantalum carbide needle arrays in a nickel-chromium matrix. Fowler-Nordheim plots for the needle arrays indicate a performance comparable to or better than that of tungsten needle arrays.

The aim of this research is to select and test metallurgical systems with refractory components, say carbides, for their potential as cold cathode needle arrays.

A prerequisite to the research is the location of suitable metallurgical systems with a eutectic reaction between the refractory component and a conducting metal. It is then necessary to assess the likelihood of these systems being suited to fabrication of needle arrays by plane-front unidirectional solidification at practical temperature gradients and solidification rates to give a rod-like morphology.

A literature search has been undertaken under the headings

1. Phase equilibria
2. Unidirectional solidification
3. Physical properties of refractory compounds.
4. Field emission.

To simplify the choice of systems the search was restricted to alloys containing one or more of the non-metallic elements carbon, boron or nitrogen and to the transition metallic elements from Groups IVA, VA and VIA and to rhenium (Group VIIA):

IVA	VA	VIA	VIIA
Ti	V	Cr	-
Zr	Nb	Mo	-
Hf	Ta	W	Re

Most of these are known to form very high-melting carbides, borides and nitrides. Furthermore, recent research has uncovered numerous cases of eutectic equilibria in which these refractory compounds are components.

Intermetallic phases have been disregarded, partly in consequence of their relatively low melting points but also because they are expected to be inferior to the refractory compounds in their stability to ion damage especially at, a pressure of, say, 10^{-7} torr.

Choice criteria for the properties of needles and matrix are:

Needles

1. Melting point over 2000°C .
2. Low vapour pressure.
3. High strength, i.e. stiffness.
4. Low sputter yield, i.e. resistant to ion damage.
5. Electrically conducting - need not be metallic.
6. Chemically inert (permitting selective etching of matrix).
7. Low work function.

Matrix

1. Melting point over 800°C .
2. Low vapour pressure at $\sim 500^{\circ}\text{C}$
3. Amenable to selective etching.

1.1. Cold Cathodes : previous work

The advantages of operating field emission cold cathodes in place of conventional thermal cathodes have been discussed extensively by Charbonnier et al. in 1963⁽¹⁾. Recently, Considine and Balsiger⁽²⁾ have summarised the advantages of using field emission sources in high density small diameter electron beams. Shelton⁽³⁾ and Wardly⁽⁴⁾ have outlined other applications for cathodes of this type. It is not intended to discuss in detail the relevant properties of these cathodes but the major advantages may be summarised as:

(1) A cold cathode does not require a heater to emit electrons and therefore the associated tube technology can be simplified.

(2) The absence of a heater gives instant start, eliminating the time delay encountered during switch-on of a thermal cathode. Also, failure due to heater burn-out is prevented.

(3) The mechanical robustness of the cathode is improved.

The progress in the development of cold cathodes has been limited however by the materials available for their manufacture. Previous work⁽⁵⁾ has concentrated upon using tungsten as the emitting needle (or point) both as a multi-pin array or as a discrete single point emitter of the type used in electron microscopes and some data display tubes. The limitation with tungsten however had been the need for an ultra high vacuum environment, typically 10^{-9} torr, in order, for example, to reduce damage by ion bombardment. Recent attempts⁽⁶⁾ ⁽⁷⁾ to use carbon fibre cathodes have not been very successful due to the 'noise' generated by the fibre. However, work in Japan⁽⁸⁾ ⁽⁹⁾ claims that a single fabricated point of titanium carbide works satisfactorily at pressures of 10^{-6} torr, and this pressure range is well within the limits of current tube technology. A further advantage of being able to operate under a poorer vacuum is in the area of electron microscopy. Here the current practice is to use a tungsten emitter operating at 10^{-9} torr which requires an expensive differentially pumped ultra high vacuum system.

Materials which have properties similar to those of titanium carbide therefore appear to have potential as single point emitters and as broad sources for use in devices operating at higher power.

An Attractive method of producing multi-point arrays of fine points, potentially useful for electronic applications, is by the directional solidification of suitable eutectic alloys. The

development of directionally solidified eutectic alloys has expanded considerably over recent years to produce materials for use in high-temperature gas turbines. These materials, principally refractory metal carbides, have been studied extensively to produce composites of high strength and corrosion resistance suitable for use as turbine blades. Examination of some of these alloys has revealed interesting structures which clearly lend themselves to fabrication of cold cathodes needle arrays.

1.2. Present Position

At present very little work is being undertaken on field emission cold cathodes. A limited examination of the devices was made by Baker⁽⁶⁾ and Lea⁽¹⁰⁾ using carbon fibres. Ferranti Limited have examined carbon fibres for use in an emission modulated amplifier, and Fulmer has made a small number of 'first attempt' eutectic cathodes for evaluation in this device.

In the US work is being carried out using directionally solidified eutectics at the Georgia Institute of Technology⁽⁵⁾ where current densities of 0.5 A/cm^2 at voltages between 3 to 5 kV have been obtained from tungsten needles in W/UO_2 and W/ZrO_2 composites.

In life tests, 3,000 hours of operation at 100 mA/cm^2 has been obtained and the ability of these materials to withstand pulsed operations up to 100 kV has been demonstrated⁽²⁾. Further work in the US using oriented tungsten needles has been concentrated at Linfield Research Institute⁽¹¹⁾ and at the Oregon Graduate Centre⁽¹²⁾ and the field emission of electrons from Mo cones produced by vacuum deposition has been studied by Spindt at Stanford⁽¹³⁾.

Materials development work on the production of directionally solidified eutectics for aircraft turbine blades has revealed an interesting series of alloys. These are basically a series of refractory carbide fibres, e.g. NbC and TaC which are grown in an electrically conducting metal matrix such as Co, Ni, or Cr. These fibres are typically 1 - 2 microns in diameter and can be

pointed to enhance the field emission. Melting points in excess of $2,000^{\circ}\text{C}$ can be achieved in these materials and the sputter yield is low.

These materials should therefore be superior to the tungsten-based composites and possess properties very similar to those of titanium carbide.

Preliminary results on the emission properties were obtained at Fulmer on the directionally solidified eutectic TaC fabricated into a cathode approximately 1 mm in diameter to demonstrate the feasibility. A current of 3 mA at an extraction voltage of 10 kV was obtained (Figure 1) in a sealed-off test diode.

1.3. Selection of Materials

The literature survey carried out at the early stages of this project (R744/1, ref. 14) was concentrated, at first instance, upon the refractory carbides, borides and nitrides. A review of the physical properties of these refractories, based on the transition metals from Groups IVA, Va, and VIA, showed that numerous candidate materials were to be found which met many of the minimum requirements of high melting point, low vapour pressure, low electrical resistivity (not necessarily metallic conductance), etc. (15 - 20, 23). The crucial parameter, field emission work function, is not well-documented and in consequence, the wide choice of candidate materials (listed in Tables 1 - 3 of ref. 14) had to be reviewed by means of additional criteria based in known phase equilibria, unidirectional solidification and upon thermodynamic stabilities. The binary carbides and borides were frequently to be found in one or more eutectic equilibria in their respective binary phase diagrams while nothing is known of the nitrides (Tables 4 - 5, ref. 14). Again there are many ternary and higher systems in which the binary borides and carbides crystallize by eutectic reactions - i.e. pseudo-binary systems (Tables 6 and 7, ref. 14). The literature on unidirectional solidification is now sufficiently comprehensive to show that the eutectic binary, ternary and higher systems of the carbides and, possibly, borides are amenable to unidirectional solidification giving the rod-like morphology

requisite for needle arrays in cold cathodes (Tables 9 - 11).

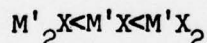
The carbides of Nb, Ta and V are examples.

Very little useful information on the phase constitution of the nitrides has been found (see Table 8, ref. 14).

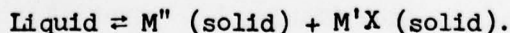
The properties of the matrix are less critical - preferential etching being one of the more important - and this allows a wide range of systems. The final choices were made from the following classes of system:

Binary eutectic	$M' - C$	$M' - B$
Ternary eutectic (pseudo-binary)	$M' - M'' - C$	$M' - M'' - B$
Quaternary eutectic	$M' - M'' - M''' - C$	$M' - M'' - M''' - B$

Here M' is a metal from our list of transition metals and forms a binary boride or carbide, while M'' and M''' may be chosen from a wider range of metals. In the binary compounds it frequently happens that M' forms more than one compound with boron or carbon and that the stability of the compound increases with increasing non-metal content, e.g.



For directional solidification in a binary system the eutectic equilibrium must be between the parent metal, M' , and the refractory component. Since the least stable compound M'_2X tends to be in equilibrium with M' , such binary systems are less suitable than pseudo-binary systems between the more stable $M'X$ or $M'X_2$ and M'' . Hence $M' - M'' - X$ compounds appear more promising provided eutectic equilibria of the following type can be found:



Literature on unidirectional solidification has many examples of this type of equilibrium, wherein the refractory component has the rod-like morphology suitable for fabrication of needle arrays. (see ref.14).

Further criteria of selection have been developed in the literature survey which are based on thermodynamic data. A ranking order of

the carbides and borides has been found by tabulating the metallic reaction pressures at some chosen temperature. According to this tabulation, borides and carbides are roughly comparable in stability but the borides are not sufficiently well documented for detailed comparison. The carbides may be ranked in stability as follows:



Nitrides are found to have too high reaction pressure and when this is taken into account together with the paucity of information on phase equilibria and other shortcomings, they are excluded from consideration.

The final short list of candidate materials is proposed in the following order:

1. $\text{Nb}_2\text{C}/\text{Nb}$; NbC/Co ; NbC/Ni ; $\text{NbC}/(\text{Co}, \text{Cr}, \text{Ni})$
2. TaC/Co ; TaC/Ni ; $\text{TaC}/(\text{Co}, \text{Cr}, \text{Ni})$
3. HfC/Ni ; HfB_2/Cr ; TaB_2/Cr

It is not yet known if suitable eutectic equilibria exist in Group 3.

2. EXPERIMENTAL METHODS

2.1. Cathode Fabrication

The ideal requirement of a field emission cathode is an array or area of equispaced points of uniform height above a surface and having a uniform tip radius. In this manner an applied field across each of the points will be uniform and hence an electron current can be extracted from each point.

With a directionally solidified eutectic structure, the ideal uniformity is never achieved; the fibres vary in diameter and the spacings between the fibres are not constant. However, the large number of fibres present ensures that some fibres experience a sufficiently high field to cause electron emission. This high field is produced by either the tip radius being very small or, alternatively, the separation of the fibres being large or a combination of these two geometric effects. Deterioration of one of the fibres by ion

bombardment, or another process, causing emission to stop, and a change in its physical shape, results in an increased field being generated on an adjacent fibre. The principle of fabrication of the emitter is to etch back chemically the matrix supporting the fibres and then by using a further etchant to remove material from the fibres to produce pointed ends. Sizes of the individual cathodes are given later.

2.2. Test Chamber

The vacuum test chamber used for evaluating the eutectic cathode is shown in Figures (2) and (3). The stainless steel chamber was pumped using a polyphenol ether based oil diffusion system for the evaluation of test cathodes. An electron bombardment filament was operated prior to the cathode test, to increase the temperature of the cathode to 500°C and complete the outgassing of the cathode. The specimen support arm could be moved vertically from outside the chamber and hence change the anode/cathode separation during a cathode test if required. A Brandenburg high voltage D.C. power supply of 10 kV, 10 mA with 0.05% ripple at full output was used for the tests and the diode current measured using a Keithley Electrometer connected to the copper anode.

2.3. Materials

The eutectic samples tested to date have been received from the sources listed below; sizes of the specimens tested are given later. The alloys listed below are nominal compositions but have not yet been analysed, with the exception of A77 - 205.

<u>Material</u>	<u>Composition</u>	<u>Source</u>
γ/γ' - α (Ni(Ni ₃ Al-Mo) (A77 - 205)	Ni-31.8 w/o-3.0 w/o Ta -5.5 w/o Al	F.D. Lemkey, UTRC East Hartford, Conn. U.S.A.
NbC	Ni-18 w/o Cr-10 w/o NbC	J. Billingham, Cranfield Inst., Bedford, U.K.
TaC	Ni-10 w/o Cr-16 w/o TaC	F.G. Wilson, Palmer Research Inst., Stoke Poges, U.K.

Electron microprobe measurements of the A77 - 205 material gave the following results for the composition of fibres and matrix in weight %:-

	<u>Fibres</u>	<u>Matrix</u>
Ni	27.9	70.1
Mo	65.7	20.8
Ta	2.0	2.8
Al	4.5	6.2

The microprobe beam is of the order of 1 μ m diameter and since the fibre diameters are of the same order the resolution between fibre and matrix is not good and the overlap must be expected to reduce the accuracy of the analysis.

3. RESULTS

The current test programme contains results which are only preliminary ones obtained from fragments of material from different sources. The specimen sizes used so far have been determined by the material available rather than the ideal shape selected. However, these initial experiments have produced worthwhile results and help to formalise the experiment now in progress.

3.1. Fowler-Nordheim Equation

The emission characteristics of a field emission cathode are governed by the Fowler-Nordheim ⁽²⁴⁾ equation.

$$J = \frac{1.54 \times 10^{-6} F^2}{\phi t(y)} \exp \left(\frac{-6.83 \times 10^7 \phi^{3/2} V(y)}{F} \right) \text{ Acm}^{-2}$$

where F is the field strength in V/cm

ϕ is the work function of the cathode in eV, $t(y)$ and $V(y)$ are tabulated ⁽²⁵⁾ (slowly varying) functions of $y = 3.79 \times 10^{-4} F^{1/2} / \phi$

The slope of the Fowler-Nordheim (F-N) equation is

$$\frac{d(\log_{10} J/F^2)}{d(1/F)} = 2.98 \times 10^7 \phi^{3/2} S(y)$$

where $S(y)$ is a tabulated function of y . As the applied field (F) is directly proportional to the applied voltage (V) assuming the geometry and the work function of the cathode does not change during testing, a plot of $\log_{10} (I/V^2)$ versus $1/V$ will produce a straight line provided field emission is the dominant charge carrier and that space charge* does not occur. The results are plotted as Fowler-Nordheim functions of $\log_{10} (I/V^2)$ against $1/V$.

3.2. $\gamma / \gamma' - \alpha$ Material (A77-205)

This specimen was an 0.78 cm diameter cylinder oriented so that the face of the cylinder was parallel to the copper anode.

* Space charge effects are associated with electrons in the interelectrode space, which at high volume densities effects the structure of the external field, changing the electron path.

The structure of the cathode is shown in Figures (4) and (5) before testing. The structure shown in Figure (6) is an area of the cathode at the completion of the test runs.

This test lasted a total of 50 hours when run at varying emission current up to the onset of arcing. Figure (7) shows an area of the cathode where arcing has occurred but no overall deterioration in the performance of the cathode was apparent resulting from the arcing.

The Fowler-Nordheim (F-N) plots for this composition are shown in Figure (8) at two anode to cathode separations of 0.5 and 1.0 mm.

The maximum current obtained was $2.5 \times 10^{-3} \text{ A}$, corresponding to a current density of $5.2 \times 10^{-3} \text{ A cm}^{-2}$ at an extraction voltage of 10kV.

3.3 Tantalum Carbide

This specimen was machined to a right circular cylinder 1 mm in diameter prior to etching of the matrix to expose the fibres. It proved impossible to maintain the cylindrical geometry during the etching which resulted in the specimen becoming cone shaped at the end as shown in Figure (9). This specimen shape was finally tested but the overall emitting area was difficult to estimate. After testing, an emitting area of $2.56 \times 10^{-5} \text{ cm}^2$ was measured from the scanning electron microscopy examination. This area could be in error since it was not possible to be certain of the exact emitting area.

The F-N plots for this cathode are shown in Figure (10) at anode-to-cathode separations of 1 and 2.2 mm. Marked deviation from the linear F-N plot occurs at both separations showing that probable space charge effects are starting when $1/V$ is approximately 4. Figures (11) and (12) show the fibres before testing in the cathode.

The deterioration of the fibres is shown in Figure 13 where the apparent melting of the fibre ends has occurred, producing a dome. It is not possible to decide at this stage however, if the domes at the ends of the fibres are caused by the melting of the fibres or if they are associated with high voltage arcing. The maximum current obtained was 8×10^{-4} A at 10 kV corresponding to a current density of 31 A cm^{-2} assuming an emitting area of $2.56 \times 10^{-5} \text{ cm}^2$.

3.4. Niobium Carbide

The niobium carbide material was square-shaped approximately $1.7 \times 1.7 \text{ mm}$. During the etching of this material the square geometry was maintained. The fibres proved impossible to etch to fine points and were eventually tested as shown in Figures (14) and (15). The cathodes operated satisfactorily producing the F-N plot in Figure (16). Examination of the cathode after testing for 50 hours has shown no significant deterioration of the cathode. The only areas of damage are small regions where an arc has occurred removing the fibres.

The maximum current obtained was 3.56×10^{-4} A and corresponded to a current density of $1.3 \times 10^{-2} \text{ A cm}^{-2}$. For this test however an extraction voltage of only 7kV was used since it was required to avoid damage to the array so that a life test could be made to the cathode. This test is currently underway.

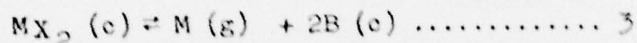
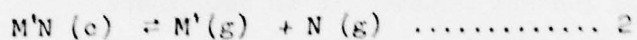
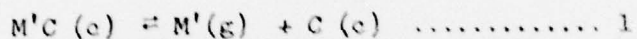
4. DISCUSSION

4.1. Thermodynamic Stabilities

These have been referred to in the Introduction and in the previous report (ref. 14) and are based on refs. 17 and 21. Since the work of assessing reaction pressures was completed further studies, carried out on our behalf by Drs. T.G. Chart and T.I. Barry (22), have extended and confirmed our first conclusions. For convenience when comparing our results with those of the NPL some of the material from the previous report is reproduced here.

Reaction pressures in this report are quoted in atmospheres and not, as hitherto, in torr.

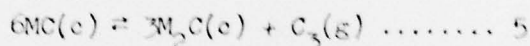
Our initial assessment postulated simple and intuitively obvious decomposition at 3000K (an assumed operating temperature)



(c = crystalline phase g = gaseous phase)

The NPL analysis of carbides, borides and nitrides takes into account several possible reactions for each of the three classes of materials.

4.1.1. Carbides



Calculations for the carbides of metals from Groups IVA, VA and VIA are based on the first reaction are set out in the following table for three different temperatures

TABLE 1 METAL REACTION PRESSURES OF CARBIDES ACCORDING TO REACTION 4

Group	Carbide	Log ₁₀ (Reaction Pressure) of Metal, M ₀ , atmospheres		
IVA		1000K	2000K	3000K
	TiC	-25.9	-9.0	-3.5
	ZrC	-34.4	-13.4	-6.4
VA	VC	-23.8	-7.8	-
	NbC	-36.7	-14.4	-7.0*
	TaC	-40.7	-16.8	-8.8
VIA	Cr ₃ C ₂	-14.6	-4.0*	-
	WC	-38.8	-15.5	-7.6

* Values determined by extrapolation beyond the temperature range of reliability.

The figures indicate that if, as seems to be the case, 3000K is on the high side then decomposition will be very low at normal operating temperatures which may be below 1000°C.

Good agreement between NPL and FRI figures can be seen where comparisons are possible, for example:

TABLE 2 METAL REACTION PRESSURES OF SELECTED CARBIDES, ACCORDING TO REACTION 4.

Candidate Material	Log ₁₀ (Reaction Pressure) of Metal, M', at 3000K, in atmospheres.	
	FRI (14)	NPL (22)
TaC	-8.77	-8.8
ZrC	-6.28	-6.4
NbC	-6.00	-7.0
HfC	-5.74	-
TiC	-3.56	-3.5
VC	-2.88	-

A comparison has been made of WC and TaC according to the second reaction for carbides which postulates the participation of Ta₂C or W₂C in the decomposition reaction. The results are presented in terms of the reaction pressure of gaseous carbon in equation 5.

TABLE 3 CARBON REACTION PRESSURES OF THE CARBIDES OF Ta AND W ACCORDING TO REACTION 5

Carbide	Log ₁₀ (Reaction Pressure) of Carbon, C ₃ , atmospheres		
	1000K	2000K	3000K
TaC	-44.1	-17.2	-8.7
WC	-37.8	-12.8	-7.9

(at 2500K)

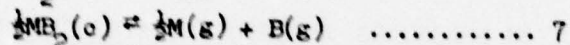
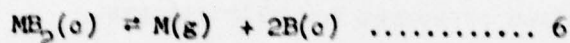
(If the expression is in terms of C (monatomic) it would be realistic for the low pressure conditions; the conclusions are unaffected, however).

Comparison of these data with the previous table shows that for TaC the reaction pressure of $C_3(g)$ is about equal to that of Ta(g) i.e. congruent evaporation is to be expected.

For WC a tendency to decompose to the sub-carbide is indicated by the somewhat higher reaction pressures of carbon. The comparison has not been extended to other carbides but, at this point, agreement between FRI and NPL assessments of stability is good.

4.1.2. Borides

Reactions postulated by the NPL for borides were as follows:



Calculations for the first reaction may be expressed in terms of the metal reaction pressure.

TABLE 4 METAL REACTION PRESSURES OF BORIDES, ACCORDING TO REACTION 6

Group	Boride	Log ₁₀ (Reaction Pressure) of metal, M, atmospheres	
		1000K	2000K
IVA	TiB ₂	-32.9	-12.3
	ZrB ₂	-40.3	-15.9
	HfB ₂	-41.9	-17.2
VA	VB ₂	-29.0	-10.4
	NbB ₂	-42.3	-17.1
	TaB ₂	-43.0	-17.6
VIA	CrB ₂	-17.5	- 5.0

For the second reaction the boron gas reaction pressures are as follows:

TABLE 5 BORON REACTION PRESSURES OF BORIDES, ACCORDING TO REACTION 7

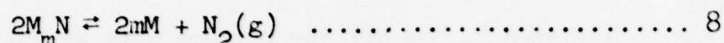
Group	Boride	Log ₁₀ (Reaction Pressure) boron gas, atmospheres		
		1000K	2000K	3000K
IVA	TiB ₂	-30.1	-10.9	4.5*
	ZrB ₂	-30.1	-10.8	4.4*
	HfB ₂	-30.5	-11.3	-4.9
VA	VB ₂	-27.1	- 9.6	-3.7*
	NbB ₂	-28.3	-10.3	-4.4*
	TaB ₂	-26.9	- 9.5	-3.8*
VIA	CrB ₂	-24.3	- 8.2	

*Not valid above the melting point of the metal due to variable compositions in resulting liquid phase.

The preferential vaporisation of boron in Zr, Hf and for Nb, Ta borides indicates that reaction 2, i.e. formation of sub-borides is a contingency which should be allowed for.

4.1.3. Nitrides

Calculations for the nitrides according to the following reaction



have yielded high reaction pressures for nitrogen gas.

TABLE 6 NITROGEN REACTION PRESSURES OF NITRIDES, ACCORDING TO REACTION 8

Group	Nitride	Log ₁₀ (Reaction Pressure) of N ₂ gas, atmospheres		
		1000K	2000K	3000K
IVA	TiN	-25.3	-7.8	-1.7
	ZrN	-28.3	-9.3	-2.9*
	HfN	-29.5	-10.4	-3.8*
VA	Nb ₂ N	-16.4	-3.5*	-
	Ta ₂ N	-19.8	-6.4	-2.3

*Values from data extrapolated beyond range of reliability.

The values are very high compared with those for borides and carbides and confirm the decision not to consider nitrides further as candidate materials.

Thermodynamic criteria of stability can provide, at best, only a partial guide to the response of refractory needle arrays to temperature/pressure conditions. They serve to isolate those compounds which are most likely to give long operating lifetimes but cannot give information on sputtering response, while the influence of physical properties such as the work function is still a matter for experiment. The short list of compounds given earlier represents a group of materials designed for test our working assumptions and is not a final short list of proven compounds.

4.2. Emitter Geometry

The geometry of a field emission cathode in relation to the total current generated has been discussed earlier by Levine ⁽²⁶⁾ and by Feeney et al. ⁽²⁷⁾. The total current generated is related to the fibre protrusions above the matrix, the fibre diameter, tip radius of the fibre, fibre density and the physical properties of the cathode (as listed in the F-N equation). Correlations attempted to date have not proved successful due to the limited amount of experimental results obtained.

4.3. Sputtering Damage - ion bombardment

Sputter induced degradation is certain to have an adverse effect upon all filament materials, but systematic data is available. For elements the sputter yield under ionic bombardment is related to the heat of sublimation and hence to the vapour pressure ⁽²⁸⁾. The inference is that elements suitable for filaments have low vapour pressures and, by the same token, compounds with low decomposition (i.e. reaction) pressures should be prime candidates. This is consistent with the role of tungsten as a thermionic and field emitter. Similarly it has been established that ZrC and LaB_6 are both superior to tungsten in stability to ionic bombardment when emitting in the field mode ⁽²⁹⁾. For further information on sputtering rates see refs. 30 and 31.

4.4. Comparison of Materials.

Detailed comparison of the results from the materials tested so far is not possible at this stage. The relatively poor performance of the A77 - 205 material does, however, give a starting point. It is described as nominally γ (γ' - α) - i.e. three-phase. Optical microscopical examination succeeded in revealing only two which formed a typically eutectic morphology with dark fibres or lamellae in a light matrix. The identity of the two phases is still somewhat uncertain and microprobe analysis indicated only that the matrix is nickel-rich while the fibres are molybdenum-rich.

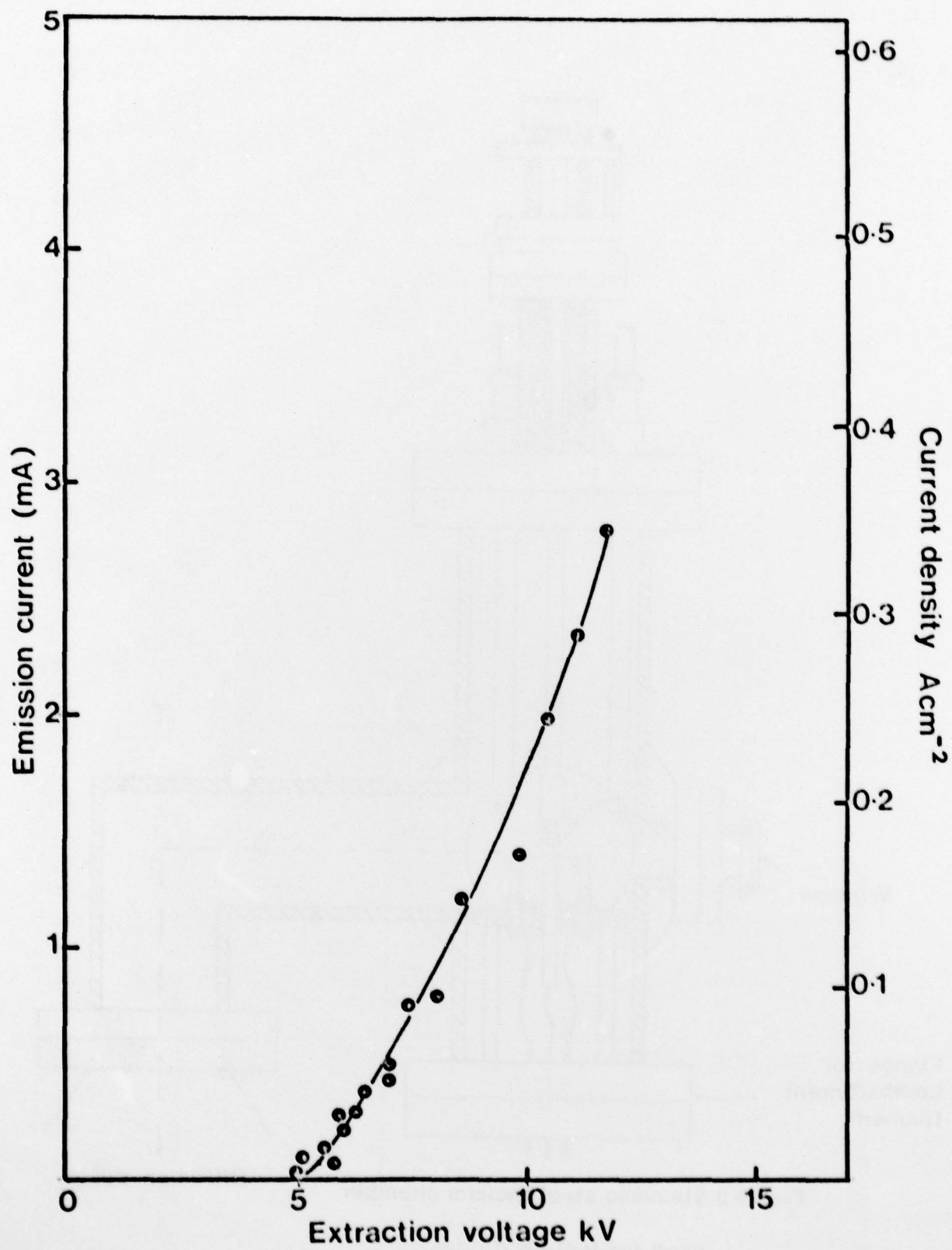
The distribution of the remaining elements Ta and Al between matrix and fibres is roughly equal. Previous work on the phase equilibria and unidirectional solidification in the Ni-Mo-Al system (33) describes the growth of α (Mo) rectangular fibres in a γ' (Ni_3Al) matrix while the γ -phase (Ni), instead of being randomly distributed between fibres and matrix appears to develop a preferred orientation with γ' . The phase diagram is still controversial (see ref. 33, p.2080) but it has been shown (34) that Ni_3Al dissolves only a very little Mo at 1150°C which is consistent with a pseudo-binary liquidus between the two components.

It has been found that the current density of the A77 - 205 material is poor compared with TaC and NbC and this may be accounted for by the irregularity of the fibre alignments (Figure 5). More important, the erosion of the fibres (Figure 6) exceeds anything found for the refractory compounds; an observation consistent with the expectation (Section 1, page 6) that metallic phases, even those based on high-melting elements like molybdenum, are unlikely to compete with borides or carbides in resistance to ion damage.

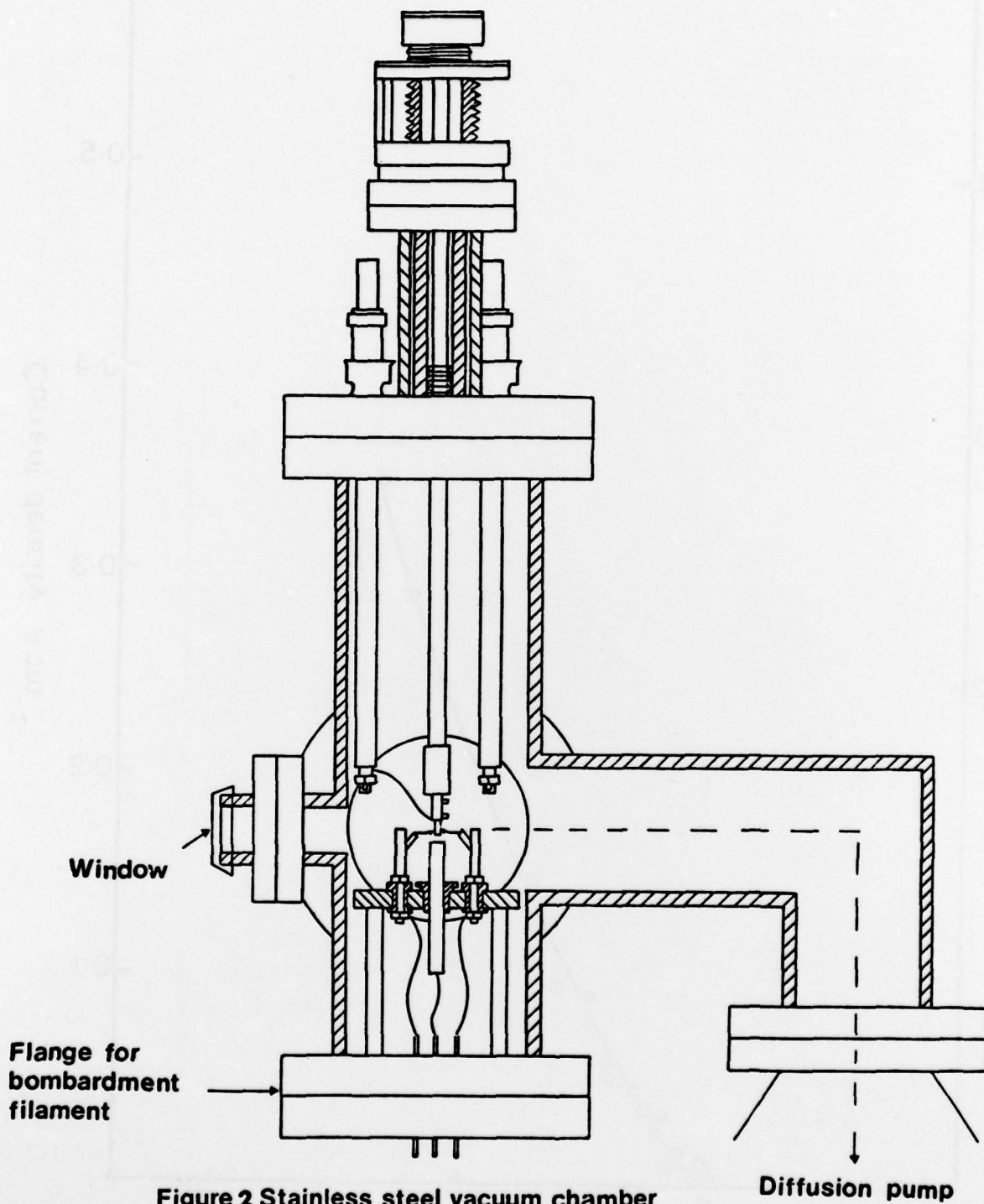
REFERENCES

1. F.M. Charbonnier et al., Proc. IEEE, 1963 July 991-1004.
2. K.T. Considine and M.M. Balsinger, Research/Development, 1976 April, 38-44.
3. J. Shelton., Field Effect Electron Emission, Army Missile Command, Redstone Arsenal, AD 738 529, August 1971.
4. G.A. Wardly, J. Vac. Sci. Techn. 1973, 10 (6), 975-978.
5. R.K. Feeney, A.T. Chapman and B.A. Keener, J. Appl. Phys., 1975, 46(4), 1841-1843.
6. F.S. Baker et al., Nature, 1972, 239, Sept. 8, 96-97.
7. E. Braun et al., Vacuum, 1975, 25, (9/10), 425-426.
8. Y. Kumashiro et al. J. Less-Common Metals, 1973, 32 21-37.
9. K. Senzaki and Y. Kumashiro, Proc. 6th Int. Vac. Congress, 1974. in: Jap. J. Appl. Phys. Suppl. 2, Pt. 1, 1974, 289-292.
10. C. Lea, J. Phys. D: Appl. Phys., 1973, 6, 1105-1114.
11. W.P. Dyke, IRE Transactions on Military Electronics 1960, January, 38-45.
12. L.W. Swanson, Practical TF Cathode Studies in: 21st International Field Emission Symposium, p.46, July 1974, Marseilles, France.
13. C.A. Spindt et al., J. Appl. Phys. 1976, 47 (12), 5248-5263.
14. V.G. Rivlin and D. Stewart, Field Emission Cold Cathode Devices Based on Eutectic Systems: A literature search, Interim Scientific Report, 1 May 1977 - 31 October 1977, AFOSR-77-3292.
15. M.A. Filyand and E.I. Semonova, Handbook of the Rare Elements, Vol. 2 Refractory Elements (Trans. M.E. Alferieff), London, MacDonald, pp 12-15, Tables 388-392.
16. V.S. Fomenko, Handbook of Thermionic Properties (G.V. Samsonov, Ed) Transl. and Published - Plenum Press Data Division, New York, 1966.
17. E.K. Storms, The Refractory Carbides, New York and London, Academic Press, 1967.
18. H.J. Goldschmidt, Interstitial Alloys, London, Butterworths, 1967.
19. C.J. Smithells and E.A. Brandes (Eds), Metals Reference Book, 5th Edition, London and Boston, Butterworths, 1976
20. G.V. Samsonov (Ed), Boron, Its Compounds and Alloys Book 2, Kiev, Akad. Nauk Ukr. SSR, 1960, see especially pp 394-436 (USAEC Trans AEC-to-5032) (Book 2).
21. D.R. Stull et al., JANAF Thermochemical Tables, NSRDS-NBS, 37, 1971.
22. T.G. Chart and T.I. Barry, National Physical Laboratory, Teddington, Middlesex, U.K. Private Communication.

23. W. Kurz and P.R. Sahm, *Gerichtet Erstarrte Eutektische Werkstoff*, Berlin Springer-Verlag, 1975 (see especially Appendix, pp 305-335).
24. R.H. Fowler and L. Nordheim, *Proc. Roy. Soc.*, 1928 A, 119, 173-181
25. R.H. Good Jr. and E.W. Muller "Field Emission" in *Handbuch de Physik* edited by S. Flugge (Springer-Verlag, Berlin, 1956), Vol 21, pp 181-191.
26. J.D. Levine, *RCA Review*, 1971, 32, 144-149).
W.L. Ohlinger, A.T. Chapman and J.K. Cochran.
27. R.K. Feeney, *Investigation of Field Emission Electron Guns for Gas Lasers*, 1976, Final Report 12 Oct 1973 - 31 Aug 1975. DAA-74-C-0229. Georgia Inst. of Technology.
28. L.J. Maisel, *Physics of Thin Films*, 1966, 3, 61 - 129.
29. M.I. Elinson and G.A. Kudintseva, *Radiotekh i Elektron (USSR)*, 1962, (9), 1511 - 1518.
30. E.G. Spencer and P.H. Schmidt, *J. Vac. Sci. and Techn.*, 1971, 8, (5), 552 - 570.
31. G. Carter and J.S. Colligan, *Ion Bombardment of Solids*, Heinemann Educational Books Ltd., 1968.
32. Yu. Borisov, S. Gershenzon and V. Yushkov, *Fiz. Khim. Obrabot. Mater.*, 1975, (4), 20 - 22.
33. H. Spenger, H. Richter and J.J. Nickl, *J. Mat. Sci.*, 1976, 11, 2075 - 2081.
34. R.W. Guard and J.H. Westbrook, *Trans, A.I.M.E*, 1959, 215, 807 - 814.



TaC eutectic cathode in test diode before sealing off.



**Figure 2 Stainless steel vacuum chamber
used for testing diodes.**

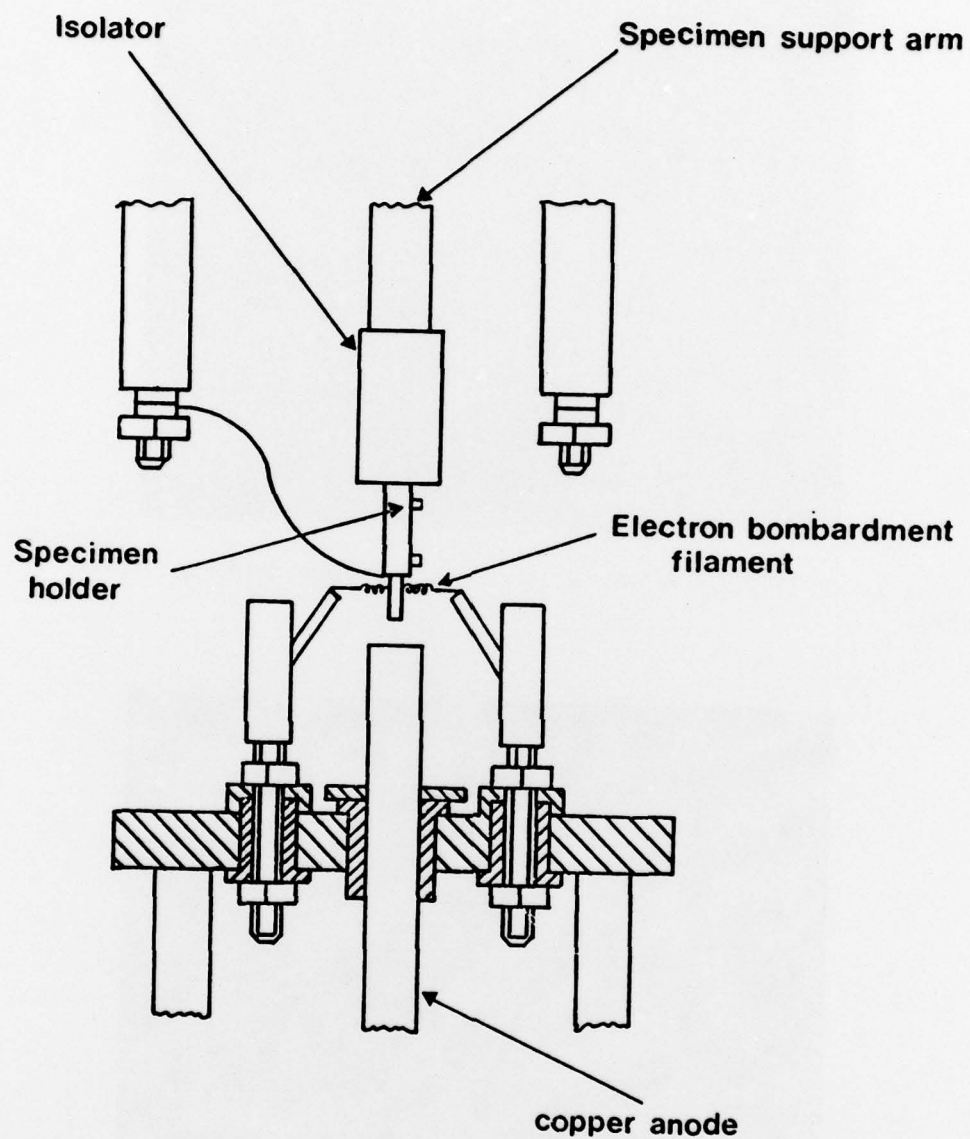


Figure 3 Cathode assembly

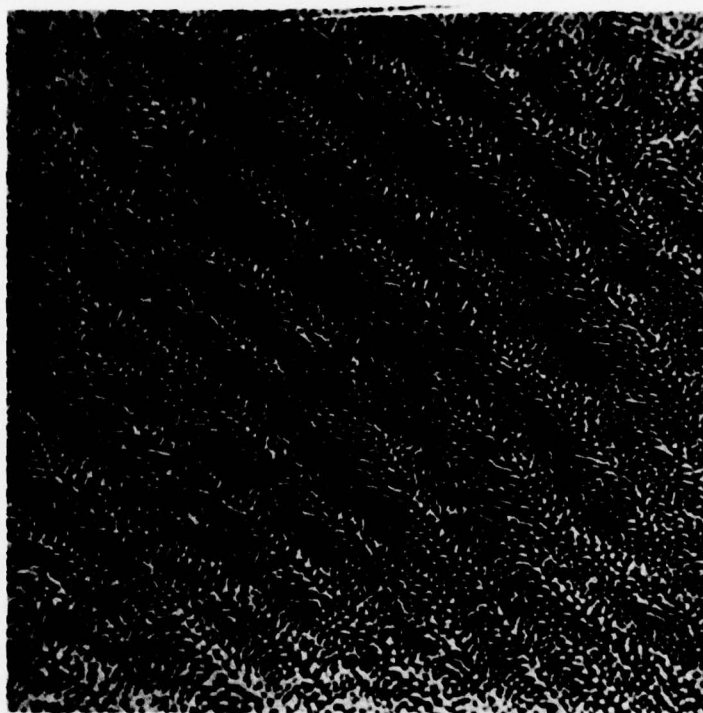


Figure 4. A-77-205 γ - γ' - α (Ni Mo Ta Al) before testing
C4500

x 900

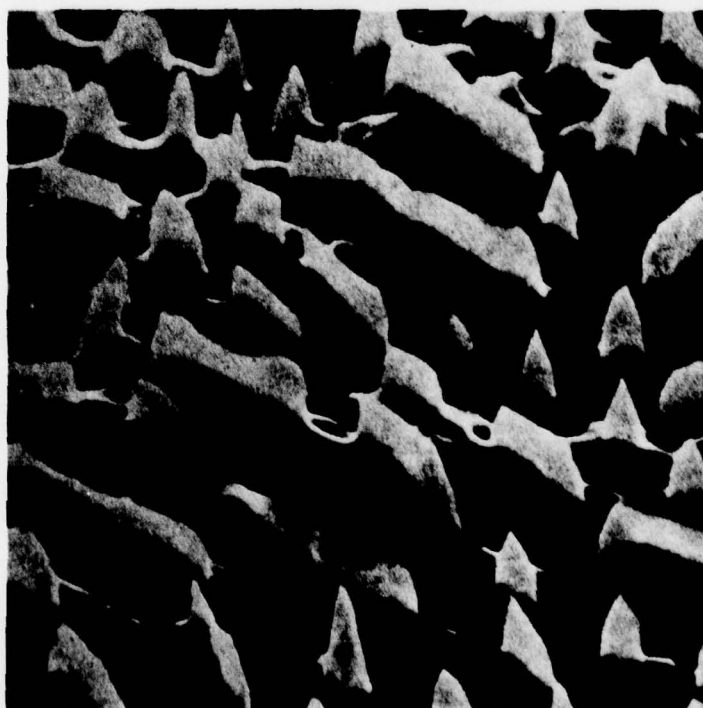


Figure 5. A-77-205 γ / γ' - α (Ni Mo Ta Al) before testing
C4499

x 10K

R744/2

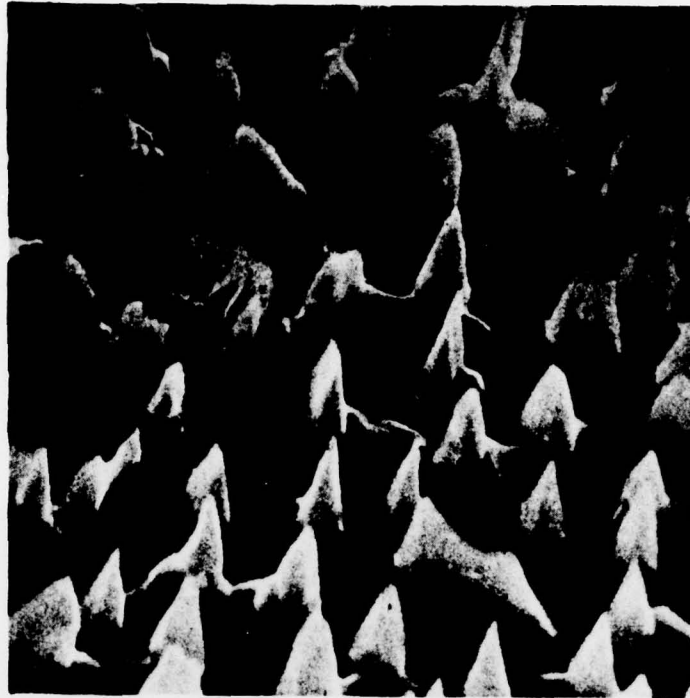


Figure 6. A-77-205 γ/γ' - α (Ni Mo Ta Al) after testing
C4848

x 10K

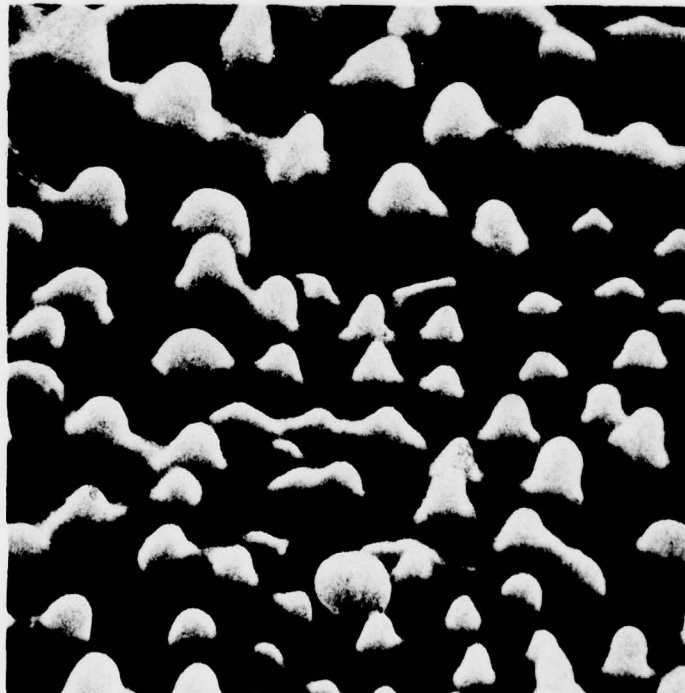


Figure 7. A-77-205 γ/γ' - α (Ni Mo Ta Al) after testing showing
area of arcing
C4847

x 2K

R744/2

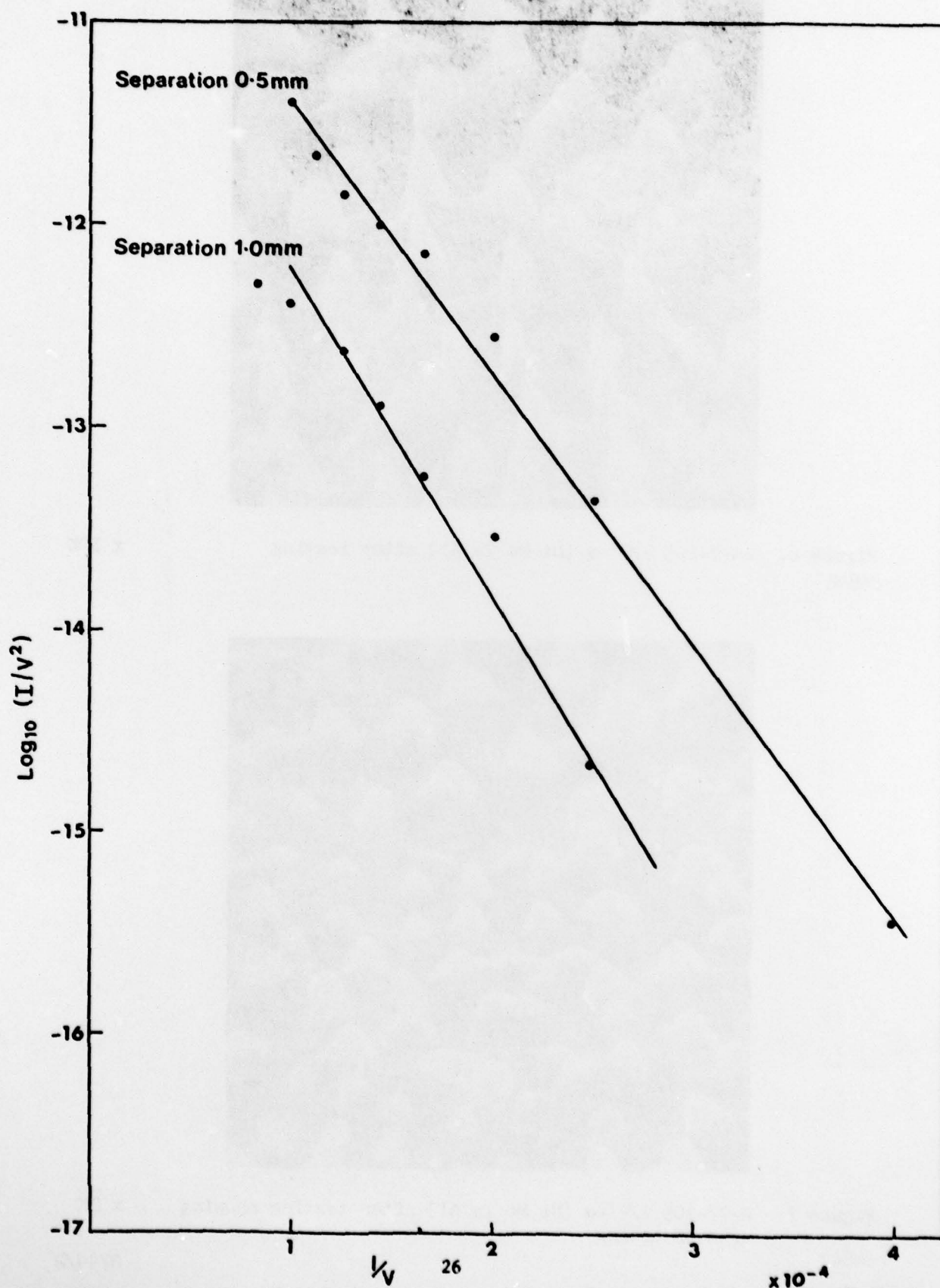


Figure 8 Fowler-Nordheim Plots with Materials A77-205 as the Cathode and at the Anode-to-Cathode Separations Shown



Figure 9. TaC cathode before testing
C3911

x 500

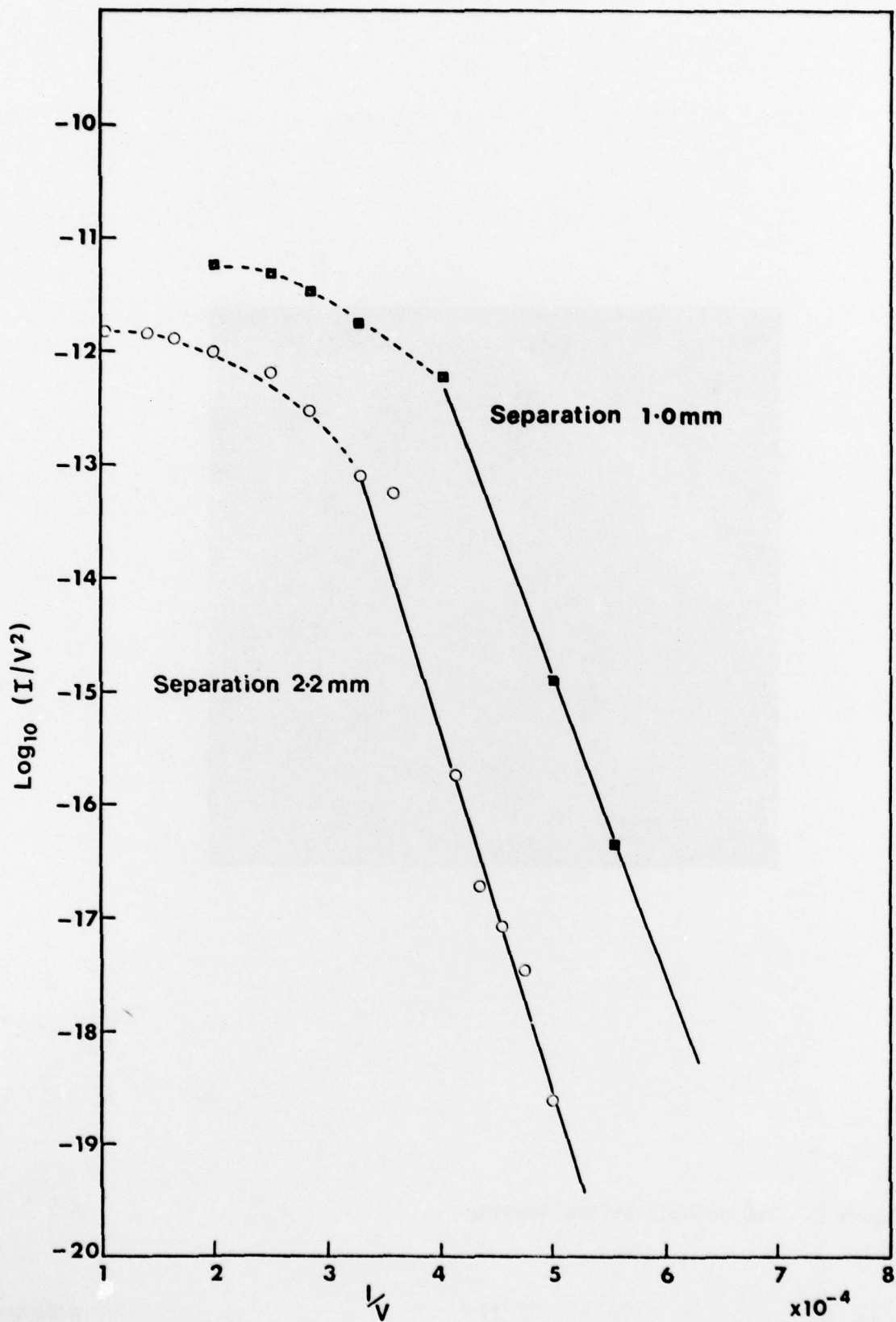


Figure 10 Fowler-Nordheim plots for TaC cathode at the anode to cathode separations shown.

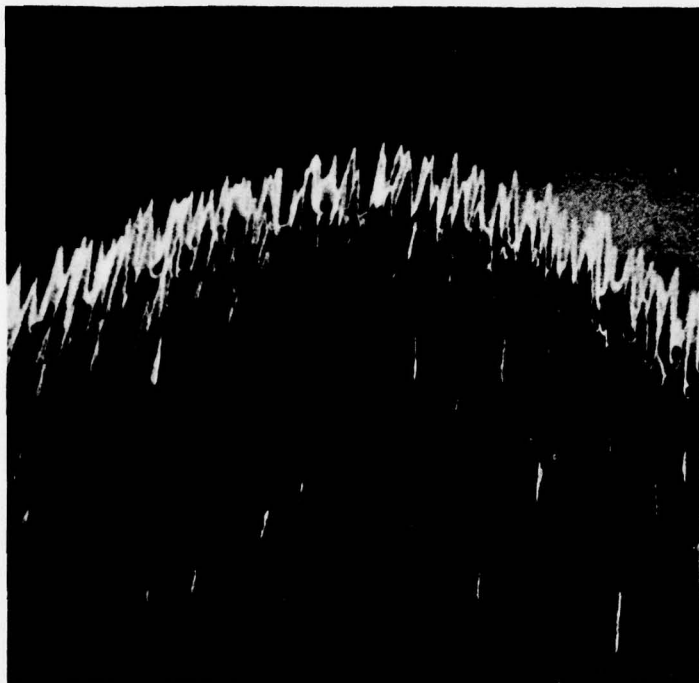


Figure 11. TaC cathode before testing
C3912

x 2K

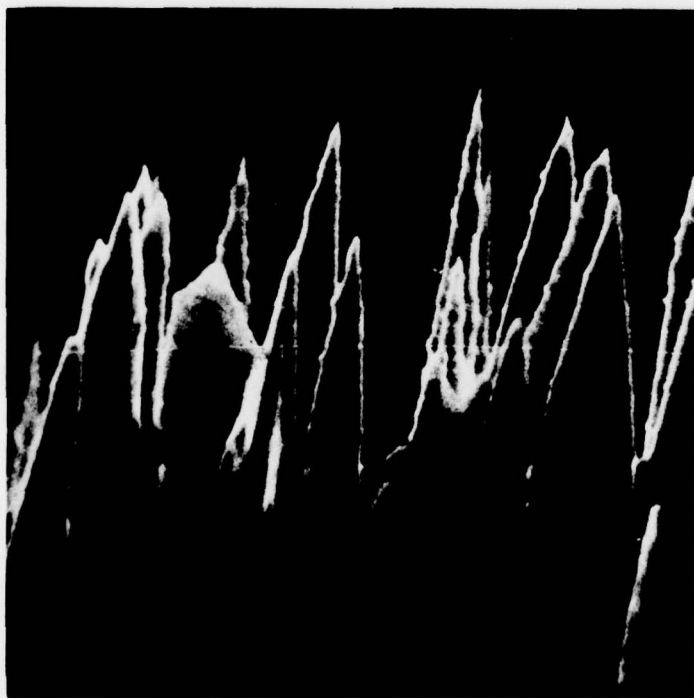


Figure 12. TaC cathode before testing
C3913

x 10K

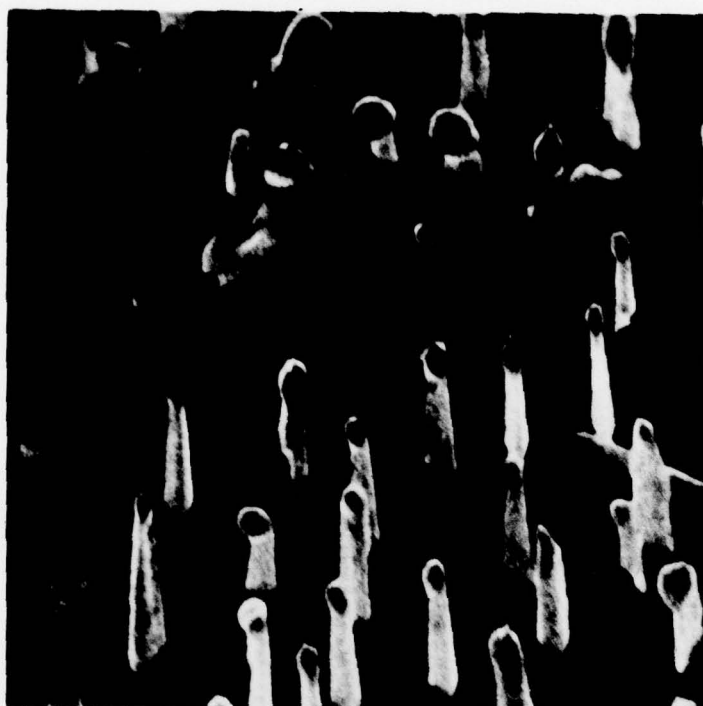


Figure 13. TaC after testing.
C3502

x 5.5K

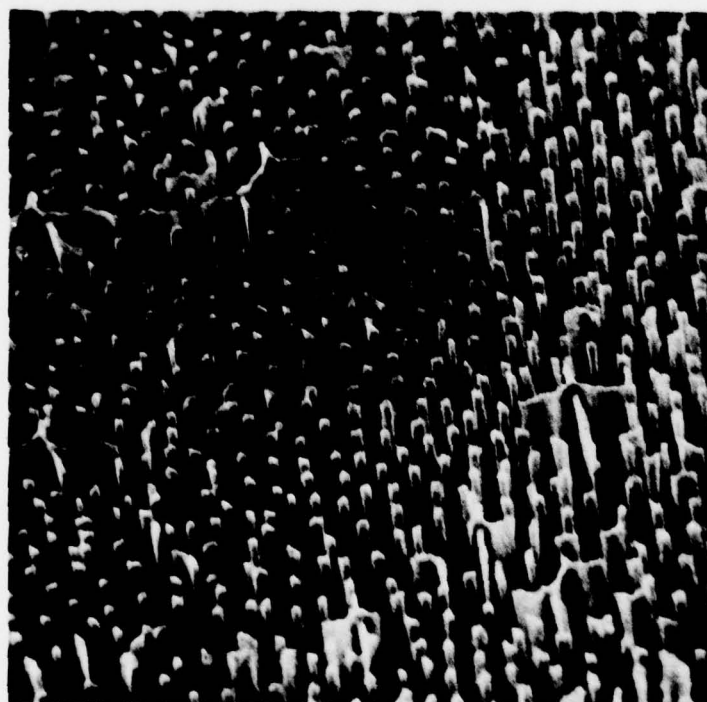


Figure 14. NbC cathode before testing.
C5578

x 730

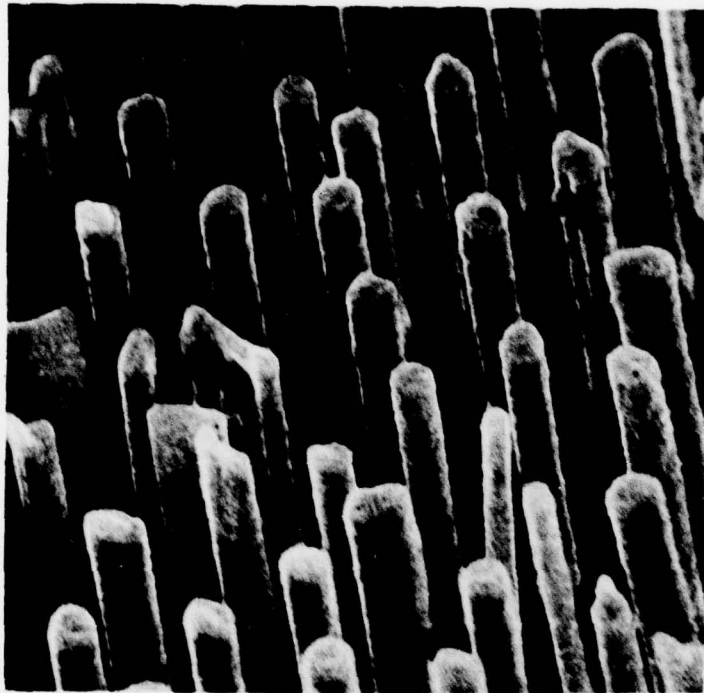


Figure 15. NbC cathode before testing
C5577

x 2,9K

R744/2

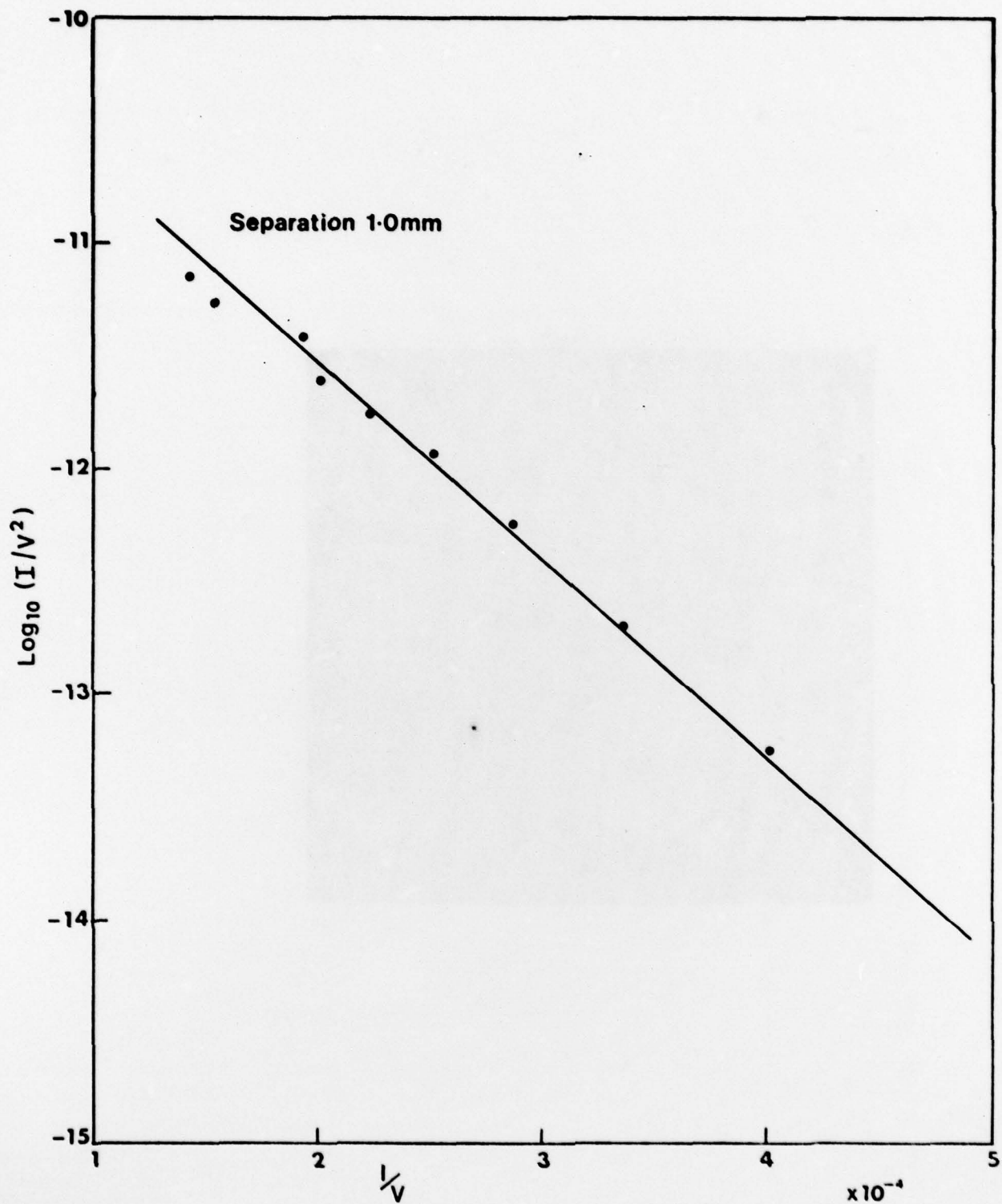


Figure 16 Fowler - Nordheim plot for NbC cathode at the anode to cathode separation shown.

*MISSION
of
Rome Air Development Center*

RADC plans and executes research, development, test and selected acquisition programs in support of Command, Control Communications and Intelligence (C³I) activities. Technical and engineering support within areas of technical competence is provided to ESD Program Offices (POs) and other ESD elements. The principal technical mission areas are communications, electromagnetic guidance and control, surveillance of ground and aerospace objects, intelligence data collection and handling, information system technology, ionospheric propagation, solid state sciences, microwave physics and electronic reliability, maintainability and compatibility.