THE SELECTIVE CHEMICAL ETCHING OF CeO_2

DOPED Gd_2O_3-Mo COMPOSITES

A THESIS

Presented to

The Faculty of the Division of Graduate

Studies and Research

by

Robert Allen Rieger

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Ceramic Engineering

Georgia Institute of Technology

December, 1973

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Approved:

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Chairman

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Date approved by Chairman: Oct. 15, 1973

ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to Dr. A. T. Chapman for his interest, patience, assistance and funds which made this research possible. Many thanks are also expressed to Dr. J. F. Benzel and Dr. J. K. Cochran of the reading committee who gave freely of their support and recommendations.

Special notice is given to Mr. James Stendera for his suggestions on etchants and their effect on composites.

And lastly, the patience and understanding of my wife, Susan, was indispensable and lent me encouragement during trying periods.

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SUMMARY

The chemical etching of CeO_2 doped Gd_2O_3-Mo composites formed by unidirectional solidification was investigated to develop techniques for forming an optimum emitting array for electron field emission by the selective removal of both the gadolinia and the molybdenum. Etchants and techniques for the exposure and lengthening of the Mo fibers, the pointing and rounding of the fiber tips, the formation of holes in the matrix by the selective dissolution of Mo, and the recessing of pointed fibers in holes was studied. The exposure and lengthening of the pins was accomplished by the use of concentrated sulfuric acid which selectively dissolved the gadolinia. The pointing of the pins was best achieved by the use of a solution consisting of 5 grams of ammonium nitrate in 100 ml of sulfuric acid. Thermal annealing formed rounded fiber tips from pointed ones. The selective dissolution of Mo to form holes in the surface was accomplished by the use of an etchant composed of potassium ferricyanide and sodium hydroxide. Production of sample morphologies consisting of pointed fibers recessed in holes was attained to limited success, uniformity being a major problem.

CHAPTER I

INTRODUCTION

Unidirectionally solidified oxide-metal composites consist of metal fibers grown in a refractory oxide matrix. The fibers, which may range in length from several microns to a fraction of an inch, are aligned in one direction and bonded very strongly to the matrix. A modified floating-zone technique is used to grow the composites. Fiber densities[1] up to 70 million per cm^2 have been obtained.

In the CeO_2 doped Gd_2O_3-Mo composite, the molybdenum fibers are present in the ceria-gadolinia matrix in roughly a hexagonal array. The inter-fiber spacing is approximately 1 micron, as determined by scanning electron microscope pictures. Ceria doping[2] resulted from experiments which determined that its addition increased the solubility of molybdenum in the composite, thereby causing better fiber growth.

Within the past few years, these composites have found many applications in the electronics field. One of the most important applications is the so-called cold cathode emitter. Replacing a typical thermoidnic electron emitter, the composite could pass an appreciable electron current without heating, thereby greatly increasing the operating life of many filament devices. An ideal electron emission geometry results when the matrix is stripped away to yield millions of exposed fibers, and the individual fiber tips are shaped to provide optimum electron emission. The large density of molybdenum fibers in a high

resistivity gadolinia matrix makes the CeO_2 doped Gd_2O_3-Mo composites excellent candidates for field emission.

The objective of this research was to investigate etchants and techniques for selectively removing metal and oxide, and shaping metal fibers in the composite system CeO_2 doped Gd_2O_3-Mo. The factors influencing the formation of different length fibers will be described, followed by a discussion of the pointing and rounding of the fiber tips and concluding with the variables concerning hole formation and the recessing of fibers in holes.

CHAPTER II

SURVEY OF LITERATURE

Since the oxide-metal class of composites are so new, scarcely any literature is available on their etching characteristics. Pepper[3] studied the chemical etching of UO_2-W composites for electron emission applications. Some of her results, notably the determination of an optimum speed of sample rotation during etching were utilized in this thesis. Stendera[4] initially investigated the etching characteristics of the CeO_2 doped Gd_2O_3-Mo system and formulated the etchants used for the fiber lengthening and fiber pointing procedures.

In this survey, the theory behind using oxide-metal composites as field emitters will be discussed, along with the etching requirements necessary to ensure a good emitting array. The individual etching characteristics of molybdenum, gadolinia, and ceria will be described separately, since no literature is available for these materials incorporated in an oxide-metal composite.

Composites as Field Emitters

Contemporary electron emission devices are oxide-doped refractory metals which emit electrons at a high temperature. This technique is employed in vacuum tubes, televisions and numerous other electronic devices.

One of the many problems associated with this conventional filament is the tremendous heat produced. The high temperatures in filament

devices lead to such problems as electrical shorting, destruction of vacuum, and short tube life.

The production of electrons from a filament or filaments at ambient temperature is known in theory as field effect emission. Shelton[5] states that the most promising approach to this is to employ oxide-metal composites; their tiny metallic fibers, each one emitting electrons would be able to pass an appreciable current when millions of fiber emitters are used together.

The ideal individual field emitter can be shown mathematically to consist of a lengthened shaft several microns in length with a tip in the shape of a prolate spheroid. While this would be very difficult, if not impossible, to obtain, it is postulated that spherical hemispheres[6] for pin tip geometry would be sufficient.

Etching techniques for lengthening the fibers by selectively removing the oxide matrix and forming the various fiber tip shapes must yield geometries that are variable at will, uniform and reproducible. Another emission geometry, recessed pointed pins, requires that holes be etched in the matrix by the selective dissolution of the molybdenum fibers.

Molybdenum

Molybdenum is a refractory metal, silver-gray in color, having a melting point of $2622^{\circ}C$. Hjelm[7] first isolated the pure metal in 1782. It is primary used in alloys wherever high strength is demanded at elevated temperatures, such as tool steels, saw blades, and cutting tools in which heat is generated by friction. In corrosion resisting

steels molybdenum increases the ability of the austenitic 18-8 chromium nickle grades to withstand sulfuric acid in certain concentrations, and also acetic acid. Molybdenum is also much in demand for making filaments and glass to metal seals.

The reactions of molybdenum with corrosive reagents have been known for a long time and are reported extensively in the literature. Molybdenum is not attacked by dilute sulfuric acid or concentrated hydrochloric acid, but hot sulfuric acid attacks it readily as does nitric acid. It generally reacts slowly with the fused alkalies[8], but it is rapidly attacked by fused oxidizing salts such as KNO_3, $KClO_3$ and Na_2O_2. Molybdenum is also soluble[9] in warm Aqua Regia, hot dilute hydrochloric acid, mixtures of hydroflouric and nitric acids, and very hot sulfuric acid (around 200-250°F).

The American Society for Testing Materials, ASTM, specifies a number of etchants[10] to be used in the metallographic preparation of molybdenum samples. These etchants are employed to heighten structural details of the metal, while performing other specialized functions depending upon the specimen. For the microetching of molybdenum, the ASTM suggests an etchant consisting of the following:

     10 ml hydroflouric acid

     30 ml nitric acid

     60 ml lactic acid

They indicate that the metal sample should be swabbed with the etchant for 10-20 seconds. The quantity of hydroflouric acid can be varied to either increase or decrease the activity of the etchant.

A second etchant suggested by the ASTM for the microetching of

as-cast molybdenum samples is:

    5 ml hydroflouric acid

    10 ml nitric acid

    30 ml lactic acid.

The sample should be swabbed with the etchant, using heavy pressure, for 5-10 seconds. This is followed by a water rinse, an alcohol rinse, and an air drying.

For the macroetching of molybdenum, the ASTM again specifies two etchants to be used. They differ only in their strength, or activity. The weaker of the two consists of:

    15 ml 48% hydroflouric acid

    35 ml concentrated nitric acid

    75 ml distilled water

This etchant is to be applied by immersing the sample in it at room temperature for a period of 10-20 minutes. The second and stronger etchant contains:

    30 ml concentrated hydroflouric acid

    15 ml concentrated nitric acid

    30 ml 48% hydroflouric acid

This etchant is again applied by immersing the sample in it at room temperature, but for the shorter period of 5-20 minutes.

Lastly, the ASTM indicates that a good etchant for the rapid dissolution of molybdenum is:

    10 grams $K_3Fe(CN)_6$ (potassium ferricyanide)

    10 grams KOH or NaOH

    100 ml distilled H_2O

This etchant is to be swabbed on the specimen for a period of 5-60 seconds. It should be followed with a water rinse, alcohol rinse, and air drying.

The previous etchant specified by the ASTM, containing the potassium ferricyanide, has been proposed by other researchers, using differing proportions. Smithells[11], in his industry-wide recognized reference book states: "The general structure of molybdenum may be developed by immersion for 5 to 10 seconds in the following reagent":

$K_3Fe(CN)_6$	360 grams
NaOH	36 grams
distilled H_2O	1000 cc

Wendell[12], in his United States Patent improved upon this basic molybdenum etchant. He cites the reagent-etchant of Smithell as the standard formulation for the etching of thin molybdenum sheets. Although he recommends that the temperature of the etchant be maintained around $200^\circ F$, he says that neither the temperature nor the concentration of the constituants is very critical. The object of his invention was to increase the rate of etching by a factor of about 3 or 4. Wendell found that adding sodium oxalate to the basic etchant allowed the etching temperature to be lowered to around $110^\circ F$, while decreasing the time required to etch 2 mils of molybdenum away from 30 minutes to 6 or 7 minutes. It was found that while increasing the temperature of the etchant does tend to accelerate the etching, the etchant solvent evaporate faster. Wendell also discovered that the etchant tended to foam a great deal while being mechanically agitated, so he added from one tenth to three-tenths of a milliliter of foam reducer, such as di-

ethylene glycol monostearate to each liter of etchant. This apparently had no detrimental effect upon the characteristics of the etchant.

An additional United States Patent[13] indicates the etchants to be used for removing scale from the surface of molybdenum metal. This etchant and its two-bath procedure is intended primarily for large scale industrial application. The first bath consists of 10% by weight of sodium hydroxide, 5% by weight of potassium permanganate, and 85% by weight of water. The temperature of this etchant bath is about 75°C. After a sample of molybdenum metal is immersed in the solution for seven minutes, the oxide scale is converted by the etchant to substances that can be easily removed by a pressure-spray rinse. After the water rinse a black smut layer still remains on the surface of the molybdenum sample. This smut layer is removed in the second etchant bath which consists of 15% by weight sulfuric acid, 15% by weight hydrochloric acid, 70% by weight of water, and from 60 to 100 grams of chromic acid per liter of etchant. The temperature of this bath is held at room temperature.

Preist[14] describes the precision etching of molybdenum by gases. In her experiments, thin films of molybdenum were exposed to a mixture of oxygen and hydrogen chloride gases. The exposure to these gases resulted in the formation and subsequent removal of a layer of molybdenum trioxide. Etch rates of 1,000 to 10,000 angstroms per minute were obtained with gas pressures between 0.1 and 1 torr, and specimen temperatures of 400 to 600°C. The resultant final etched surface was found to be as smooth, if not smoother than the original surface. It was determined that a residue of very thin MoO_2 existed on the surface after etching. This residue, in the form of an adherent layer, was

very difficult to remove. The gaseous etching process demonstrated promise for etching with dimensional control accurate to better than 0.1 μm. Greater precision may be possible in films thinner than 1 μm.

A number of Soviet authors did extended research on the reactions and reaction kinetics occuring between molybdenum and various reagents.

Boehni[15], in studying the corrosion behavior of several rare metals in aqueous acid solutions found that in non-oxidizing dilute acid solutions, except hydroflouric acid, molybdenum was not attacked. He postulated that in oxidizing acid solutions molybdenum is not corrosion resistant because no passivating layers are formed. He further states that molybdenum is quite corrosion resistant to hydroflouric acid.

Boxin, Uspenskaya and Maksudov[16] in their studies of the corrosion resistance of metals and alloys in flourosilicic acid found that of the components of stainless steel the most resistant in 10% H_2SiF_6 (flourosilicic acid) were chromium, molybdenum and tungsten.

Zotikov and Semenyuk[17] investigated the high temperature corrosion of molybdenum and other rare metals in hydrogen flouride. They found that the exposure of molybdenum to the vapor of a 40% hydroflouric acid solution at temperatures of 300, 400, 500, 600 and 700°C caused losses of .004, .013, .017, .027 and .170 grams/m^2 of molybdenum per hour, respectively.

The differences in etching rates and characteristics within one particular molybdenum sample were examined by Tartakovskaya, Mel'nikova, Kozlova and Makarenko[18]. They found that selective dissolution of polycrystalline molybdenum leads to a change in the surface relief of

the sample because of the different rates of etching in various crystal-
lographic directions. Further, the roughness of the etched surface was
found to depend on the differences in grain size and the development of
etching figures. In their particular experiments the height of the
surface relief non-uniformity was 280 μm for an average grain size of
1000 μm. They state: "X-ray and microscopic analysis in combination
with roughness measurements established the following order for the dis-
solution rates of molybdenum in < 70% sulfuric acid solutions: (111) >
(110) > (100)."

Putilova and Suponitskaya[19] reported on the reaction kinetics of
the molybdenum dissolution in 2N nitric acid containing urea. The
purpose of using urea was as a possible etching regulator. The molyb-
denum samples used in their studies were annealed in a reducing atmos-
phere of H_2 at $1000^{o}C$ for 5 minutes, after which they were kept in a
dessicator. They determined that the dissolution of molybdenum in 2N
nitric acid proceeds as a self-accelerating process, the autocatalyst
of which is probably nitric acid. When they introduced some $NaNO_2$ into
the nitric acid before etching, they found that this addition strongly
stimulated the dissolution of the molybdenum and eliminated the in-
duction period. It was postulated that the corrosion could be inhibited
by the removal of the catalyst, such as the reduction of the nitric acid
with urea. The addition of urea apparently decreased the dissolution
rate of the metal. The amount of urea added that yielded the greatest
decrease in corrosion was determined to be 10 millimoles/liter.

A similar study was conducted by Kochanova, Putilova and
Suponitskaya[20]. They studied the rate of solution of molybdenum and

nickle in 2 molar nitric acid using thiourea as an etching regulator. It was determined that at 20°C, the rate of solution of molybdenum was significantly reduced when .005 to .05 moles of thiourea was added to the 2 molar nitric acid. The samples of nickle used were found to be more easily protected than the samples of molybdenum. This was attributed to the fact that the thiourea appeared to react with the HNO_2 in the solution and formed a protective film on the nickle, but not on the molybdenum.

The corrosive effect of distilled water on various metals at elevated temperatures was studied by Byalobzheskii and Anurova[21]. Using chromatographic, gravimetric, and x-ray techniques, they calculated corrosion rates for some metals exposed to steam at 250°F. The oxygen absorption rates and hydrogen evolution rates were determined and tabulated for Al, W, Cd, Cu, Mo, Ni, Nb, Pt, Ta, Ti, Cr and Zr. The amount of metal dissolved from each sample was calculated from a developed equation, a knowledge of amounts of oxygen absorbed and from the resulting oxide film composition.

The electrolytic etching of molybdenum is also covered extensively in the literature. While it is generally unrelated to the practice of chemical etching, several researchers have employed electrolytic techniques which partially utilize acid or alkali etchants.

Putilova, Maslova and Suponitskaya[22] examined the NO bubbles formed during the electrolytic etching of molybdenum in 2N nitric acid to which $K_2Cr_2O_7$ was added. The bubbles were photographed at different time intervals. The addition of $K_2Cr_2O_7$ to the nitric acid was found to considerably increase the size of the bubbles and change the rate of

bubble growth within relatively narrow limits (25 to 200 m/minute).

Demkin[23] reported the formula for an electrolytic etchant used to reveal grain boundaries and dislocations in molybdenum. The etchant is composed of 5 ml sulfuric acid and 100 ml of EtOH. He used an emf of about 1 volt for an area of 10-40 square millimeters for 45-60 seconds.

In an experiment similar to the preceding one, Koroleva and Pikunov[24] studied the structure of molybdenum revealed by electrolytic etching in a solution containing 5 milliliters sulfuric acid and 100 milliliters MeOH. They discovered that the $\{100\}$ planes were best etched electrolytically in 10% NaOH.

Finke and Schulze[25] investigated the structure of zone refined molybdenum crystals containing less than 50 ppm impurities utilizing a combination of chemical and electrolytic etching techniques. The molybdenum crystal was cut and ground with abrasive paper, and then electropolished at 12-50 volts with a current density of 1-6 amp/cm^2 in 7 parts MeOH and 1 part sulfuric acid. This was followed by immersion of the sample for 20 seconds at room temperature in Murakami Solution. The Murakami Solution is an etchant consisting of 10 grams KOH, 10 grams $K_3Fe(CN)_6$ and 100 ml of H_2O. The authors plotted the radius and depth of the etch figures expressed in μm as a function of etching time in seconds. The influence of mechanical preparation on the surface of the crystal was not detected for an etching time of greater than 15 minutes.

Gadolinia

Gadolinia is the name given to the most common oxide form of

gadolinum, Gd_2O_3. In the sintered state it has a greenish-black color and a melting point of $2330 \pm 20^{\circ}C$. The primary industrial application of gadolinia is as a phosphor for color television screens.

Very little information is available on the etching of gadolinia or the reaction of it with corrosive reagents. A small amount of work has been done on the thermochemistry of gadolinia, notably the measurement of heat of solution.

The ASTM[10] specifies three etchants to be used to prepare a sample of a gadolinium based metal for microscopic examination. The first consists of:

    1 ml sulfuric acid

    15 ml nitric acid

    10 ml acetic acid

    5 ml H_3PO_4

    20 ml lactic acid

The sample of metal should be swabbed gently with this solution for 10-15 seconds. A rinse of methanol and air drying follows.

The second etchant is:

    30 ml nitric acid

    10 ml HPO_4

    20 ml acetic acid

    10 ml lactic acid

The sample is swabbed gently with this solution for 5-15 seconds. A rinse with methanol or ethanol and air drying again follows.

The final etchant is composed of:

    75 ml acetic acid

    20 ml H_2O_2 (30%)

The ASTM states that the sample of metal should be immersed in this solution for 6-15 seconds.

The normal Ln_2O_3 oxides, where Ln represents any rare earth, are typical basic oxides only slightly soluble in water. The oxides are dissolved quantitatively by strong acids. The rate of dissolution, however, varies greatly with the particular form of the oxide, depending on the method of preparation of the oxide and the temperature of calcination. All rare earth oxides are dissolved by the stronger acids. The most soluble forms react with weak acids also, such as chromic, acetic, and carbonic. The salt-forming nature of the oxides is confirmed by the reaction with acid oxides, which causes the production of various salts. In these salts[26], the rare earth oxides always act as the alkaline component. The marked basic character of the rare earth oxides becomes weaker along the series La-Lu. All other conditions being equal, the rate of dissolution[27] of the rare earth oxides drops noticeably with increasing atomic number.

As with molybdenum, several Soviet investigators performed experiments concerned with the reactions between gadolinia and various corrosive reagents.

Val'tsev and Breusova[28] examined the solubility of Gd_2O_3 and other rare earth oxides in molten NH_4NO_3. Their solubility was defined as the amount of oxide in the melt at the moment the reaction product appeared as a precipitate. They used the method of isothermal saturation at a temperature of $180^\circ C$. It was found that the solubility of rare earth oxides including Gd_2O_3 increased with increasing atomic number from 16.7% for La to 29.8% for Gd and then decreased to 23.5% for

Er. It was also found that the process of dissolution was faster for the elements of the cerium group than for those of the yttrium group.

In a similar experiment Koz'min, Davydov and Shul'gin[29] determined that the solubility of Gd_2O_3 in KOH depended upon the temperature and the partial pressure (P) in the coexisting gas phase. The dependence of solubility on P was attributed to the formation of a $K_3\{Ln(OH)_6\}$ type complex compound (Ln = rare earth element). The activity of the water and the KOH was also reported to play an important role in the formation of such a complex.

Ryabchikov and Vagina[30] investigated the interaction of rare earth oxides with ammonium salt solutions at high temperature. In their procedure, the oxide batch was placed in a calibrated vessel with a stirrer, the salt solution was added, and the solution was kept at $97^{\circ}F$ for 3 hours. The authors discovered that with increasing salt solution concentration, the solubility of the rare earth oxides increases noticeably. The greatest increase was observed with La, the smallest with Eu and Gd. On the basis of these results, they postulated that the rare earth oxides are selectively soluble in ammonium salts of various acids.

Ceria

Ceria, CeO_2, is the most common oxide form of the rare earth cerium. Like gadolinia, it has a very high melting point and is used industrially for television screen phosphors.

Practically nothing has been written on the etching or solubility of ceria, because of its comparative newness to the ceramic field.

The chemistry of ceria is well known. It is soluble in nitric

or hydrochloric acids only in the presence of a reducing agent. Concentrated sulfuric acid converts it into ceric sulphate. Fused bi-sulphate[31] attacks it very readily.

Williams and Calabra[32] describe an etching method to prepare ceria samples for microscopic examination. They ruled out the use of severe etching methods, such as boiling concentrated acids, because they wanted to preserve a complex microstructure. The best etching method that these investigators found was immersion in a 1:1 solution of 48% hydroflouric acid and distilled water for 15 minutes at ambient temperature. This was followed by swabbing for 1 to 2 seconds with a 1:1 solution of concentrated hydrochloric acid and distilled water to remove a thin residue formed during etching with HF. The specimens were then washed in cold water and dried.

CHAPTER III

PROCEDURE

All the CeO_2 doped Gd_2O_3-Mo composite samples used in this re-
search were prepared by unidirectional solidification using an rf gen-
erator by a modified internal floating zone technique. Regardless of
the type of etching to be conducted, several standard procedures were
performed. These standard procedures will be described first, followed
by a discussion of the rotating technique, the ultrasonic technique
and the combination stirring-ultrasonic technique used for etching.
The equipment and conditions used for thermal annealing in an attempt
to form rounded fiber tips and to relieve stresses in the gadolinia
matrix are explained lastly.

Sample Polishing and Cleaning

The samples to be etched were flat wafers obtained by slicing the
original 5/8 inch diameter unidirectionally solidified pellet into
sections approximately 3/32 inch in thickness perpendicular to fiber
growth with a diamond saw blade. To remove saw blade marks, the wafers
were first ground on successively finer silicon carbide paper (180, 320,
600 grit) until they were visually smooth. The finer grooves and grind-
ing scratches were removed by lap polishing the wafer with 1 μm diamond
paste on a nylon cloth. Water was used as a lubricant during this
process. Samples were washed thoroughly in cold water, ultrasonically
cleaned in acetone for several minutes, and air dried. Optical exami-

nation was used to determine both the extent of fiber growth and the quality of polish. This procedure will be referred to in the remainder of this thesis as the "standard method of preparation".

A second standard procedure was used for the rinsing and cleaning of the samples immediately after etching. Once the sample was removed from the particular etchant, it was immersed in a beaker of cold tap water for a few seconds and immediately placed in a second clean beaker of cold tap water for several minutes. This somewhat elaborate precaution was necessary to prevent the oxidation of any etchant which might stain the surface of the specimen if allowed to remain on it exposed to the air. The sample was then placed in a beaker of acetone in an ultrasonic cleaner as described previously. This procedure will be referred to as "standard washing and cleaning" in the remainder of this thesis.

Etching Procedure

The first technique used to expose, lengthen and point the molybdenum fibers consisted of rotating the specimen in the apparatus pictured in Figure 1. This device consisted of a low speed motor mounted on a drill press which turned the specimen holder, and was controlled by a variable speed switch. The speed of rotation was variable, but it was found by Pepper[3] that 20 rpm was the optimum value for good etching characteristics on UO_2-W composites. Rotation was necessary to ensure an even distribution of etchant over the face of the sample, and to allow the transport of fresh etchant to the sample. For etching, the sample was clamped in a special holder, rotated for a few seconds,

and then lowered into the beaker of etchant. After the required amount
of time the sample was raised, the beaker of etchant removed, and the
washing procedure was begun with the sample still rotating.

The second technique used to obtain a more uniform matrix surface
was almost identical to the one described above, except that the beaker
of etchant was placed in the small electrosonic "SONAC"* device on the
pedestal of the apparatus in Figure 1. The SONAC was filled with
methyl alcohol to transfer the agitation to the etchant. This setup
allowed the simultaneous stirring and agitation of the sample.

The last technique, which was used primarily for etching holes
in the composites, was called the "vertical ultrasonic method". It
consisted of a small beaker of etchant placed in the tank of the ultra-
sonic cleaner with the power unit set to 47 ma to give the maximum
amount of cavitation. The ultrasonic cleaner was manufactured by the
Acoustica Associates Corporation, and operates at a frequency of 40 KH_z.
The wafer was gripped in a pair of tweezers, and held vertically in the
etchant for the required period of time. Standard washing and cleaning
followed.

A special specimen holder was constructed for etching with solu-
tions containing sulfuric acid. Since the sulfuric acid attached both
metal tweezers and porcelain tipped tweezers, a teflon holder was made,
shown in Figure 2. The nylon screws, however, deteriorated rapidly and
had to be changed frequently.

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* SONAC is the trade name of a small device marketed for the cleaning
  of dentures by electrosonic agitation.

Thermal Annealing

Etching an unannealed sample resulted in extremely rough surfaces, Figure 3. Before any etching could be satisfactorily done, it was found that the wafers had to be annealed to remove cracks and strains. Samples were annealed in an H_2 atmosphere using a 4 MHz rf generator. The annealing equipment is shown in Figure 4. The rf field coupled to a Mo tube surrounding the sample, and heating progressed. The sample was raised in temperature rapidly to around $1500^{\circ}C$, held for 10 minutes, and cooled slowly over a period of 3 or 4 hours to ambient temperature.

A similar annealing process was used to round the pin tips, and the temperature and time conditions are described in the discussion.

Figure 1.   Apparatus used for Etching Gd_2O_3-Mo Samples

Spindle Chuck to go in Etching Apparatus

Nylon Screws to hold Samples in place
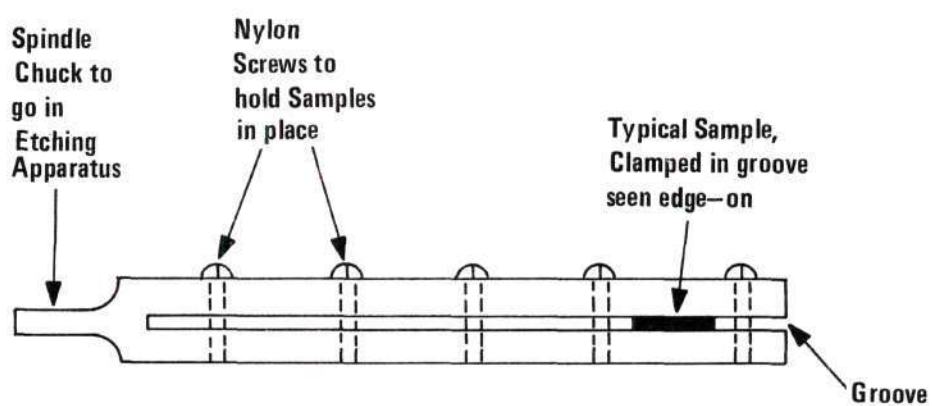
Typical Sample, Clamped in groove seen edge—on

Groove

Figure 2.   Special Teflon Gd_2O_3-Mo Sample Holder
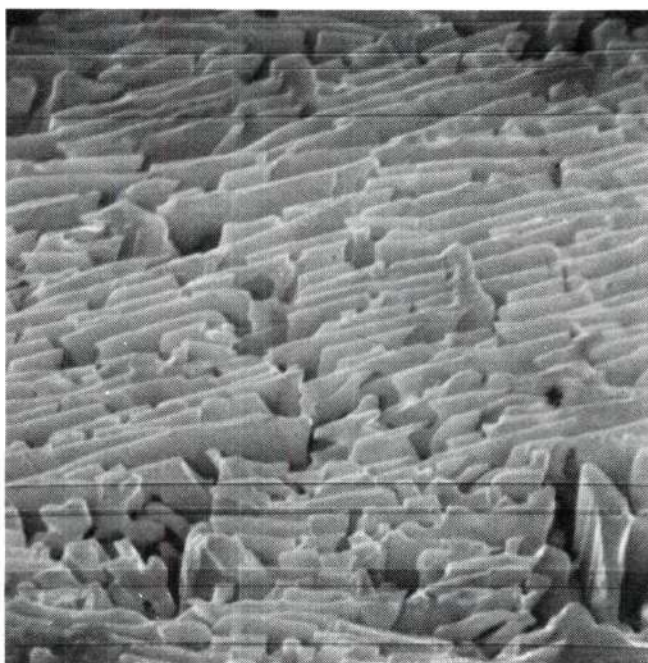
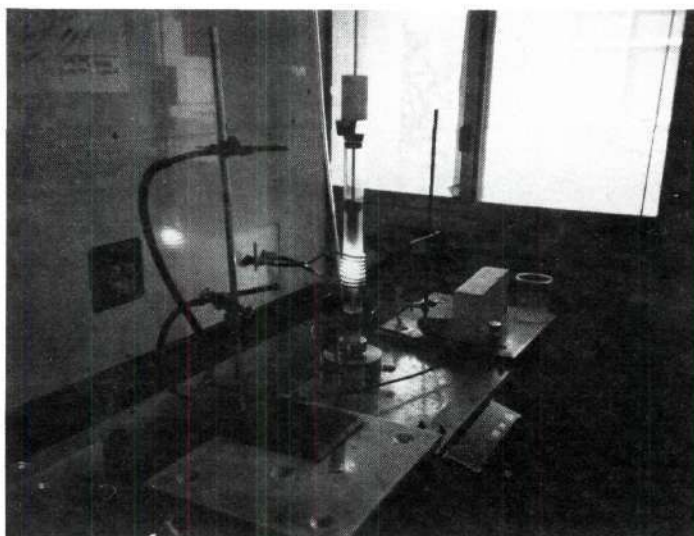Figure 3. Sample Etched Without Stress Relieving
Annealing Treatment (X4800)

Figure 4. Rf Apparatus used for Annealing Studies

CHAPTER IV

RESULTS AND DISCUSSION

The goal of this investigation was to formulate etchants and etching procedures that would allow flexibility in forming desired emitting geometries. In order to accomplish this goal, the experimentation was divided into six sections. The first section describes the thermal annealing procedures that must be followed before any etching could be attempted in order to relieve stresses in the gadolinia matrix. The second section is concerned with the selective removal of the gadolinia matrix in order to expose and lengthen molybdenum fibers. The next section explains the formation of various fiber tip shapes for electron emission, and the fourth section covers the selective removal of the molybdenum fibers in order to form holes in the matrix. The fifth section discusses the formation of recessed pointed fibers in holes in the matrix, and the last section describes attempts at using other etchants than the ones covered in the previous sections.

Preetch Thermal Annealing

A CeO_2 doped Gd_2O_3–Mo sample which was etched in pure, reagent grade sulfuric acid for 30 minutes at room temperature is shown in Figure 3. The solution apparently preferentially etched the regions of stress, because areas of stress are areas of higher energy. The preferential etching of microcracks is probably also responsible for the texture, and the pictured surface is a combination of the two effects.

Annealing removes stresses and closes microcracks thereby allowing good etching to occur. The thermal annealing allowed subsequent chemical etching to produce a smooth surface.

Etching to Expose Molybdenum Fibers

The etchants used to expose the molybdenum fibers by the selective removal of the gadolinia matrix were investigated, and the rate of fiber lengthening was determined.

The primary etchant used to lengthen fibers was concentrated reagent grade sulfuric acid. The sulfuric acid did attack the molybdenum fibers to a small degree, but over the time interval required to etch away 8 μm of matrix (20 minutes) no significant attack on the fibers was observed. The etched matrix was generally smooth, although a large variation from one section of the sample to another may exist. Figure 5 shows a typically etched specimen.

The rate of etching away of Gd_2O_3 to expose Mo fibers was determined by etching a sample in concentrated sulfuric acid for periods of 5, 10, 15, and 20 minutes. The sample was reground and polished in the standard manner before each individual etch run, and fresh acid was used for each run. This was done to eliminate the possibility of catalysts or reaction products being formed between the gadolinia and sulfuric acid which might affect the etching rate of the next time period. The height of the resulting fibers was determined by the difference in focal planes between the fiber tips and matrix in the reflected light microscope. In the light microscope the differences between different focal planes is independent of the magnification being
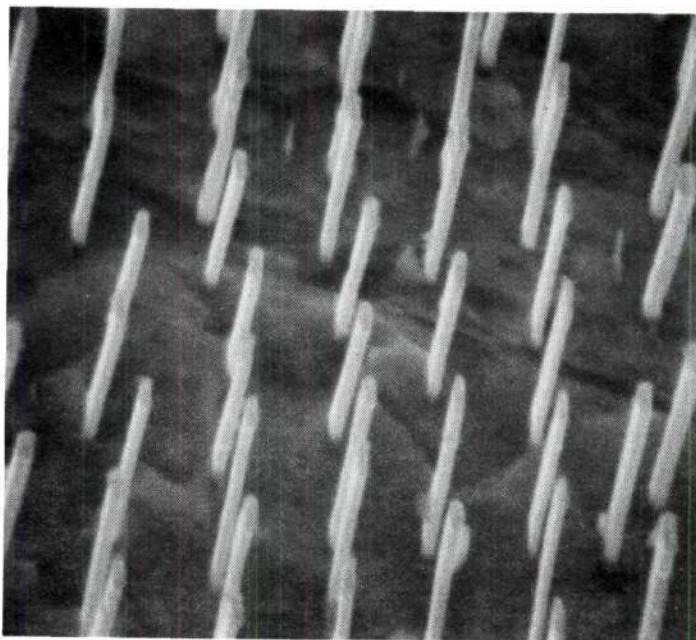
Figure 5. Gd$_2$O$_3$-Mo Sample with Selectively Etched Matrix Showing Exposed Fibers Prepared by Etching in Pure Concentrated H$_2$SO$_4$ (X10,500)

used. The microscope has a fine-focusing knob which is graduated in μm. The fiber height was measured as the difference between the values of the fine adjustment when focused on the matrix and fiber tips. Almost every sample examined showed roughly a 0.5 μm spread in fiber heights in various sections of the surface. The value for the fiber height was taken as the average of the maximum and minimum fiber height values. Figure 6 is a plot of fiber height versus etching time.

The above experiment was conducted twice, with a 3 month time period between runs. The exact same conditions were used both times. The data points for both runs are plotted in Figure 6. The data points are remarkably close to one another, and this is considered verification of the accuracy of this experiment. The two sets of data in Figure 6 show a rough linear dependence, but further analysis was performed. Each set of two corresponding data points was averaged, and these values were used to perform a straight line regression and a parabolic regression on a PDP-8E minicomputer. The equations of both these fits are also graphed in Figure 6. Copies of the computer programs and instructions for their use can be found in Appendix A. The correlation index, or degree of fitness of this data to the particular regression is .990976 for the parabolic and .978384 for the linear or straight-line. Since a 0 index designates no fit, and an index of 1 indicates a perfect fit, it can be seen that the etching rate of Gd_2O_3 to expose fibers more closely resembles a parabola than a straight line. Both fits are good, however, just by judging from their correlation coefficients. The parabola which describes the data is very close to linear because the data is located on the extreme "tail" or flat region of the parabola.
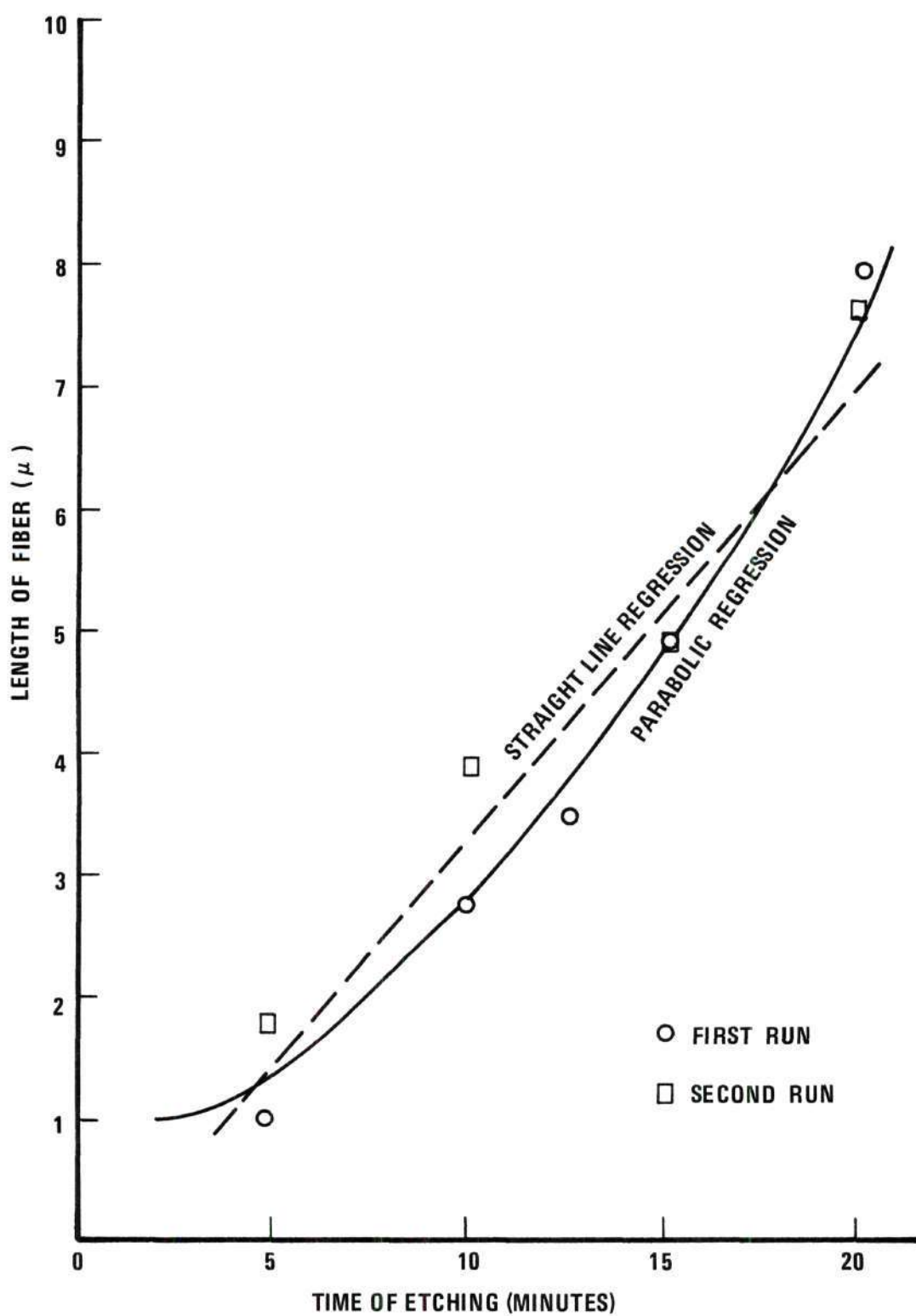
Figure 6. Exposed Fiber Height Versus Etching Time for Gd_2O_3-Mo Sample using Sulfuric Acid

The parabolic trend of the data, rather than a linear one, is not disturbing. The slight parabolic relation is considered accurate because of a "shielding" effect. As etching proceeds, the fiber length increases. Since the fibers in a Gd_2O_3-Mo composite are so fine and close together to begin with, the spaces between fibers act as tiny "channels" as the etching proceeds. Fresh etchant must be transported down these channels to the gadolinia matrix, and old used etchant must be transported out for etching to continue at a steady rate. Catalysts or reaction products may be formed between the H_2SO_4 and the gadolinia and become trapped at the bottom of such a channel, either accelerating the etching action at that point, or stopping the etching by shielding the surface from fresh etchants. This effect becomes more pronounced as time increases, and is also exhibited in the etching of holes which will be discussed later.

Forming Fiber Tip Geometries

Two methods were investigated for shaping molybdenum fibers to produce tips suitable for electron emission. The first method is the chemical pointing of the fibers and the factors influencing this pointing, and the second is the use of annealing treatments for the formation of rounded hemispheres, which were shown in the survey to yield a good emission geometry.

The etchant to point fibers as determined by Stendera[4], consists, of a small amount of NH_4NO_3 (several grams) in 100 ml of concentrated sulfuric acid (reagent grade). The exact amount of NH_4NO_3 is a subject of later discussion, but 4 grams yields good pointing. Figure 7 shows

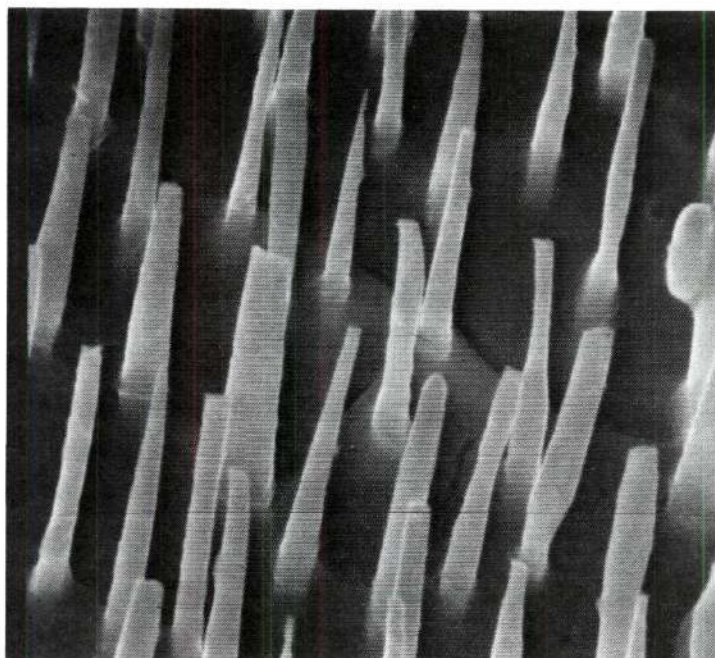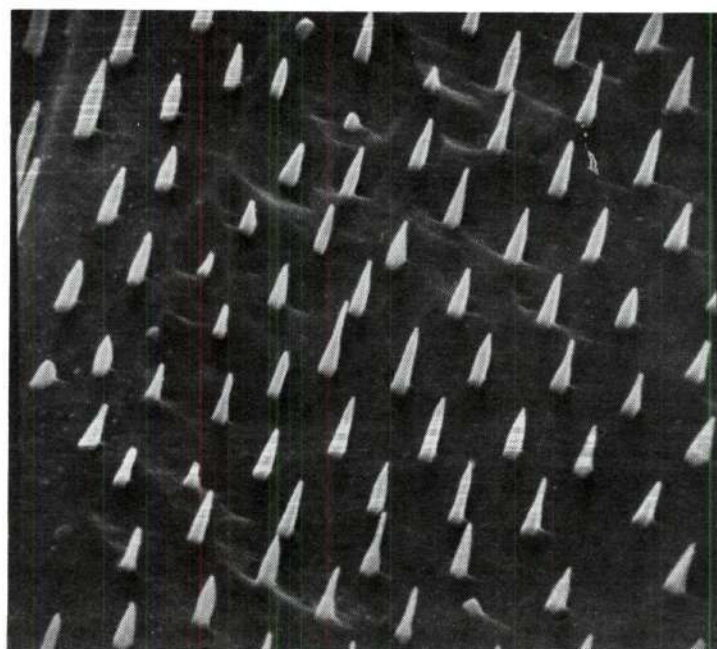Figure 7. Gd_2O_3-Mo Sample Etched for 8 Minutes in Pointing Solution Containing 4 grams NH_4NO_3 (X11,700)

Figure 8. Sample Etched for 8 Minutes in Ultrasonic Cleaner Only using Solution Containing 4 grams NH_4NO_3 (X5600)

a sample etched in this solution for 10 minutes. With only rotation the fibers tend to be irregular in shape, with wide variations in shape from one section of the sample to another. No explanation can be given for this except to say that a shielding effect is occuring, similar to the one observed for the fiber lengthening etchants, with the one difference being that the $NH_4NO_3-H_2SO_4$ solution is more sensitive to this effect that the H_2SO_4 etchant was alone.

It was this non-uniformity in etching behavior that initiated research into the ultrasonic agitation method of etching. The rational behind it was that if there was truly a shielding effect occuring, then ultrasonic cavitation would promote the transport of fresh etchant down the previously discussed channels, producing a smoother matrix. The very process of etching pointed fibers is complicated in nature. The pointing is accomplished by the etchant attacking the gadolinia at a slightly faster rate than it attacks the molybdenum. As etching proceeds, the tips of the fibers get smaller because they have been exposed the longest, while the bases undergo a small amount of attack, resulting in the formation of a pointed geometry.

The first attempt at ultrasonic etching was made utilizing the ultrasonic cleaner described in the procedure. The sample was held in a beaker containing 4 grams NH_4NO_3 in 100 ml of H_2SO_4 for 8 minutes with the ultrasonic cleaner on. Standard washing and cleaning followed. Figure 8 is a scanning electron micrograph of the sample. It is seen that while the fibers are well pointed and uniform, the matrix is poorly etched in a somewhat random fashion. The fact that the ultrasonic etching technique greatly improved the fiber pointing can be seen by com-

paring Figures 7 and 8. The unevenness of the matrix of the sample in Figure 8 is attributed to the lack of rotation during etching. Thus, ultrasonic etching alone is not sufficient to ensure a good penetration of etchant between the fibers at the same time providing a good distribution of etchant over the surface.

In order to provide agitation with a stirring motion, a SONAC device was employed with rotation. This device is not ultrasonic, but it does produce rather vigerous agitation. A sample of Gd_2O_3-Mo composite prepared in the standard manner was rotated at 20 rpm at room temperature for 8 minutes, with the etchant beaker sitting in the SONAC. Standard washing and cleaning followed. Figure 9 is a scanning electron micrograph of the sample. The overall improvement in the composite geometry is readily visible. The fibers are well pointed and uniform, and the matrix is generally quite smooth. Although it can't be surmised from the photograph, the sample was much more uniform from one area to another. The small rectangles at the base of each fiber may be a result of the cubic crystal structure of gadolinia.

The effect of the addition of NH_4NO_3 to concentrated H_2SO_4 was studied in order to determine how it affected pointing. Using just the basic etching technique of rotating the sample at 20 rpm at room temperature, different etchants containing 1, 2, 3, 4, and 5 grams of NH_4NO_3 per 100 ml of H_2SO_4 were tried. The time of etching of each sample was kept constant at 8 minutes. Standard washing and cleaning techniques were exercised. Figures 10, 11, 12, 13 and 14 show the samples etched in 1, 2, 3, 4 and 5 grams of NH_4NO_3 respectively. An obvious conclusion of this study as seen from the photographs is that the degree of point-
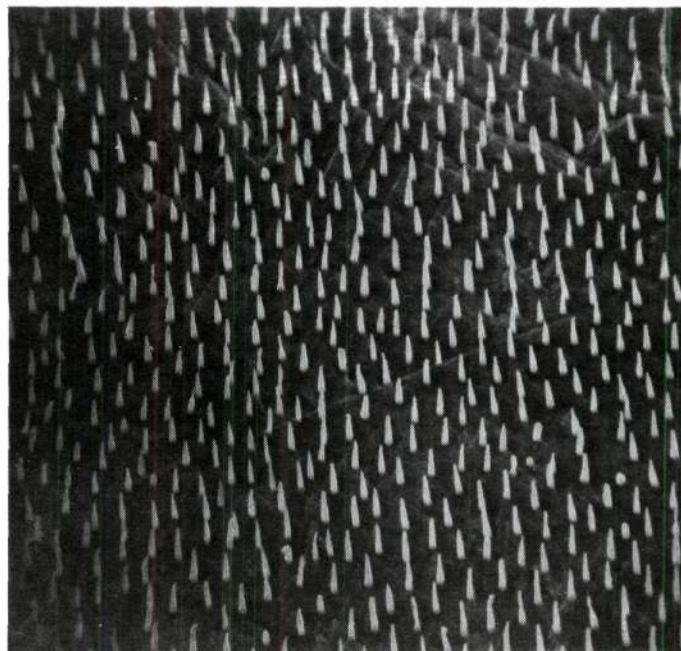
Figure 9. Gd_2O_3-Mo Sample Etched using Both Stirring Motion and and SONAC Vibration (X2350)

Figure 10.   Sample used in Pointing Study, Etched with 1 Gram NH_4NO_3 in 100 ml H_2SO_4 (X11,200)

Figure 11.   Sample used in Pointing Study, Etched with 2 Grams NH_4NO_3 in 100 ml H_2SO_4 (X11,500)

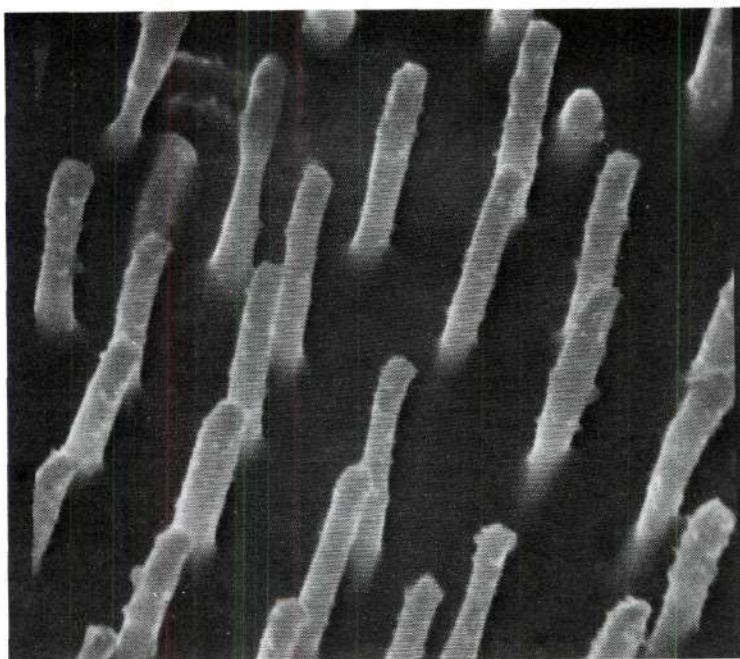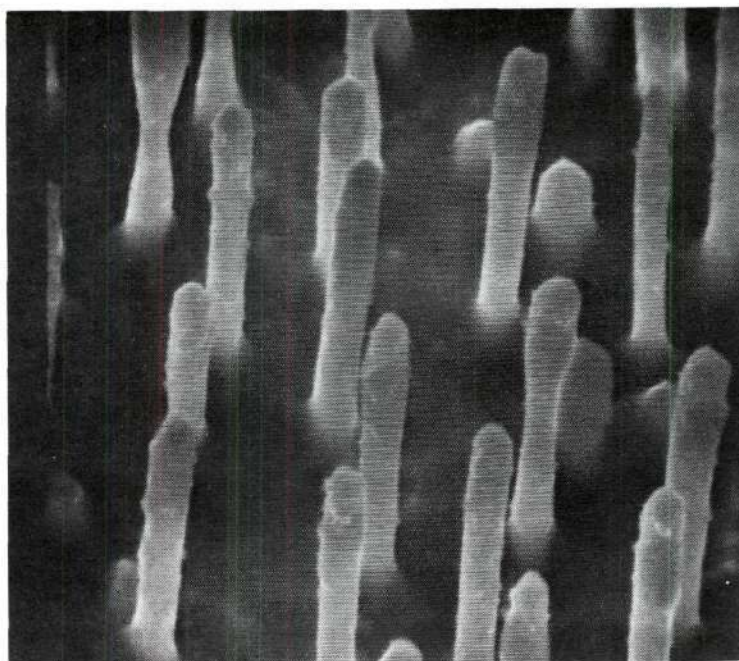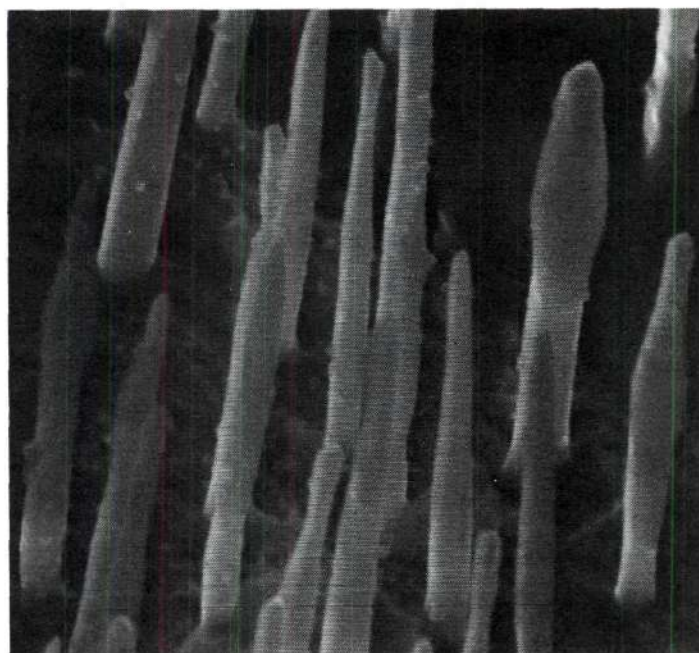Figure 12. Sample used in Pointing Study, Etched with 3 Grams NH_4NO_3 in 100 ml H_2SO_4 (X 11,700)
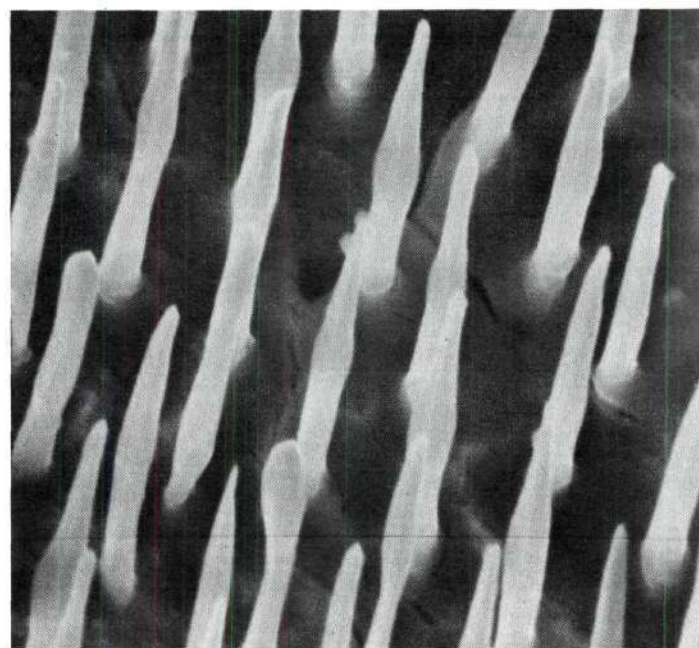

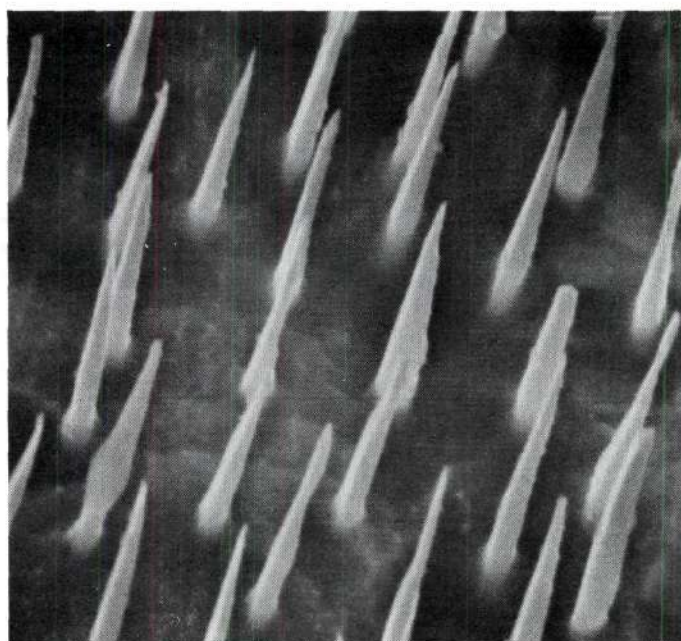Figure 13. Sample used in Pointing Study, Etched with 4 Grams NH_4NO_3 in 100 ml H_2SO_4 (X 11,900)

Figure 14. Sample used in Pointing Study, Etched with 5 Grams NH_4NO_3 in 100 ml H_2SO_4 (X 11,600)

ing increases with the amount of NH_4NO_3 added. It is also seen, however, that the roughness of the matrix similarily increases with increasing NH_4NO_3. Since both a smooth matrix and good pointing are necessary for any emission sample, a compromise must be reached. Based on the experimental results the 5 gram solution is best because of the good pointing produced. The matrix can always be smoothed out a little by etching for a short period of time in the lengthening etchant. There also appears to be a threshold at which pointing begins to occur. There is no appreciable difference between 1 gram or 2 grams of NH_4NO_3, as neither causes any appreciable pointing. Figure 12 shows that a definite pointing is achieved with 3 grams of NH_4NO_3. It is therefore concluded that it takes a certain amount (about 3 grams) of NH_4NO_3 to attack the molybdenum fibers at all, but that when it does attack it does so quickly.

A short experiment was performed to try to provide some insight into what actually does the pointing of the fibers in the CeO_2 doped Gd_2O_3-Mo system. Five grams of NH_4NO_3 were added to 100 ml of distilled water, and a sample was just rotated in this solution at 20 rpm for 8 minutes. Light microscope examination revealed that no attack on either the fibers or matrix had taken place at all. The sample was then placed in the normal pointing solution of 5 grams of NH_4NO_3 in 100 ml of H_2SO_4 to which a few milliliters of water was added. It was again revolved at 20 rpm for 8 minutes. This time the surface of the sample was completely destroyed. Apparently some complex is formed between the NH_4NO_3 and the H_2SO_4 which actually provides the pointing, and this complex is changed radically by the presence of just a small

amount of water.

The second area of investigation was concerned with annealing already pointed specimens to try to round the pin tips into spherical hemispheres which are of interest for field emission testing.

The rf unit in which the composites were originally grown and in which they were annealed to remove strains and stresses was used for this process. The study was concerned with finding the effects of both temperature and length of soak at a certain temperature on the shape of the fiber tips. Two temperatures, $1200^{o}C$ and $1600^{o}C$, and two times, 15 minutes and 25 minutes were chosen for investigation. Four of the better Gd_2O_3-Mo specimens were selected, and were pointed in a solution containing 5 grams of NH_4NO_3 in 100 ml of H_2SO_4 by the SONAC rotational method, followed by lengthening by the rotational method in concentrated H_2SO_4. The fibers were in the shape of right circular cylinders with pointed tips. The overall length of the exposed fibers was around 5 μm. The temperature was kept as close as possible to 1200 and $1600^{o}C$, reproducable to $\pm$ $25^{o}C$.

The rounding of the fiber tips by annealing for 15 and 25 minutes at $1200^{o}C$ can be seen in Figures 15 and 16, respectively. It can be seen that good rounding has been produced by surface tension effects, but the rounding at 15 minutes soak is much rougher than the rounding at 25 minutes soak. Apparently the rounding process was not completed by the end of 15 minutes. This is supported by the presence of little "blebs" of material on each pin tip that is not rounded, and the somewhat irregular rounding of some tips. The blebs may or may not be composed of Mo. The matrix of both specimens is somewhat rough, but is due
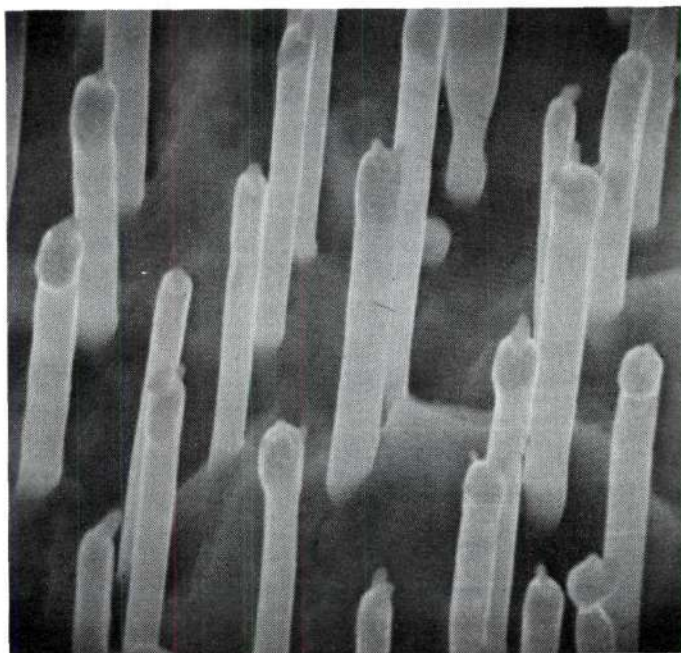
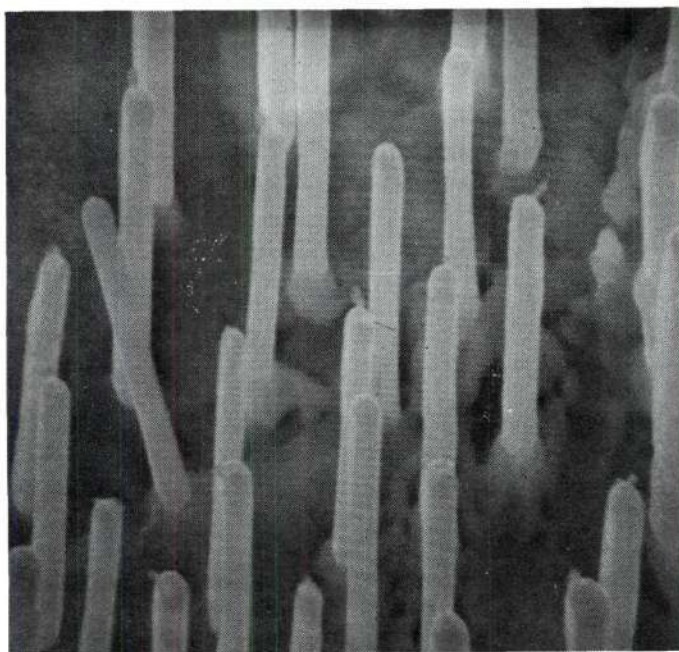Figure 15.   Gd$_2$O$_3$-Mo Sample After Annealing at 1200°C for 15 Minutes for Tip Rounding Study (X 12,300)

Figure 16.   Gd$_2$O$_3$-Mo Sample After Annealing at 1200°C for 25 Minutes for Tip Rounding Study (X 12,200)

to the annealing conditions.

The rounding of the pin tips and the destruction of the exposed fiber structure by annealing for 15 and 25 minutes at $1600^{o}C$ are exhibited in Figures 17 and 18, respectively. For the sample at 15 minutes soak, the matrix is very rough, the pins are poorly rounded and slumping, and the whole array appears to be meeting. Figure 18 verifies this, for at a soak of 25 minutes everything has completely melted. As a result of this data, an annealing condition of $1200^{o}C$ for 25 minutes was chosen as that yielding good hemispherical tips for the molybdenum fibers.

The fact that the fibers must be chemically pointed before annealing to give good rounding is exhibited in Figure 19. This figure shows a sample with fibers that are just lengthened and not pointed, after annealing at the optimum conditions of $1200^{o}C$ for 25 minutes. The rounding was generally poor.

Etching of Mo to Form Holes

The selective etching of the Mo fibers to form holes in the Gd_2O_3 matrix was first attempted using the hole etch for tungsten employed by Pepper[3]. This etchant consists of:

> 7.5 grams $K_3Fe(CN)_6$
>
> 2.5 grams NaOH
>
> 250 ml distilled H_2O

A typical sample, prepared in the standard manner, was rotated at 20 rpm at room temperature for 30 seconds. Standard washing and cleaning followed, and light microscope examination revealed that the Mo had been
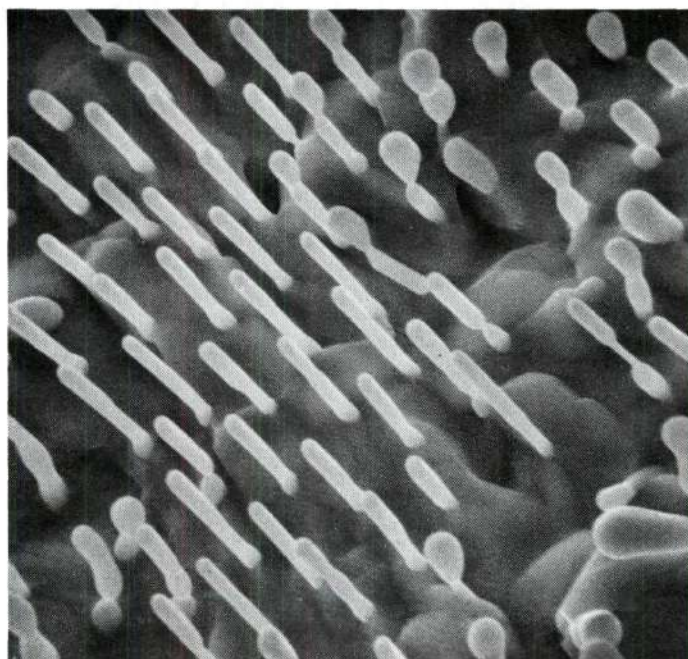
Figure 17. Gd_2O_3-Mo Sample After Annealing at 1600^oC for 15 Minutes, for Tip Rounding Study (X 6200)

Figure 18. Gd_2O_3-Mo Sample After Annealing at 1600^oC for 25 Minutes, for Tip Rounding Study (X 6400)

selectively etched away to yield holes. A scanning electron micrograph of such a structure is shown in Figure 20.

The method of determining the depth of a hole included the known etching rate of the gadolinia. In practice, a sample that had holes was placed in the standard fiber lengthening etchant for a known period of time. The gadolinia matrix was selectively etched away. This etching was conducted for a time sufficient to expose fibers once again. After cleaning, the length of the exposed fibers was measured. The depth of the original hole was then simply the known amount of Gd_2O_3 removed in microns (as determined from the etching time) minus the height of the exposed fibers.

Experiments conducted by a collegue[33] on the etching behavior of the UO_2-W system yielded the information that hole depth was, after a certain point, independent of etching time. This is an exaggerated case of the shielding effect discussed in the section covering the etching of exposed fibers in this chapter. These conclusions were verified in the Gd_2O_3-Mo system by etching two samples in the above hole etchant for 30 seconds and for 2 minutes. The measured hole depths were, for all practical purposes, identical. The fresh etchant cannot get down to the etching face fast enough, and some reaction products may be shielding the Mo against further dissolution. Using the standard hole etch, the maximum hole depth attainable by rotational etching is about 1 μm.

In an attempt to increase the possible hole depth, an investigation was conducted into changing the concentration of the etchant. An etchant, composed of the same chemicals, but 5 times the initial con-
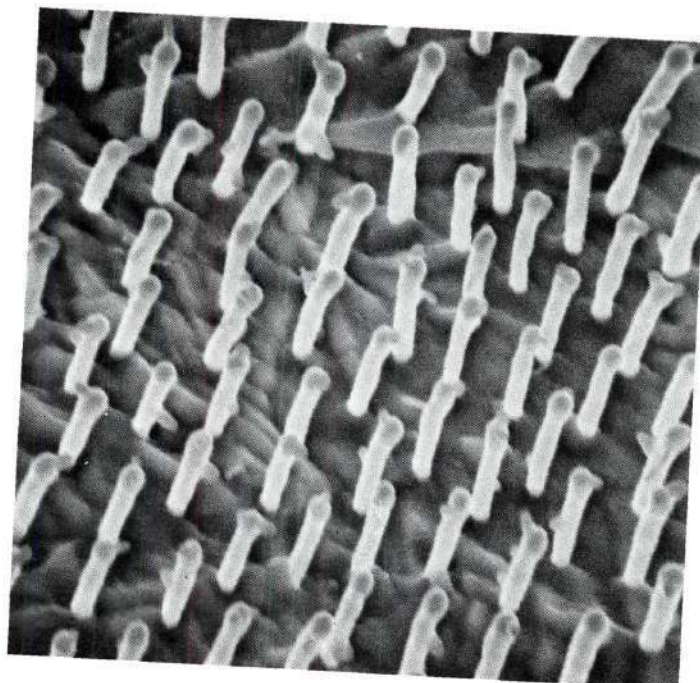
Figure 19. Sample with Unpointed Fibers After Annealing at 1200°C for 25 Minutes (X 5000)

Figure 20. Removal of Mo Fibers using $K_3Fe(CN)_6$ and NaOH Solution

centration was tried. It consisted of:

$$37.5 \text{ grams } K_3Fe(CN)_6$$

$$12.5 \text{ grams } NaOH$$

$$250 \text{ ml distilled } H_2O$$

Using the standard rotational etching technique, holes of 2.5-3 microns were produced.

The same etchant was then prepared in a concentration 10 times normal. It was composed of:

$$75 \text{ grams } K_3Fe(CN)_6$$

$$25 \text{ grams } NaOH$$

$$250 \text{ ml distilled } H_2O$$

Holes 3 microns deep were produced, using the same etching techniques. It is apparent that past a certain point, an increase in etchant strength has no effect on hole depth.

The "vertical ultrasonic technique" as described in the procedure was attempted next. It was postulated that the ultrasonic vibrations would greatly increase the transport of fresh etchant into the holes. The concept of rotating while etching was abandoned, since any effect this produced in moving etchant would be negligable compared to the action of the ultrasonic waves.

Using a 10 times normal concentration etchant, a sample prepared in the standard manner was held in the vertical position in the ultra-sonic cleaner for 1 minute. The resulting holes were measured to be 4.5 μm in depth. When the experiment was repeated with the sample immersed for 2 minutes, the holes were 7.5-8 μm deep.

The rate of etching holes was determined next. Using the 10

times normal etchant and the ultrasonic technique, samples were treated for periods of 30, 60, 90 and 120 seconds. Standard washing and cleaning and measuring techniques were used. Figure 21 is a plot of hole depth versus time of ultrasonic etching.

The above data was analyzed in the same manner as the fiber length etching rate data. Linear and parabolic regressions were run on the PDP-8E minicomputer. The results this time were remarkable. The linear fit had a correlation index of .994255 to the data. This indicates a good fit, but the parabolic fit had an index of .999875 to the data. This says that the relation of hole depth to ultrasonic etching time is almost perfectly parabolic. The equations of the fits are also drawn on Figure 21. The shape of the parabola indicates that the rate of etching is slowing down with time. All this supports the theory that there is a difficulty getting fresh etchant into the holes, for as the time increases and the holes get deeper the etching rate decreases.

Formation of Recessed Pointed Pins

The etching of CeO_2 doped Gd_2O_3 composites to form recessed pointed fibers in holes in the oxide matrix was investigated. The partially sucessful initial work will be explained in this section.

The etching was attempted as a two-step process. In the first step shallow holes, around 2-3 deep were etched in the sample by the use of the $K_3Fe(CN)_6$-NaOH-H_2O etchant. The second step is the application of a pointing etch composed of 5 grams NH_4NO_3 in 100 ml of sulfuric acid, which it is postulated, will point the fibers in the holes while only etching away a small amount of the matrix. Initial experiments were
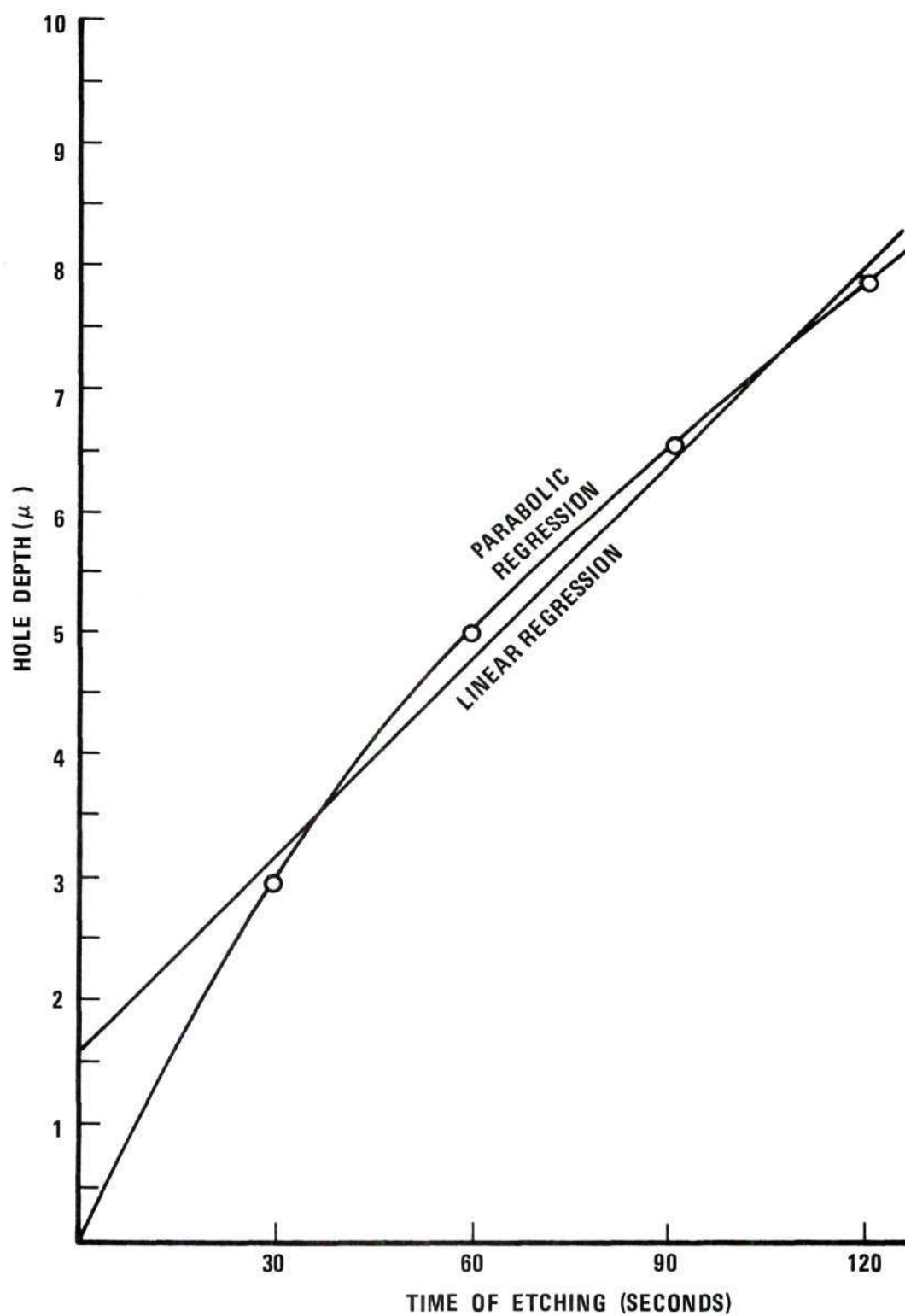
Figure 21. Hole Depth Versus Etching Time for Gd_2O_3-Mo Sample using
Vertical Ultrasonic Method

performed with the rate of hole depth formation in the first step set equal to the rate of fiber pointing and lengthening in the second step. Figure 22. It can be seen that not all the holes contain fibers, and that the shape of the holes is rather perculiar. The shape of the holes correspond to the surface markings which are probably related to the crystallographic orientation of the gadolinia matrix that was seen in Figure 9.

The same sample exhibiting recessed pins is shown at lower magnification in Figure 23. The holes are clearly visible, and some fibers are even apparent in the holes, especially in the area just a little above the exact center of the photograph. The fibers do not appear to be pointed however. Uniformity is a very big problem. The fibers seen exposed between some of the holes are a result of the fact that they were recessed in shallow holes which were completely obliterated by the second step of etching. This alone shows the variation in hole depth within one small region of sample.

Other Etchants

Throughout the course of this investigation, several additional etchants were tried. Although none of them were successful to any degree, the effect they had upon the composite samples will be briefly discussed.

An etchant containing equal parts of concentrated sulfuric acid and concentrated propionic acid was tried at room temperature. No attack whatsoever was observed in the light microscope.

A solution containing 20 grams of $K_3Fe(CN)_6$ in 100 ml of concen-

Figure 22.   Recessed Fibers in Holes in a Gd_2O_3-Mo Sample (X 4700)

Figure 23.   Recessed Fibers in Holes in a Gd_2O_3-Mo Sample Indicating
the Non-Uniformity of the Present Technique (X 1000)

trated H_2SO_4 was used as a possible etchant for recessed pointed fibers. The etchant gave off deadly cyanide fumes, and generally was difficult to work with. The surface of the composite sample was destroyed.

Seventy percent perchloric acid diluted with water was tried next. This acid caused a slight corrosive action on the gadolinia. The reaction was much too slow to be further considered.

Fuming sulfuric acid was substituted for concentrated sulfuric acid in the standard lengthening etchant. This acid was very difficult to work with, and completely destroyed the surface of the gadolinia-molybdenum sample.

CHAPTER V

CONCLUSIONS

1. The sample wafers of CeO_2 doped Gd_2O_3-Mo must be annealed at $1500^{\circ}C$ and cooled slowly to remove stresses and microcracks prior to any etching being conducted.

2. The exposure of gadolinia-molybdenum composites to an etchant consisting of concentrated, reagent grade sulfuric acid causes the gadolinia matrix to be selectively etched away thereby exposing and lengthening the molybdenum fibers.

3. The rate of fiber lengthening with time is parabolic, probably caused by the finess of the molybdenum fibers and their high number density.

4. The molybdenum fibers were pointed most efficiently using an etchant composed of 5 grams ammonium nitrate in 100 ml of concentrated reagent grade sulfuric acid.

5. An increase in the amount of ammonium nitrate in the pointing etch caused the fibers to be more sharply pointed, but with increasing matrix roughness.

6. Annealing a previously chemically pointed composite sample at $1200^{\circ}C$ for 25 minutes caused the molybdenum fiber tips to form good uniform spherical hemispheres.

7. The formation of holes in the gadolinia matrix by the selective dissolution of Mo is accomplished by the use of an etchant contain-

ing 75 grams $K_3Fe(CN)_6$, 25 grams NaOH, and 250 ml distilled water.

8. Due to the shielding effect, the relation of hole depth to ultrasonic etching time is perfectly parabolic.

CHAPTER VI

RECOMMENDATIONS

Uniformity was the largest problem associated with the selective chemical etching of CeO_2 doped Gd_2O_3-Mo composites. It is not known whether this non-uniformity stems from the initial growth of the composite by unidirectional solidification, or whether it is truly an etching variable. Work should be conducted to first isolate and qualify the nature of this non-uniformity problem, and then steps should be taken to correct it.

Different etchants should be investigated for all phases of etching. A different etchant for a particular geometry might be the answer to the problems of uniformity.

Further investigation of the combination of different etchants and annealing conditions should be pursued. Lower annealing temperatures for longer periods of time might accomplish the same result without severe deterioration of the sample.

Changes in the pointing etch should be made to determine if the taper of the pointing could be changed, and if the matrix could be damaged less.

The recessing of pointed fibers in holes must receive continued study. The two-step process is a start, but other etchants and techniques will have to be found that will finally yield a good uniform geometry.

Greater uniformity in the depth of etched holes should be obtained. New techniques of etching, particularly in the ultrasonic area, might prove useful.

APPENDIX A

COMPUTER PROGRAMS USED IN REDUCTION OF FIBER LENGTH
AND HOLE DEPTH VERSUS ETCHING TIME DATA

The computer programs used in all calculations were written in Focal 69 designed for use on a PDP-8E minicomputer manufactured by the Digital Corporation of Maynard, Massachusetts, with at least four thousand words of memory. Focal 69 is a conversational language, and the programs were written taking full advantage of this feature so that even an inexperienced researcher could apply them.

The parabolic and linear, or straight-line regressions are computer programs that fit the input data to either a parabola or a straight line. Figure 24 is a computer generated copy of the parabolic regression program, and Figure 25 is a computer generated copy of the linear regression program. Both programs function identically insofar as data input and output.

The programs accept as input data N, the number of pairs of data points consisting of $X(i)$, $Y(i)$....$X(N)$, $Y(N)$. The program automatically increments i, so all the researcher needs to do is type in the appropriate data values when the computer "asks" for them. In this research, the variable X was considered to be the length of time of etching, and the variable Y was either the fiber length in microns, or the hole depth in microns depending on the particular experiment. The output consists of the equation of the fitted parabola or straight line with Y as a function of X. This equation is followed by the correla-

tion coefficient, which indicates the degree of closeness of the in-serted data to either a parabola or a straight line. The computer then generates a list of the original X and Y data points with the corre-sponding calculated value of Y that fits the parabola or straight line.

```
C  FOCL/F   05/08/72

01.01  F
01.10  A  ?N?,!
01.20  F  I=1,N;D 1.25
01.22  G  1.3
01.25  T  %2,?I?,"   ";A ?X(I),Y(I)?, !
01.30  F  I=1,N;D 2
01.40  S  A(21)=A(12);S A(22)=A(13);S A(31)=A(13);S A(32)=A(23);
 01.41  S  A(11)=N
01.50  F  K=1,2;F I=K+1,3;D 3
01.51  S  C(3)=B(3)/A(33);S I=3
01.53  S  S=0;S I=I-1
01.54  F  J=I+1,3;S S=S+A(10*I+J)*C(J)
01.55  S  C(I)=(B(I)-S)/A(10*I+I)
01.56  I  (I-1)1.58,1.58,1.53
01.58  T  %, !, "EQUATION",!!!
01.59  T,"Y =",C(1)," + ",C(2),"* X + ",C(3),"* X↑2",!!
 01.60  F  I=1,N;S YC(I)=C(1)+C(2)*X(I)+C(3)*X(I)↑2
01.61  S  YB=B(1)/N
01.62  F  I=1,N;S NB=NB+YC(I)/N
01.64  F  I=1,N;D 5
01.68  T  !!, "INDEX =",FSQT(CN/CY),!!!
01.69  T  "        *X*                 *Y*                 *Y CAL*",!!
 01.70  F  I=1,N; D 1.81
01.75  G  6.1
01.81  T  %,"  ",X(I),"        ",Y(I),"        ",YC(I),!!

02.10  S  A(12)=A(12)+X(I);S A(13)=A(13)+X(I)↑2;S A(23)=A(23)+X(I)↑3
 02.15  S  A(33)=A(33)+X(I)↑4;S B(3)=B(3)+Y(I)*X(I)↑2
02.20  S  B(1)=B(1)+Y(I);S B(2)=B(2)+Y(I)*X(I)

03.10  S  M=-A(10*I+K)/A(10*K+K)
03.20  F  J=K,3; S A(10*I+J)=A(10*I+J)+M*A(10*K+J)
03.30  S  B(I)=B(I)+M*B(K)

04.10  S  NB=NB+YC(I)/N

05.10  S  CN=CN+(YC(I)-NB)↑2;S CY=CY+(Y(I)-YB)↑2

06.01  S  SMDIF=0
06.10  F  I=1,N;S SMDIF=SMDIF+(Y(I)-YC(I))↑2
06.20  S  V=FSQT(SMDIF/(N-1))
06.30  T  !,"STANDARD ERROR OF ESTIMATE =",V,!;Q

07.10  F  I=1,3;F J=1,3;S A(10*I+J)=0
07.20  F  K=1,3;S B(K)=0;S C(K)=0
07.30  S  NB=0;S CN=0;S CY=0
```

Figure 24. Computer Generated Copy of Parabolic Regression Program

```
C FOCL/F  05/03/72

01.01 F
01.10 A ?N?,!;F I=1,N;T #2, ?I?," ";A ?X(I),Y(I)?,!
01.15 F I=1,N;S X=X+X(I);S Y=Y+Y(I)
01.20 S XB=X/N;S YB=Y/N
01.25 F I=1,N;D 2
01.30 S S1=SX/N;S S2=SY/N;S S3=SZ/N
01.35 S A=S3/S1;S B=YB-(XB*S3/S1)
01.50 F I=1,N;S YC(I)=A*X(I)+B
01.60 T !!!!,"EQUATION",!!,%," Y =",A,"* X +",B,!!
01.65 T !, "INDEX = ",S3/FSQT(S1*S2),!!
01.70 T !!,"        *X*              *Y*            *Y CAL*",!!!
 01.72 F I=1,N;D 1.75
01.73 D 4
01.75 T %," ",X(I),"        ",Y(I),"        ",YC(I),!!
01.99 Q

02.10 S SX=SX+(X(I)-XB)↑2;S SY=SY+(Y(I)-YB)↑2
02.20 S SZ=SZ+(X(I)-XB)*(Y(I)-YB)

04.05 S X=0
04.10 F I=1,N;S X=X+(Y(I)-YC(I))↑2
04.20 S V=FSQT(X/(N-1))
04.30 T "STANDARD ERROR OF ESTIMATE =",V,!;Q

05.10 S X=0;S Y=0;S SX=0;S SY=0;S SZ=0
```

Figure 25. Computer Generated Copy of Linear Regression Program

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