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New Techniques for the Synthesis of Metals and Alloys

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SEMI-ANNUAL TECHNICAL REPORT NO. 5

UCLA-ENG-7328
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NEW TECHNIQUES FOR THE SYNTHESIS OF METALS AND ALLOYS

R.F. BUNSHAH

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SEMI-ANNUAL TECHNICAL REPORT NO. 5

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13. ABSTRACT

I. New Techniques for the Synthesis of Metals and Alloys

The high rate physical vapor deposition (HRPVD) process is to be used for the following:

1. Preparation and characterization of Ni and Ni-20Cr alloy sheet.
2. Synthesis of compounds Y_2O_3, TiC, Si_3N_4 by reactive evaporation and their characterization.
3. Dispersion strenghtened alloys, Ni-20Cr-Y_2O_3, Ni20Cr-TiC and Ti-Y_2O_3.

This report describes:

1) Preparation of Nickel foil by HRPVD techniques and evaluation of its properties.
2) Experiments on high rate deposition of Y_2O_3, TiC, Si_3N_4 by direct evaporation and of Y_2O_3 and Si_3N_4 by reactive evaporation and activated reactive evaporation.

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High Rate Physical Deposition Process						
Lattice parameter						
Microhardness						
Nichrome						
Nickel						
Nitrides						
Oxidation						
Oxides						
Pressure barrier						
Reactive evaporation						
Refractory carbides						
Silicon nitride-Si_3N_4						
Substrate						
Synthesis of Materials						
Thickness distribution						
Titanium carbide						
Yttria-Y_2O_3						
Yttrium						

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Security Classification

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PART I

New Techniques for the Synthesis of Metals and Alloys (Tasks I, II, III)

INTRODUCTION

This report describes research activities on ARPA Grant No. AO 1643. The scope of the work is divided into two major areas of effort and further subdivided into four tasks as shown below:

1. New Techniques for the Synthesis of Metals and Alloys - Tasks I, II, and III. (Professor R.F. Bunshah - Principal Investigator)
2. The Properties of Rare Earth Metals and Alloys - Task IV (Professor D. L. Douglass - Principal Investigator)

In the following, progress on Tasks I, II and III is reported. Progress on Task IV will be reproted in a subsequent report.

PART I

NEW TECHNIQUES FOR THE SYNTHESIS OF METALS AND ALLOYS
(TASKS I, II, AND III)

R. F. Bunshah

I. Background

High rate physical vapor deposition (HRPVD) techniques$^{(1-8)}$ are to be used to prepare metallic alloys, ceramics, and metal-ceramic mixtures (dispersion strengthened alloys). The method consists of evaporation of metals, alloys and ceramics contained in water cooled crucibles using high power electron beams. The process is carried out in a high vacuum environment. The use of high power electron beams makes it possible to produce very high evaporation rates. The vapors are collected on heated metallic substrates to produce full density deposits at high deposition rates.

There are three tasks in this section:

Task 1: The preparation and characterization of nickel and Ni-20Cr alloy sheet by the high rate physical vapor deposition process.

Task II: Synthesis and characterization of compounds by Reactive Evaporation. The compounds to be prepared are Y_2O_3, TiC and Si_3N_4.

Task III: Dispersion strengthened alloys produced by HRPVD Process, and their characterization. The specific alloys to be studied are:

A. Ni-20Cr-Y_2O_3 B. Ni-20Cr-TiC C. Ti-Y_2O_3

Single source and two source evaporation methods will be used to produce these alloys.

The HRPVD process has several attractive features:

A. Simple, full density shapes (sheet, foil, tubing) can be produced at high deposition rates, 0.001" per minute thickness increment thus making it an economically viable process.

B. Metals and alloys of high purity can be produced.

C. Very fine grain sizes (1μ grain diameter or smaller) can be produced by controlling substrate temperature. Grain size refinement is produced by lowering the condensation temperature.

D. An alloy deposit may be produced from a single rod fed source. This occurs because the molten pool at the top of the rod is about 1/4" deep only. The vapor composition is the same as that of the solid rod being fed into the molten pool. At equilibrium, the composition of the molten pool differs from that of the vapor or the solid feed. It is richer in those components having a low vapor pressure. The composition of the vapor is the product of the vapor pressure times the mole fraction of the component. For example, a Ti-6Al-4V alloy deposit where the differences in vapor pressure of Al and V are a factor of 5,000 at 1600°C can be produced by evaporation from a single source. The feed-rod is Ti-6Al-4V and the molten pool is much richer in V than in Al.

E. Two or more sources can be used to simultaneously deposit on the same substrate thus conferring the ability to produce complex alloys. For example, an alloy with a 2 or 3 component solid solution matrix may be evaporated from one source and another metal or ceramic for the dispersed phase from another source. The dispersion size and spacing should be very fine since the deposition is occurring from the vapor phase.

The unique feature of this process is that all of the above benefits can be obtained simultaneously.

It should be noted that the condesnation temperature is a very important process variable. Bunshah and Juntz(8) found that for titanium, as the deposition temperature is lowered the grain size of the fully dense deposit becomes finer. At very low temperatures (~25% of the melting point) the deposit has less than full density. Since a fine grain sized microstructure represents an optimum condition of strength and toughness in a material, the importance of control over the deposition temperature becomes obvious.

II. Scope of Work and Progress in Reporting Period (September 1, 1972 - February 28, 1973)

The main tasks on this contract are the preparation and testing of the various alloys, ceramics and dispersion strengthened alloys as outlined in Section I above. Very essential to the preparation of suitable test specimens are two other factors:

A. Design of the apparatus for high rate physical vapor deposition.

B. Theoretical calculation of the thickness distribution and temperature distribution of the deposited material which is in this case in the form of a sheet.

Both of these tasks are essential preliminaries to the main scope of work. They were completed and described in semi-annual technical report No. 1.(9)

Two papers based on item B above have been published.(10,11)

A NEW process for the synthesis and high rate deposition of compounds was developed.(12) The process is called Activated Reactive Evaporation and two papers(13,14) have been presented and accepted for publication.

During this period, two tasks were carried out. Nickel foils were prepared by HRPVD techniques and their properties evaluated. This is described in Appendix 1. Experiments with direct evaporation of Y_2O_3, Si_3N_4 and TiC were carried out to investigate the feasibility of producing deposits of these compounds. The synthesis of Y_2O_3 by reactive evaporation and activated reactive evaporation was further explored. These results are described in Appendix 2.

III. Future Work

In the next half-year period, the following work is scoped.

A. Continuation of the work on deposition of Ni and Ni-20Cr alloy sheets and a study of their structure and properties.

B. Continuation of the work on the synthesis and testing of Y_2O_3, TiC, and Si_3N_4 by reactive evaporation and activated reactive evaporation.

C. Initiation of the work on production of Ni-20Cr alloys containing dispersed phases by HRPVD processes from two evaporation sources.

IV. Personnel

The following personnel have been working on this project in this reporting period.

Principal Investigator - Professor R. F. Bunshah

Post Doctoral Fellows: Dr. H.A. Beale

Graduate Students: Mr. Rao Nimmagadda and Mr. Neil Kane

Technician: Mr. Fred Weiler

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APPENDIX I

High Rate Physical Vapor Deposition of Nickel Foils

I. Introduction

The objective of this program is to determine if fully dense structures of nickel produced by high rate physical vapor deposition techniques can be classed as engineering materials. This can be achieved by investigating the relationship between microstructure and properties. Characterization of the material was carried out by determination of grain size, grain morphology, density, tensile properties, bend ductility, and hardness. Samples of conventionally produced (cast and rolled) nickel foils were also subjected to the same testing procedures in order to form a basis of comparison for the vapor deposition technique.

II. Experimental Procedures

A. Vapor Deposited Samples

The deposited nickel foils were produced by high rate physical vapor deposition (HRPVD) techniques. This process was carried out in high vacuum by evaporation of a 2" (nominal) diameter nickel billet placed in a rod fed electron beam heated source. Fig. 1 shows a schematic representation of the deposition set-up. Nickel vapors were condensed on a flat, rotating substrate located above the molten pool. In order to produce a uniform thickness distribution in the deposit, the substrate axis was tilted 30° from horizontal. All substrates were preheated prior to deposition by a spirally wound, tungsten wire, radiation heater located on the back side of the substrate. Temperature was monitored and controlled by use of a chromel-alumel thermocouple spot-welded to the substrate.

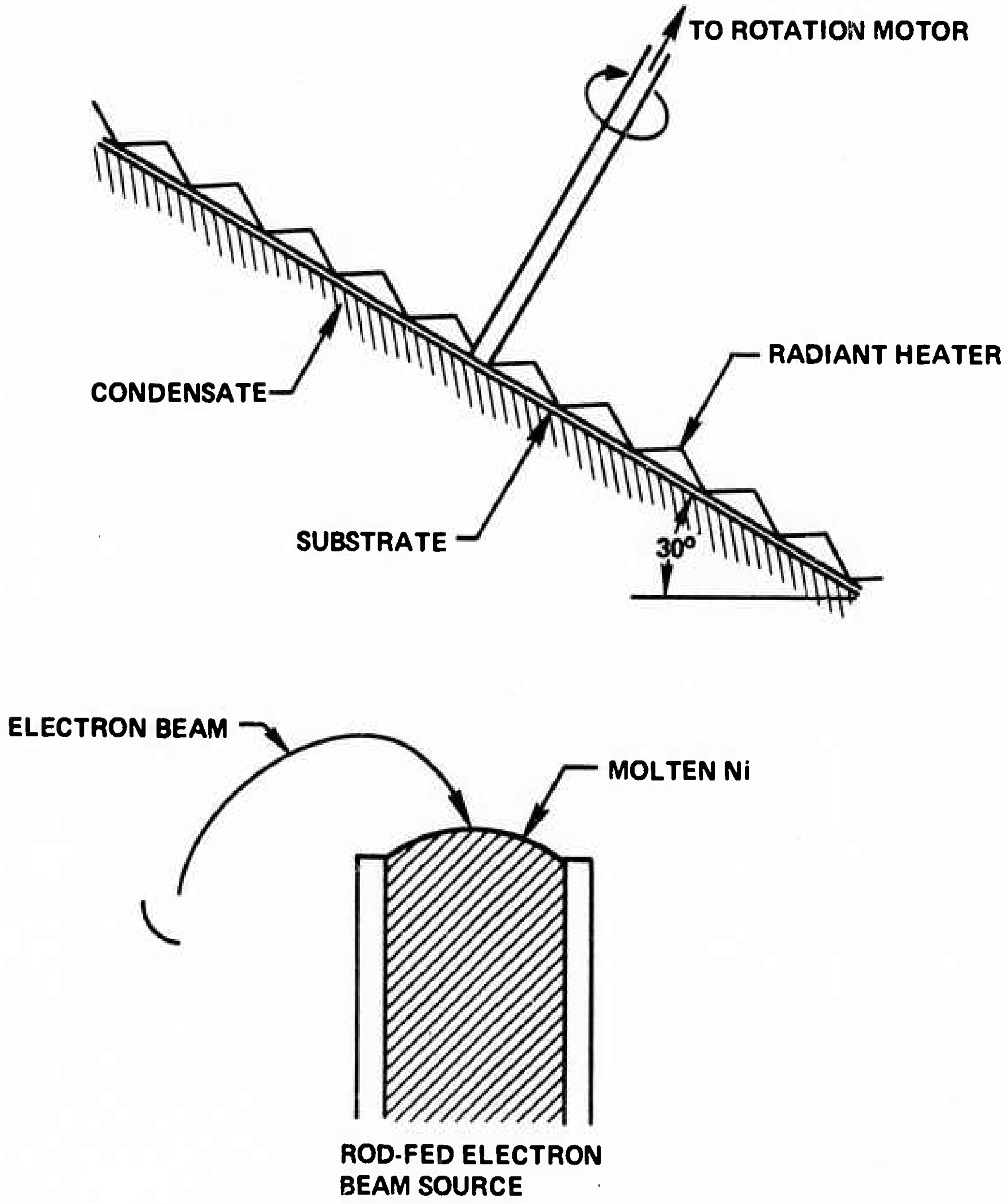

Figure 1. Schematic of Deposition Set-Up.

The substrate material was .005" thick, 11" diameter stainless steel. Removal of the deposited nickel foil from the substrate was facilitated by application of a thin halide film on the stainless steel prior to evaporation of the nickel. In addition to the data presented in this report, certain calibration runs were conducted to become familiar with the characteristics of nickel evaporation.

B. Rolled Samples

The conventionally produced nickel foils were cold-rolled from slabs cut from the same billet used in the evaporation process. Samples were 95% cold-worked and then recrystallization annealed in a vacuum of 10^{-5} torr.

C. Grain Size Determination

The grain size of the deposit was controlled by selection of the substrate temperature. In the rolled foil, grain size was controlled by choice of annealing temperature and time. Grain size determination was done on all samples as follows. The samples were mounted in lucite, hand sanded on a series of fine grit emery papers, and then mechanically polished on a cloth with an 0.3μ Al_2O_3 polishing compound slurry. A variety of etchant solutions were tried. The best results were obtained with glyceregia and aquaregia. Photomicrographs of the samples were taken on a Bausch and Lomb metallograph. The average grain diameter was determined using a linear intercept method.(1)

D. Density

Using a Westphal analytical balance, the sample density was determined by the immersion technique. The difference between sample weight in air and immersed in a liquid divided by the liquid specific gravity yielded the sample volumes. Air weight divided by volume gave the density.

E. Mechanical Properties

1. Tensile Properties

The samples were tested to determine their tensile properties: 0.2% offset yield stress, ultimate tensile strength, percent elongation and percent reduction in area. Tensile sample dimensions conformed to ASTM specification E8-69 for subsize specimens. The nickel was machined to size using a rotary blade Tensilkut machine. All sample edges were sanded to remove roughness. Testing was carried out on an Instron machine using a strain rate of .02"/min and a maximum load of 500 lbs. The deposited samples were tested in both the as deposited state and after a recovery anneal while the rolled samples were tested after recrystallization annealing. Duplicate samples were used for each data point.

2. Hardness

Hardness measurements were made using a Tukon Microhardness Tester with a 136° diamond pyramid indentor. Loads used ranged from 100 to 500 g. The foil samples were mounted in lucite to assure rigidity. The size of indentation was chosen such that multigranular hardness, rather than intergranular hardness, was being measured.

3. Bend Ductility

Room temperature bend ductility tests were performed using mandrels made of wires of diameter approximating sample thickness. Samples underwent 180° bends around these mandrels and the bent surface was then checked in a metallograph for any evidence of cracking.

III. Results and Discussion

A. Grain Size and Morphology

In vapor deposited foils the grain size is strongly dependent on the deposition temperature. Table I lists a compilation of the pertinent

Table I

Deposition Parameters

Sample	Beam Current (amps)	Pressure (Torr)	Deposition Temp. °C	Evaporation Rate g/mn	Condensation Rates	
					g/min	mil/min
Ni-8	1.00	1.10^{-5}	554	3.14	.98	.125
Ni-9	1.00	1.10^{-5}	426	3.09	1.00	.128
Ni-10	1.00	1.10^{-5}	329	2.98	.97	.125

deposition parameters. It has been shown by Movchan and Demchishin(2) that for nickel and other materials three characteristic morphology zones exist in vapor deposited foils. As shown in Fig. 2, these are: zone 1-domed surface structure with tapering grains through the cross-section; zone 2-columnar grains through the cross-section with a smooth matte surface: and zone 3-equiaxed grains in both the cross-section and surface of the deposit. From prior work on several metals and compounds,(2,3,4) the change in morphology between zone 1 and zone 2 occurs at approximately 0.25 T_m and between zone 2 and 3 at approximately 0.5 T_m. T_m is the melting point in °K. For nickel the approximate boundary temperature between zone 1 and zone 2 is 270°C (520°F) and between zone 2 and zone 3 it is 450°C (840°F). Table II lists the deposition temperatures, grain sizes and thicknesses of the samples. The morphology of our deposits conformed closely to nickel deposit morphology reported by Movchan and Demchishin.(2) In the deposits at 329°C (625°F) and 426°C (800°F) deposition temperature, columnar grains in the cross-section were observed. In the deposit at 554°C (1030°F) deposition temperature the morphology was fully equiaxed grains. The range of grain sizes in the deposits was from 12μ to 26μ.

In the rolled foils, the grain sizes were controlled by varying the time and temperature of annealing. Table II shows the annealing parameters used. All samples showed an equiaxed grain morphology with a large abundance of annealing twins.

B. Density

It has been shown for the HRPVD process that if the substrate temperature is greater than .25 T_m, the deposit will be fully dense. Our determination of the density showed this to be true. Density values for all samples, both deposited and rolled was approximately 8.9 g/cm^3.

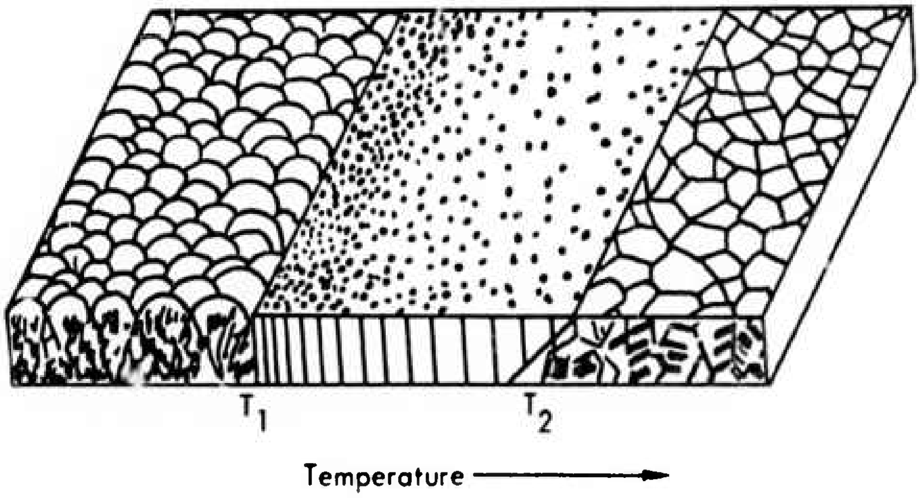

Figure 2. Structural Zones in Condensates. (After Movchan and Demchishin)(2)

Table II

Grain Sizes and Sample Thickness

Deposited Samples

Sample	Substrate Temp.	Grain Size(μ)	Thickness(mil)
Ni-8	554°C (1030°F)	26.5	15.0
Ni-9	426°C (800°F)	19.0	15.5
Ni-10	329°C (625°F)	12.7	15.0

Rolled and Annealed Specimens

Sample	Annealing Temp.(°C)	Annealing Time(min)	Grain Size (μ)	Thickness(mil)
Ni-R-1	700	90	20.5	15.0
Ni-R-3	700	75	18.0	15.0
Ni-R-4	650	20	11.5	15.0

C. Mechanical Properties

1. Tensile Properties and Hardness

In Table III, yield stress, ultimate tensile strength, percent elongation, percent reduction in area, and hardness are shown for the deposited and rolled samples. It is seen that both materials exhibit very similar properties. The Hall-Petch relationship was investigated for yield stress and hardness by plotting these values against the inverse square root of the average grain siameter.(5,6,7) The Hall-Petch relationship was developed originally to explain the dependence of yield stress on microstructure. Subsequently, work by Armstrong(6) and Bunshah and Armstrong(7) has shown that the same type of equation can be used to explain the relationship of hardness to grain size.

The Hall-Petch relationship is:

$$\sigma_y = \sigma_o + K_y d^{-1/2}$$

where σ_y = yield stress

σ_o = Hall-Petch intercept - a measure of the stresses necessary to move dislocations in a grain without resistance from grain boundaries

K_y = the Hall-Petch slope - a measure of grain boundary resistance to slip at yield

The value of the Hall-Petch slopes is altered by impurity atoms in the matrix, since this slope is often considered as a measure of dislocation locking by solute atoms.

For hardness, the Hall-Petch type relationship is:

$$H = H_o + K_H \ell^{-1/2}$$

applied, where H_o and K_H are experimental constants analogous to the above

Table III

Mechanical Properties

Sample	Method of Preparation	Grain Size(μ)	Yield Stress (.2%)(Ksi)	Ultimate Tensile Strength (Ksi)	% Elongation	% Reduction in Area	DPH Hardness (Kg/mn^2)
Ni-8	Deposited	26.5	18.4	48.1	39.0	20.8	96.6
Ni-9	Deposited	19.0	19.2	47.9	32.5	20.7	109.1
Ni-10	Deposited	12.7	22.6	51.6	34.5	21.4	103.7
Ni-10*	Deposited and Stress Relieved	12.7	23.0	52.4	26.0	16.3	-
NiR-1	Rolled & Annealed	20.5	20.4	58.7	50.7	33.2	93.0
NiR-3	Rolled & Annealed	18.0	20.6	57.6	44.5	30.0	90.8
NiR-4	Rolled & Annealed	11.5	25.5	60.9	45.0	27.2	92.5

mentioned Hall-Petch yield stress constants. Fig. 3 shows the Hall-Petch plot for yield stress vs. inverse square root of grain diameter. Fig. 4 shows the plot of the hardness vs. the inverse square root of the grain diameter.

In both cases, the data is in good agreement with the Hall-Petch type relationship. As shown in Table III the hardness of the deposited samples is a few percent higher than rolled and annealed foils. This shift is in agreement with the slightly larger ductility shown in the rolled foils.

In Table IV values for σ_o, K_y, H_o, K_H, σ_o/H_o and K_y/K_H are given. Possible reasons attributing to the difference in the Hall-Petch constants between the as deposited and the rolled/annealed material may be: 1) high impurity content in the rolled foils; and 2) morphology difference in the grain structures as discussed above.

To determine whether residual stresses were affecting the mechanical properties of the deposited structures, samples of the deposits were stress-relief annealed for two hours at 300°C. Testing of these showed no change in tensile properties as shown in Table III.

Work done by Sonon and Smith(8) with 99.98% pure Ni melted and cast at 10^{-2} torr was compared with this data. Fig. 5 shows this comparison on a plot of yield stress vs. inverse square root of grain diameter. Sonon and Smith demonstrated that yield stress increased as carbon content increased from 190 ppm to 810 ppm. Table IV lists the Hall-Petch contents that they obtained as well as those from this investigation.

Our Ni was 99.95% pure with a maximum carbon content of 350ppm. As seen in Fig. 5, both vapor deposited and rolled foils from this starting materials exhibit approximately twice the yield stress, at smaller grain

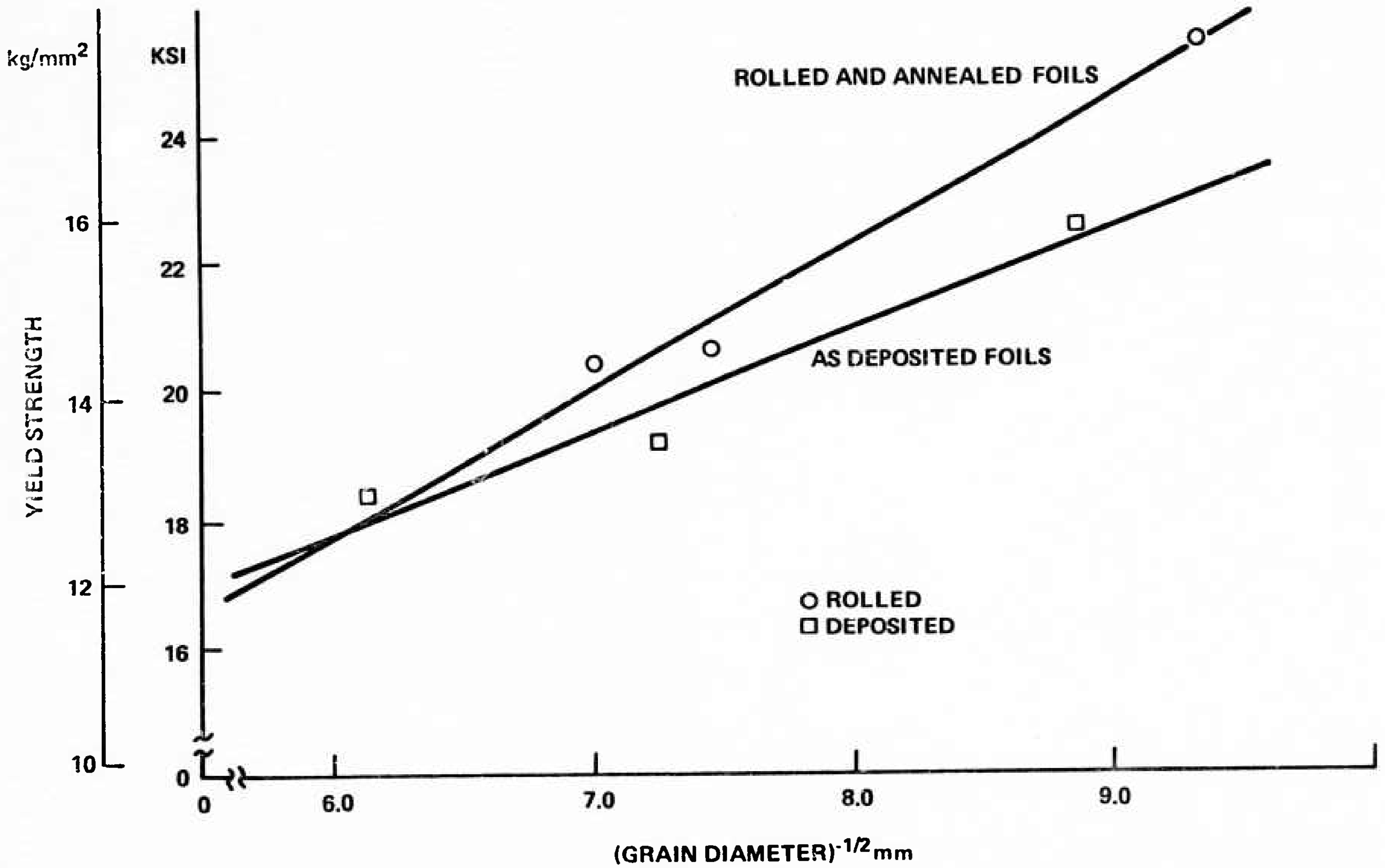

Figure 3. Yield Stress Versus Inverse Square Root of Grain Diameter.

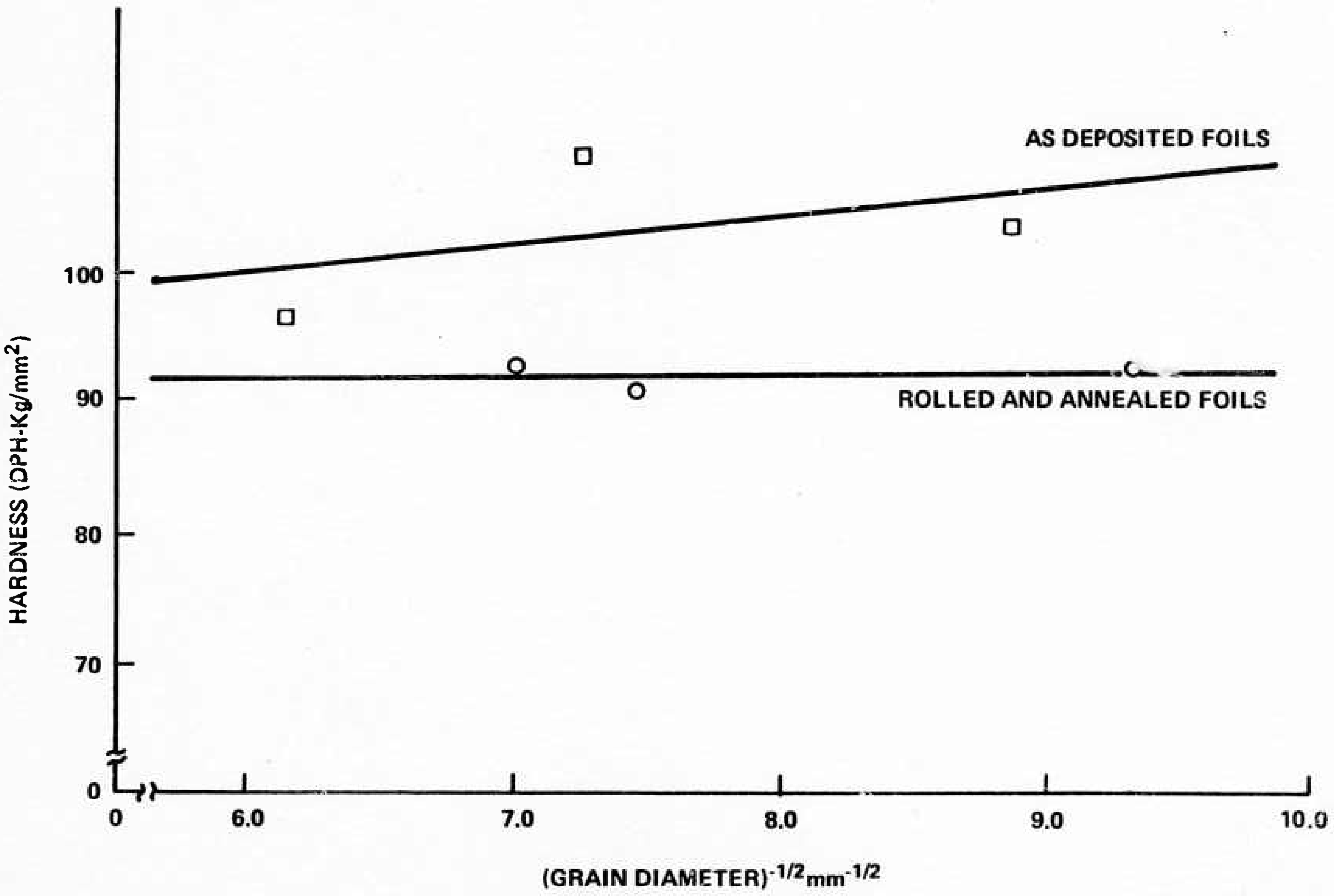

Figure 4. Hardness Versus Inverse Square Root of Grain Diameter.

Table IV

Hall-Petch Constants

Materials	σ_o (K_g/mm^2)	K_y $(K_g/mm^{3/2})$	H_o (K_g/mm^2)	K_H $(K_g/mm^{3/2})$	σ_o/H_o	$\frac{K_y}{K_H}$
Deposited Nickel	5.82	1.12	87.0	2.2	0.068	0.51
Rolled Nickel	2.75	1.62	91.2	.11	0.030	14.7
Nickel(810 ppmC)	2.82	.78	-	-	-	-
Nickel(190 ppmC)	1.97	.49	-	-	-	-

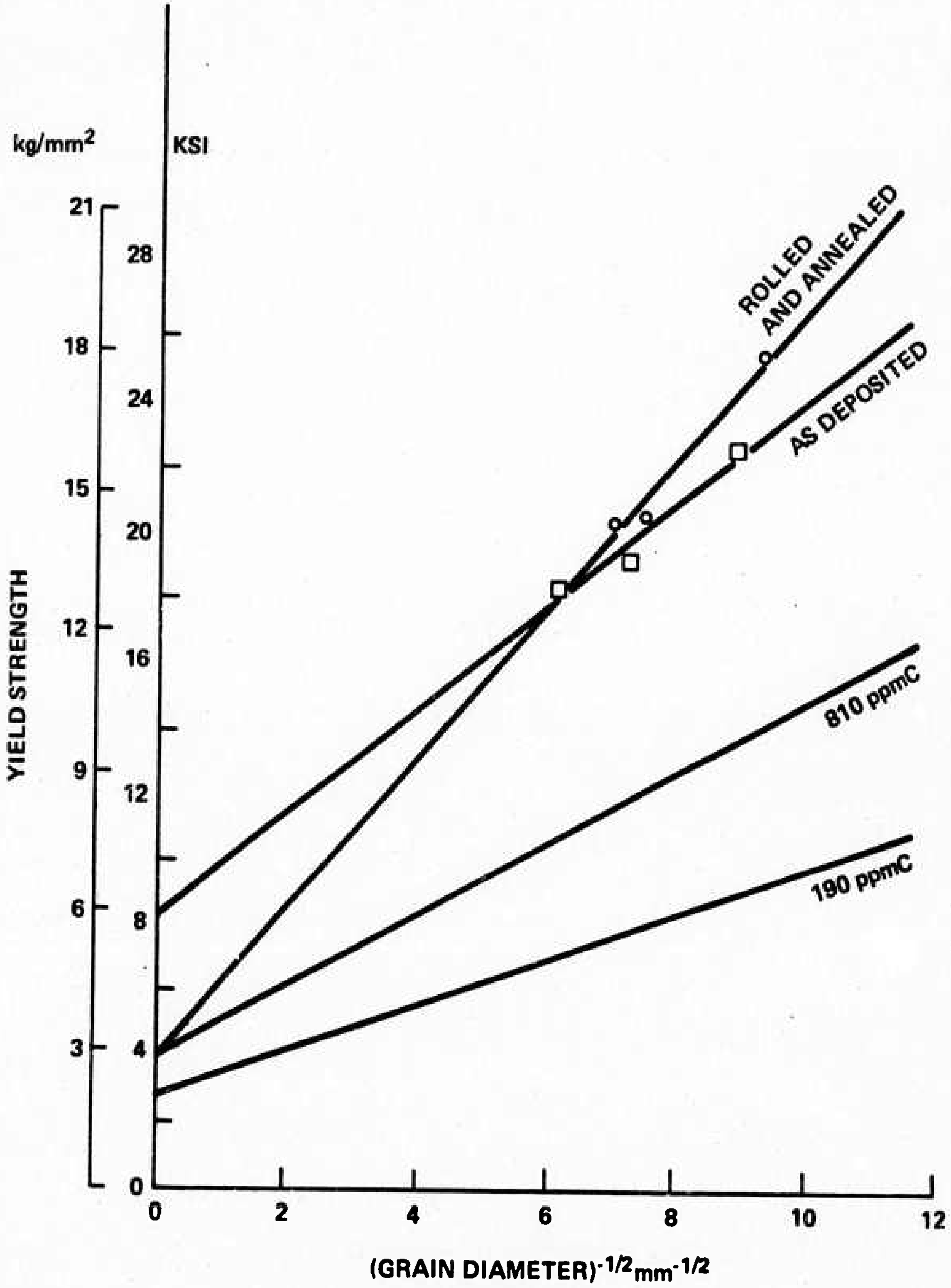

Figure 5. Yield Stress Versus Inverse Square Root of Grain Diameter for Various Nickel Deposits.

sizes as compared to Sonon and Smith's material.

2. Bend Ductility

In the characterization all samples proved to be identical, being able to withstand a less than 1 T 180° bend at room temperature. Study of the bent edge under magnification showed no sign of cracking or tearing.

IV. Summary and Conclusions

Nickel foils of full density were produced by high rate physical vapor deposition techniques. The grain size and grain morphology was varied by changing the substrate temperature. Mechanical tests on the deposited material showed strength and ductility values comparable to similar purity cast and rolled material. The yield strength and hardness values varied linearly with inverse square root of the grain diameter according to the Hall-Petch relationship. It may therefore be concluded that nickel produced by HRPVD techniques is an engineering material.

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APPENDIX 2

High Rate Deposition of Y_2O_3, Si_3N_4 and TiC deposits by Direct Evaporation and of Y_2O_3 by Activated Reactive Evaporation

I. Objective: This section deals with the following: (1) Feasibility study on high rate deposition of Y_2O_3, Si_3N_4 and TiC deposits by direct evaporation; (2) High rate deposition of Y_2O_3 and Si_3N_4 by Activated Reactive Evaporation.

II. Direct Evaporation of Y_2O_3, Si_3N_4 and TiC

Direct evaporation of a compound involves heating an evaporation source consisting of the compound to produce vapors which are then condensed to form a deposit. This is an extension of the technique of direct evaporation applied to metals and alloys. For high deposition rates, a high power density heat source, e.g. an electron beam, is used. Potential problems which can arise under these conditions for direct evaporation of compounds are:

(1) Dissociation of the compound which would result in a deposit of of less than desired stoichiometry For example, evaporation of an Al_2O_3 source material might result in an Al_2O_{3-x} deposit.

(2) Control of the source during evaporation due to high gas content or charge build up.

(3) Possible break up of the evaporant stock due to the high thermal stresses.

The evaporation stock was fabricated by hot pressing of powders into a rod.

The experimental observations are very similar for all three materials. At low electron beam currents 0.1 to 0.2 amps, sudden pressure bursts make it impossible to continue with the evaporation process. The evaporant being a hot-pressed powder compact contains a lot of gases which are released on heating. The evaporant rod also cracks up due to the high thermal stresses imposed on it by the impact of the evaporant beam. Thus high rate deposition of these compounds by direct evaporation is not a feasible technique. At the present time with the hot pressed evaporation sources deposition rates of 0.5 μ per minute at source-to-substrate distance of 8 inches is the maximum possible. There is also some evidence that for Y_2O_3 and TiC the deposit is deficient in O and C respectively indicating in change in stoichiometry between the source and the deposit. Although this deposition rate is low as compared to that for metals (25 μ/min), it should be adequate for deposition of dispersion strenghthened alloys where the volume percent of dispersed phase is small.

III. High Rate Deposition of Y_2O_3 and Si_3N_4 by Reactive Evaporation and Activated Reactive Evaporation

Reactive Evaporation is a process whereby vaporized metal atoms and gas atoms in the enviroment react to form a compound which is then deposited. For example, Y is evaporated in the presence of oxygen to form Y_2O_3 which is the phase deposited. Often the reaction between the metal and gas atoms does not take place or occurs partially. In that case the reaction can be activated by ionization of the reacting species. The process for carrying this out efficently so as to produce a high deposition rate for the compound was recently developed in this research contract and has been reported[1,2]. It is called Activated Reactive Evaporation. The experimental set-up has been described previously[1,2].

High rate of Y_2O_3 by Reactive Evaporation and Activated Reactive Evaporation was studied further in this period. The experimental variables are the rate of evaporation of Y, the pressure of O_2 and whether the reaction was activated by imposing a voltage on a probe located between the source and substrate.

The data are presented in Table I. The results do not show a consistent pattern and further experimentation is necessary.

Results of experiments on Avtivated Reactive Evaporation of Si_3N_4 are shown in Table II. The variables are the gas species N_2 and NH_3, gas pressure and deposition temperature. Deposition temperature appears to be the dominant variable. Crystalline Si_3N_4 was synthesized only at at a high substrate temperature. These results are consistent with previous work where it has been shown that silicon deposited at low temperatures is amorphous. Further works will be carried out to optimize the experimental conditions for depositing Si_3N_4.

Table I: Reactive Evaporation and Activated Reactive Evaporation of Y_2O_3

Run #	Emission Current (A)	Reactive gas	Gas pressure (torr)	Rate of deposition (μ/min)	Probe Current (A)	Probe Voltage (V)	Deposition temp. °C	Remarks
1. Y-O_2-2	0.20	O_2	1×10^{-4}	13	-	-	25	Traces of Y-in deposit
2. Y-O_2-3	0.20	"	$4\text{-}6 \times 10^{-4}$	11	-	-	25	Traces of Y-in deposit
3. Y-O_2-6	0.14	"	$1\text{-}2 \times 10^{-4}$	5.1	-	-	440	
4. Y-O_2-9	0.14	"	$1\text{-}2 \times 10^{-4}$	8.5	-	-	540	Mixture of Y&Y_2O_3 due to spitting of Y from the pool
5. Y-A-2-3	0.25	"	5×10^{-3}	12.7	-	-	480	Traces of Y-in deposit
6. Y-A-2-4	0.25	"	5×10^{-3}	5.3	0-1.3	65	480	
7. Y-A-2-5	0.25	"	$3.5\text{-}4 \times 10^{-2}$	1.1	-	-	480	
8. Y-A-2-6	0.25	"	$3.5\text{-}4 \times 10^{-2}$	4.2	0.1-1.5	55	480	Traces of Y-in deposit

Table II: Activated Reactive Evaporation of Si_3N_4

Run #	Emission Current (A)	Reactive gas	Gas pressure (torr)	Rate of deposition (μ/min)	Probe Current (A)	Probe Voltage (V)	Deposition temp. °C	Remarks
1. Si-A-3	0.57	N_2	1.5×10^{-2}	5.1	0.4-0.5	60	185-315	Mixture of crystalline & amorphous silicon and perhaps amorphous Si_3N_4
2. Si-A-4	0.55	N_2	4×10^{-4}	-	0.5-0.7	100	Ambient	"
3. Si-A-6	0.40	NH_3	$3\text{-}5 \times 10^{-2}$	-	0.2	100	540	"
4. Si-A-7	0.45	NH_3	2.7×10^{-2}	-	0.3-0.5	85	800-1000	Crystalline Si & Si_3N_4

References

1. R.F. Bunshah, New Techniques for the Synthesis of Metals and Alloys, UCLA - Eng. - 7161, Sept. 1971

2. R.F. Bunshah and A.C. Raghuram - Jnl. Vac. Sci. Tech., 9, 1385 (1972)