NASA CR- 159,701

NASA-CR-159701
1980 000 9777

National Aeronautics and
Space Administration

FINAL REPORT

INTERNAL COATING OF AIR COOLED GAS TURBINE BLADES

by

P. L. AHUJA

November, 1979

GENERAL ELECTRIC COMPANY
Aircraft Engine Group
Lynn, Massachusetts/Cincinnati, Ohio

Prepared For

National Aeronautics and Space Administration

NASA Lewis Research Center
Contract NAS3-21038

1. Report No.
NASA CR - 159701

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle
INTERNAL COATING OF AIR COOLED GAS TURBINE BLADES

5. Report Date
October, 1979

6. Performing Organization Code

7. Author(s)
P. L. AHUJA

8. Performing Organization Report No.

9. Performing Organization Name and Address
General Electric Company
Aircraft Engine Group
Cincinnati, Ohio 45215

10. Work Unit No.

11. Contract or Grant No.
NAS3-21038

12. Sponsoring Agency Name and Address
National Aeronautics and Space Administration
Washington, D. C. 20456

13. Type of Report and Period Covered
Final

14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

Six coating systems were evaluated for internal coating of DS Eutectic high pressure turbine blades. Sequential deposition of electroless Ni by the hydrazine process, slurry Cr, and if desired, slurry Al, followed by heat treatment provided the coating composition and thickness for internal coating of DS eutectic turbine blades. Both NiCr and NiCrAl coating compositions were evaluated for strain capability and ductile to brittle transition temperature and both met the objectives of this program.

17. Key Words (Suggested by Author(s))
DS NiTaC, Air-Cooled Blades, Internal Coating, Electroless Ni, Slurry Cr, Slurry Al, DBTT, Strain

18. Distribution Statement

19. Security Classif. (of this report)

20. Security Classif. (of this page)

21. No. of Pages
65

22. Price*

* For sale by the National Technical Information Service, Springfield, Virginia 22151

NASA-C-168 (Rev. 6-71)

N80-18041 #

FOREWORD

This final report is based on the NASA Contract #NAS3-21038 in its modified form. It describes the process selected for internal coating of air cooled NiTaC HPT blades. A three layer NiCrAl Coating applied by electroless Ni, slurry Cr and slurry Al processes has been shown to possess adequate strain capability at the engine operating temperatures.

The following have been associated with this project.

John Merutka - NASA Program Manager
Ernie Kerzicnik - AEG Program Manager
Thomas Berry - Technical Program Manager
Peter Ahuja - Principal Investigator

TABLE OF CONTENTS

PAGE NO.

EXECUTIVE SUMMARY 1

(1) INTRODUCTION 3

(2) OBJECTIVES 3

(3) TECHNICAL PLAN 4

(4) EXPERIMENTAL WORK 6

(5) MECHANICAL PROPERTY EVALUATION 27

(6) RESULTS 27

(7) DISCUSSION 62

(8) CONCLUSIONS 63

(9) REFERENCES 65

LIST OF TABLES

		PAGE NO.
I.	Candidate Coating Systems and Processes	5
II.	Optimum Formulation of Hydrazine Bath	9
III.	Gas Content of Electroless Ni from Hydrazine Bath	10
IV.	Conditions for Deposition of CVD Cr	13
V.	Internal Coating Deposition Sequence, Layers Thickness and Deposition Technique	31
VI.	Thickness of Candidate Coatings #2, 4, 6 (First Iteration)	31
VII.	Thickness of Candidate Coatings #2, 4, 6 (Up to 3rd Iteration)	45
VIII.	Thickness of Candidate Coatings #1, 2, 3, 4, 6	55

LIST OF FIGURES

		PAGE NO.
1.	Electroless Ni Coating Facility at AEG-Evendale	11
2.	Hydrazine Electroless Ni on Rene' 125 Pin After Heat Treat	12
3.	As-Deposited CVD Cr on Rene' 125 Pin	14
4.	CVD Cr Coated NiTaC Pin After 300 Hours Oxidation Testing at 982C (1800F)	15
5.	Schematics of a CVD Coater	16
6.	Laboratory Coating Chamber for Blades	17
7.	Schematics of a Pin Coating System for CVD Cr	18
8.	Slurry Injection Set-Up for Blades	20
9.	Cr Deposited By Slurry Injection Technique Inside a CF6-50 Blade	21
10.	EDAX Analysis of Slurry - Injected Cr Coating	22
11.	CVD Al Deposit Using TIBA (Micro)	23
12.	Slurry Al Coating Using Modified Pack Arrangement (CF6-50 Blade)	25
13.	SEM Analysis of Slurry Al Coating Inside Blade (CF6-50)	26
14.	Specimen Configuration Used for DBTT Testing	28
15.	Pin Specimen Used for Oxidation, Hot-Corrosion and Physical Testing	29
16a.	As-Deposited Electroless Ni on AF NiTaC Pin	33
16b.	After Diffusion Heat Treat	34

PAGE NO.

17a. A NiCr Coating (#2, 1st Iteration) on NiTaC Pin 35

17b. Computer Plot of Microprobe Data 36

18a. A NiCrAl Coating (#4, 1st Iteration) on AF NiTaC Pin 37

18b. Computer Plot of Microprobe Data on Above 38

19a. NiCrAl Coating on AF NiTaC Pin (Coating #6, 1st Iteration) 39

19b. Computer Plot of the Microprobe Data 40

20. Computer Plot of Electron Microprobe Data Showing Distribution of Ni, Cr and Al in a NiCrAl Coating on AF NiTaC Pin (Coating #2, 2nd Iteration). 42

21. Computer Plot of Microprobe Data on NiCrAl Coating (#4, 2nd Iteration) on AF NiTaC Pin 43

22a. Metallographic Structure of NiCr Coating (Coating #2, 3rd Iteration) 46

22b. Computer Plot of Microprobe Data (Coating #2, (3rd Iteration) 47

23a. Phase Distribution in NiCrAl Coating (Coating #4, 3rd Iteration) 48

23b. Computer Plot of Composition Profile 49

24. Computer Plot of Electron Microprobe Data Showing Distribution of Ni, Cr and Al in NiCrAl Coating on AF NiTaC Pin (Coating #6, 3rd Iteration) 50

25a. A NiCrAl Coating on AF NiTaC Pin (Coating #6, 4th Iteration) 51

25b. Probe Data on Composition Profile 52

PAGE NO.

26. Computer Plot of Electron Probe Data Showing Distribution of Ni, Cr and Al in a NiCr Coating (Coating #1, 1st Iteration) 54

27. Photomicrograph Showing Absence of Aluminided Zone in Coating #3 56

28. Macrophotograph of DBTT Specimens with Coating #2 58

29. Photomicrograph of NiCr Coating #2 on AF NiTaC Specimens 59

30. DBTT Plot of Coating #2 Deposited on AF NiTaC Specimens 60

31. DBTT Plot of Coating #4 Deposited on AF NiTaC Sepcimens 62

32. Coating Strain Capability as a Function of Temperature and Type of Coating System 63

EXECUTIVE SUMMARY

The most advanced turbine blade designs utilizing the DS eutectic alloys will require an environmentally protective coating on the internal cooling passages. Previous work at General Electric had demonstrated the feasibility of depositing NiCr or NiCrAl internal coatings by depositing successive layers of Ni, Cr, and Al followed by a heat treatment to produce NiCr or NiCrAl coatings. In the present program, six pre-selected NiCr and NiCrAl coatings were evaluated as internal coatings for DS eutectic blades. The base alloy was DS NiTaC. The nominal coating compositions and deposition processes are summarized in Table A:

TABLE A - CANDIDATE COATING SYSTEMS AND PROCESSES

Coating #, System (wt. %)	Element/Deposition Technique*			
	1st Step	2nd Step	3rd Step	4th Step
#1 Ni-30Cr	Ni/N	Cr/C		
#2 Ni-20Cr	Ni/N	Cr/S		
#3 Ni-15Cr-20Al	Ni/N	Cr/C	Al/C	
#4 Ni-15Cr-20Al	Ni/N	Cr/S	Al/S	
#5 Ni-20Cr-10Al	Cr/C	Ni/N	Cr/C	Al/C
#6 Ni-20Cr-10Al	Cr/S	Ni/N	Cr/S	Al/S

*Deposition Techniques:
N - electroless Ni
C - chemical vapor deposition
S - slurry injection

Up to four iterations of coating applications were conducted to produce the target thickness over the range 0.0038 - 0.0050 cm. (0.0015 - 0.002 inches) and chemical compositions. The coatings were evaluated metallographically for soundness and adherence, and by the electron microprobe for chemical composition. Two coatings, #2 and #4 were also tested for ductility at temperatures up to 760C (1400F). Each coating achieved the ductility goal .006 cm/cm (0.006 in./in.) at 760C (1400F). These evaluations revealed the electroless Ni, and slurry Cr and Al as superior processes for depositing Ni, Cr and Al. The NiCr and NiCrAl coatings were deposited to the required thickness with good adherence to the DS NiTaC base alloy. This evaluation provides a portion of the base technology needed for coating internal cavities of DS eutectic and other DS alloy turbine blades.

(1) INTRODUCTION

In order to increase turbine inlet temperature, various development for improving the temperature capability of materials, such as superalloys, have been undertaken. One of the advanced alloys under development at General Electric is a DS NiTaC eutectic alloy, strengthened by TaC fibers. However, the chromium level in these alloys is reduced to enhance high temperature strength making the bare alloy more susceptible to attack by corroding environments. Hence, protective coatings are needed to increase reliability and extend part life.

Codep (aluminide type) coating, currently being employed for external surface protection and life extension of turbine parts in various engines, performs satisfactorily, but is limited in its ability to protect at higher temperatures and in its ability to coat internal cooling passages of turbine blades. There are no internal coatings and processes which will reliably provide 100% coverage on advanced design GE blades and also meet the environmental and mechanical property requirements.

The need for an internal coating has been recognized in anticipation of increasing internal operating temperatures in advanced alloy parts. Moreover, the NiTaC alloy is a directionally solidified material with a reduced elastic modulus in the height direction of the blade, i.e., it will strain more under centrifugal loads. In order to provide satisfactory environmental resistance and also meet a higher coating strain requirement, NiCr(Al) add-on type coatings are needed. Based on experience with external coatings, the best approach to form a NiCrAl type internal coating was considered to be by deposition of elemental Ni, Cr and Al layers and then thermally converting them to form NiCrAl coatings. The coating composition can be controlled by layer sequence, thickness and the post-coating diffusion cycle. This had been demonstrated previously in programs at General Electric. Because of the small diameter and complex cooling passages designed into advanced air cooled blades, only fluid flushing techniques could be relied on to provide coatings with 100% coverage.

(2) OBJECTIVES

The following goals were selected for evaluation of alternative internal coatings:

1. The coating process should have a 100% coverage capability.

2. ± 20% maximum variation in thickness and composition.

3. A minimum of 1000 hours life in oxidation at 1010C (1850F).

4. A life of 300 hours at 900C (1650F) in hot corrosion test.

5. A minimum ductility of 0.006 cm/cm at 760C (1400F) and a DBTT below 760C (1400F).

6. No more than 2 mil (0.005 cm) additive thickness in cooling hole passages.

7. The coating should have a minimum effect on carbide denudation.

(3) TECHNICAL PLAN

The effort required screening and evaluation of six coating/process combinations and selection of one coating system for use in coating blades for a process demonstration. Included in the task were verification of coating thickness, composition and measurement of DBTT. Also, candidate coatings were to be applied to specimens with simulated cooling passages to assess whether holes were coated and the extent of cooling hole blockage. Finally, the environmental resistance of the candidate coatings was also to be determined as well as its compatibility with an external coating (EA NiCrAlHf). However, during the program, the viability of NiTaC as a blade alloy became questionable. The program was then terminated and the technology developed was transferred to a Navy contract (N00140-78-C-0028) wherein coatings are being developed for DS Rene' 150.

The six internal coating composition/process combinations pre-selected as candidates were as follows:

TABLE I - CANDIDATE COATING SYSTEMS AND PROCESSES

	Element/Deposition Technique			
Coating #, System wt. %	1st Step	2nd Step	3rd Step	4th Step
#1 Ni-20Cr	Ni/N	Cr/C		
#2 Ni-20Cr	Ni/N	Cr/S		
#3 Ni-15Cr-20Al	Ni/N	Cr/C	Al/C	
#4 Ni-15Cr-20Al	Ni/N	Cr/S	Al/S	
#5 Ni-20Cr-10Al	Cr/C	Ni/N	Cr/C	Al/C
#6 Ni-20Cr-10Al	Cr/S	Ni/N	Cr/S	Al/S

* Deposition Techniques:
N - electroless Ni
C - chemical vapor deposition
S - slurry injection

The prior internal coating development work at General Electric started with single element deposition. The work was initiated in 1971 with the successful demonstration of an Al coating in the passages of a CF6-6 blade. Such Al deposits could be thermally converted to an aluminide coating like Codep. More recently, a novel idea for depositing Al by a slurry injection technique was invented and successful deposition inside CF6-50 blades have been achieved.

The chromium deposition work was started in 1976. Cr was deposited by chemical vapor deposition (CVD) techniques and thermally converted to form a chromide coating for the internal protection of F404 high pressure turbine blades. In addition, the recently developed slurry injection technique (IR&D work) has also been used successfully to deposit chromide coatings inside CF6 blades.

The Ni deposition work was started in 1975. Ni layers with good uniformity and structure have been successfully deposited on CVD Cr and Al coated specimens. Diffusion heat treatments resulted in NiCr or NiCrAl type coatings. However, efforts in efforts in using a CVD technique to deposit Ni were held up due to the concerns about handling toxic nickel carbonyl. Using a substitute method to deposit Ni from electroless Ni solutions, deposits were formed successfully inside F101 high pressure turbine blades with reasonably uniform thickness profile. Recent progress has demonstrated that the purity of electroless Ni deposit can be further improved by using hydrazine electroless Ni solution.

Although substantial progress has been made on each individual coating process, a program to integrate the individual processes to form a desired NiCr or NiCrAl type coating on a NiTaC substrate was necessary. The role of the substrate in the performance of a coating vis-a-vis diffusion characteristics is of great significance. This final report highlights efforts made toward identifying a coating system that has the potential to meet our projected goals for internal coatings.

(4) EXPERIMENTAL WORK

There are no known commercial monoplex processes available today for the deposition of NiCr or NiCrAl internal coatings. The best approach for deposition of a uniform NiCr or NiCrAl coating is to deposit individual Ni, Cr and Al elemental layers first and then diffusion heat treat to form the desired composition.

One of the promising approaches for deposition of Ni, Cr, or Al is chemical vapor deposition (CVD). In general, CVD coating techniques have been described for all the components of interest to this program; however, little work has been reported on the deposition of these coatings on the internal surfaces of channels of appreciable length/diameter ratio. An alternate technique used to deposit Ni is the electroless Ni process. The most common problem encountered during the electroless Ni process is that impurities are codeposited along with Ni. The impurities, such as phosphorous from reduction by hypophosphites and boron from reduction by borohydrides, are detrimental to coating performance. This problem has been eleminated by using hydrazine as a reducing agent. Recent work at General Electric has demonstrated the feasibility of this technique.

Cr and Al can be deposited by techniques other than CVD. The candidate techniques are slurry injection and vapor transport techniques. In the sulrry injection technique, a mixture of Al halides or Cr halides with an organic binder and an activator is injected into a blade. The blade is then heat treated at specified temperatures and environments to allow the slurry to decompose and leave an aluminide or chromide coating. The vapor phase transport technique is essentially a modification of the pack process. This technique requires the generation of a halide vapor from a pack mixture. The halides react with the base metal and deposit an aluminide or chromide coating. These techniques have been developed under General Electric in-house programs. By far, the slurry injection technique has been found to be superior to the vapor transport technique, both from the facility and process control point of view. The techniques used for this program are described below in greater detail.

(i) CVD and Electroless Ni Techniques

Nickel can be deposited from gaseous nickel carbonyl at temperatures of 150C (300F) to 250C (480F) and catalysis with H_2S or surface absorbed sulfur from other sources can yield useful deposition rates at temperatures as low as 425C (795F). This is the most highly developed and best understood CVD reaction for depositing nickel; its only limitation is the toxic nature of the carbonyl which requires that special but defined procedures to be used.

Nickel can also be deposited from acetyl acetonate vapor at 290-400C (550-750F) preferably at low pressures. However, the requirements of higher deposition temperature and low pressure operation off-set the advantage of reduced toxicity of the reactant.

Although many metals can be deposited from their chlorides, and solid nickel chloride can be reduced by hydrogen, CVD of Ni from its chloride is precluded by the low volatility of the latter. In recent years, the stabilization of volatile nickel chloride by the complexing reaction

$$Al_3Cl_6(g) + Ni\ Cl_2\ (S) = Ni\ Al_3\ Cl_{8(g)}$$

has been observed, which opens another route to CVD nickel; e.g., at 482C (900F).

$$\mathrm{Ni\ Al_3\ Cl_{8(g)} + H_{2(g)} = Ni(s) + Hcl_{(g)} + Al_3Cl_{6(g)}}$$

The obvious disadvantage is again the high deposition temperature. Handling the complex reaction is also more difficult than simply feeding nickel carbonyl from a commercially supplied tank. However, because of the toxicity of the chemical, (OSHA tolerance limit for carbonyl 1 ppb), the CVD Ni technique was not used in this program.

The foregoing arguments leave us with the choice of one promising candidate, i.e., electroless Ni.

Electroless deposition is defined as the autocatalytic chemical reduction of metal from solution. The metal deposition proceeds solely on the surface which is catalytic for the chemical reduction process. Electroless nickel plating solutions consist of nickel salts and a reducing agent with other compounds added to improve solution and deposit characteristics. Electroless nickel deposits have two important advantages over other types of nickel deposits. The first is uniformity. These deposits do not build up at sharp corners and edges. The second advantage is ease of process control.

Of the known methods, hypophosphite reduction is the most common. Electroless nickel deposits from hypophosphite-base solutions are not pure nickel, but contain phosphorous. Deposits appear amorphous to x-rays but electron diffraction studies indicate the deposits to be supersaturated solid solutions of phosphorous in finely crystalline nickel. Heating at 440C (750F) results in precipitation of a Ni_3P phase.

The phosphorous content of deposits from acid electroless nickel solutions increases with decreasing solution pH and is usually about 5 to 15 percent by weight. Deposits from alkaline solution usually contain 5 to 7 percent phosphorous. As such, these coatings are not acceptable in the present application.

Sodium borohydride has also been used as a reductant; however, residual boron adversely affects the corrosion resistance and ductility of the deposits. As much as 8% boron has been reported to be codeposited in the process.(1)

A promising candidate for internal nickel coating was recognized after an extensive literature survey. It was found that relatively pure nickel can be deposited autocatalytically using hydrazine as the reductant. Hydrazine is a powerful reducing agent theoretically capable of yielding four electrons and four protons per molecule. It is believed that metal deposition probably takes place according to the following overall reaction between nickel ions and hydrazine in an alkaline aqueous solution.

$$2\ Ni^{++} + N_2H_4 + 4\ OH^- \underset{\text{(Ni Catalyst)}}{=} 2\ Ni + N_2 + 4\ H_2O$$

The activity of Ni^{++} is maintained very low so that the solubility product of the metal hydroxide will not be exceeded. The plating rate is found to be a function of Ni^{++} activity, pH and temperature. Nickel deposits spontaneously when the catalytic substrate is immersed in the solution and reaction becomes autocatalytic after the first nickel is formed.

Dini and Coronado(2) were the first to apply the hydrazine method of Levy(3) for obtaining thick, uniform and relatively pure nickel deposits. The optimum formulation reported by them is as follows:

TABLE II - Optimum Formulation of Hydrazine Bath

Nickel Acetate	60 g/1
Glycollic Acid	60 g/1
Tetra Sodium EDTA	25 g/1
Hydrazine (64%)	100 Ml/1
Temperature	90C (192F)
PH	11

Thick and pure deposits having good adhesion to the substrates using this process were obtained. The main drawback of this formulation was found to be the higher residual stress due to the gas content of the deposit produced in the hydrazine bath. This also accounted for poor corrosion resistance. Gas analysis by a fusion technique showed 0.003-0.0067 percent hydrogen, 0.09-0.463 oxygen and 0.241 to 0.287 percent nitrogen.

Based on the available information, work was started at General Electric to develop a procedure for electroless nickel plating of Rene' 125 by modifying the hydrazine process to suit our requirements (Figure 1). Several variations were tried to obtain relatively pure, thick deposits with a minimum residual stress. This involved variation of the bath composition, surface preparation and heat treatment. The results of gas analysis of the deposits made on Rene' 125 pins have been promising. The gas content on a number of specimens was analyzed and is reported in Table III.

TABLE III - Gas Content of Electroless Ni (wt %)

		(Hydrazine Method)	
	Bare Pin (Rene' 125)	As Deposited	After Heat Treat
N_2	0.0005	0.0044	0.0005
O_2	0.0105	0.0226	0.0144
H_2	0.0002	0.0007	0.0003

Consistently uniform deposits of nickel have been obtained at a rate of 0.0012-0.0015 cm (0.5 - 0.6 mil/hour) which diffuse well into the substrate after heat treatment. (Figure 2)

Further work was conducted to monitor nickel and hydrazine contents of the solution during deposition. Surface preparation, stabilization of the bath and plating of electroless Ni on Cr were some of the activities pursued for this program to obtain an internal NiCrAl type coating on the blades as an ultimate goal.

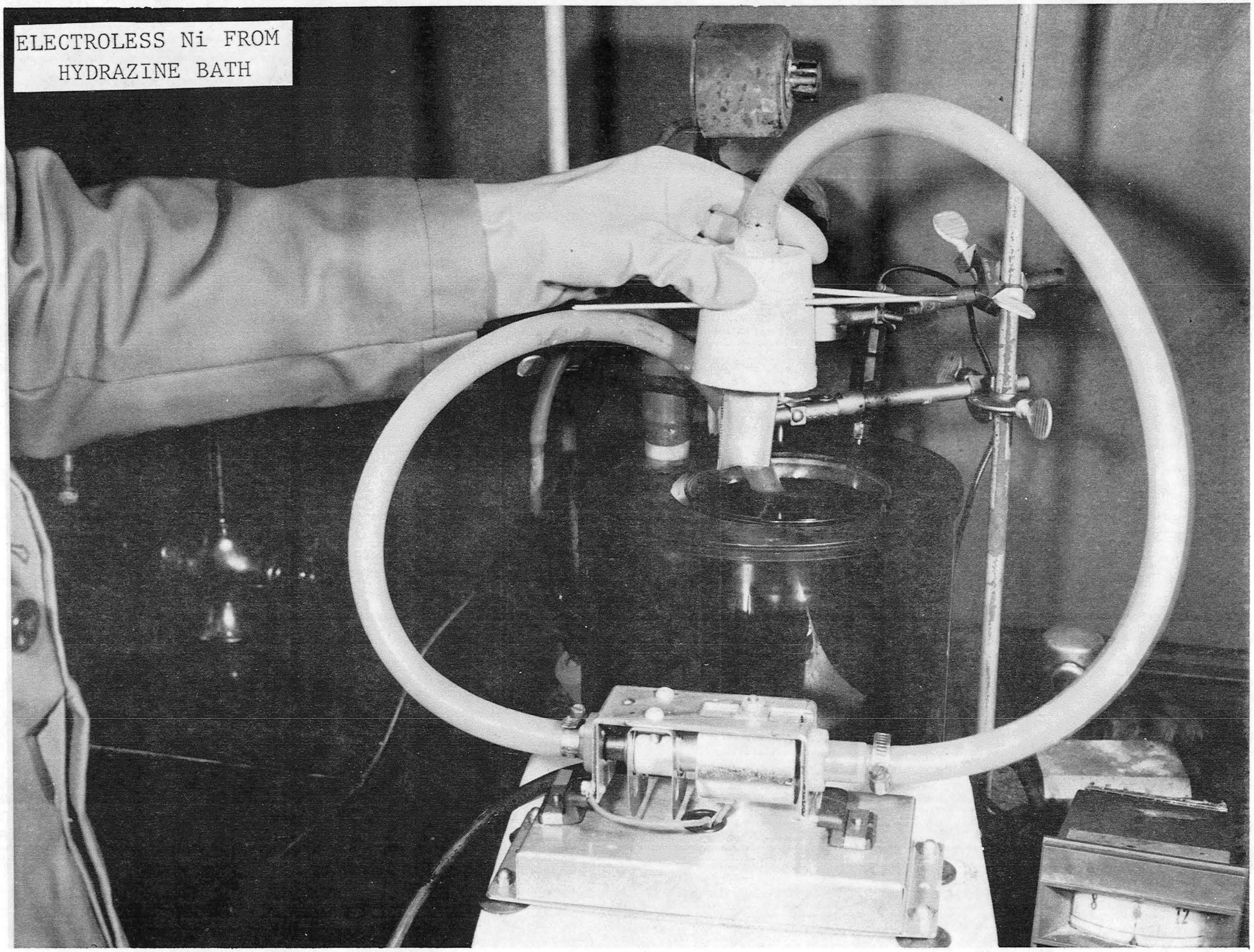
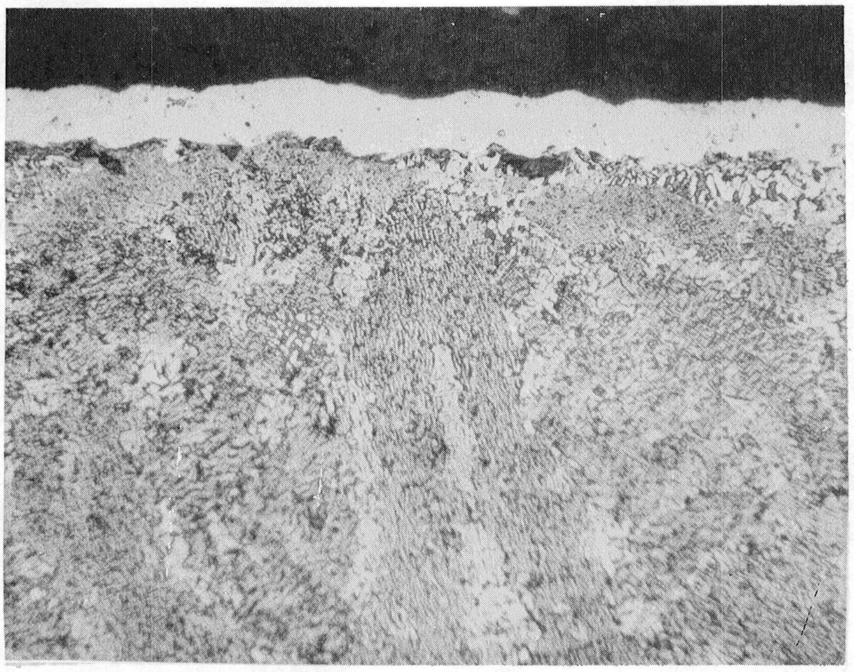


Figure 1
Electroless Ni Facility



500X, Etched

Figure 2
Hydrazine Electroless Ni on Rene' 125 Test Pins,
Heat Treated 10 Hrs. at 760C (1400F)

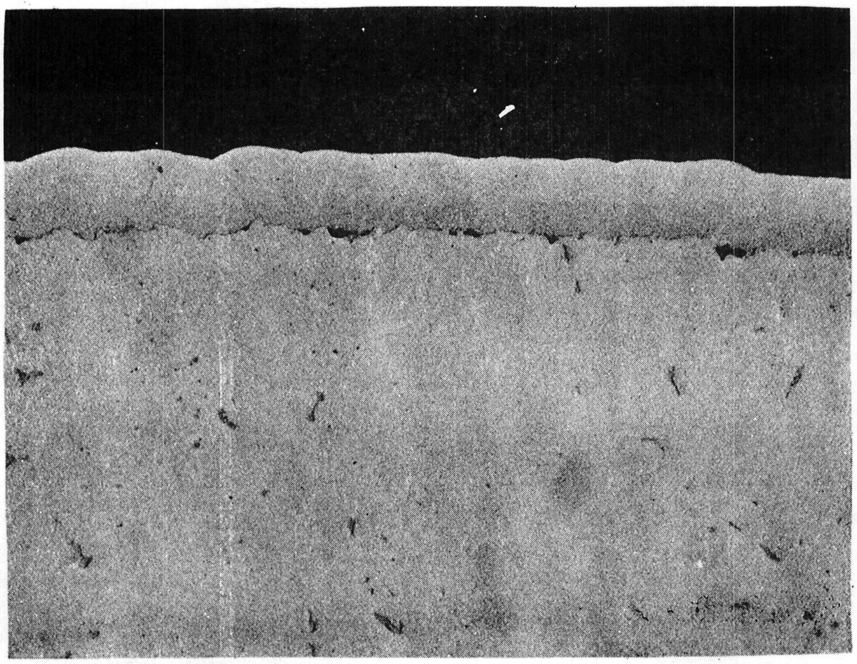
(ii) CVD Cr Technique

The most promising CVD Cr process for the present program involved organo-metallic compounds of chromium, such as chromium dicumene, which has been used most extensively at Battelle-Columbus Lab(3). The major limitation in the use of dicumene chromium is the fact that, depending upon the reaction conditions, 4-12% carbon can be codeposited with the chromium. However, where it must be eliminated, the addition of 0.1 percent of a halide, e.g., HCl or HI has been effective. For example, the addition of 0.06m% HI to 0.6m% dicumene chromium in hydrogen has resulted in products containing as low as 1000 ppm carbon.

The amount of carbon codeposited is extremely important to the performance of the resultant coating. Too much carbon is detrimental to the environmental resistance of the coating. Yet, on the other hand, a controlled amount of carbon is desired for coating a NiTaC alloy(5). A problem with some NiTaC alloys is that the TaC reinforcement fiber near the coating tends to disassociate when the coating is deposited. In some cases, a .025 - .038 cm (10 to 15 mils) of carbide denudation, due to the coating has been observed. This affects the substrate mechanical properties. The work performed by Rairden and Jackson under NASA Contract(4)(5) has demonstrated that the carbide denudation phenomenon can be minimized by adding a controlled amount of carbon to the coating. Figure 4 is a cross-section of a NiTaC pin coated with CVD Cr+C and tested in oxidation for 300 hours at 980C (1800F). The TaC fibers were retained in the coating. The CVD Cr deposited from dicumene Cr with a halide catalyst was selected as one of the candidates for this program. Preferred conditions for deposition of a Cr coating are listed in Table IV. Figures 5-7 show the schematics and assembly of a CVD coater.

TABLE IV - Conditions for Deposition of CVD Cr

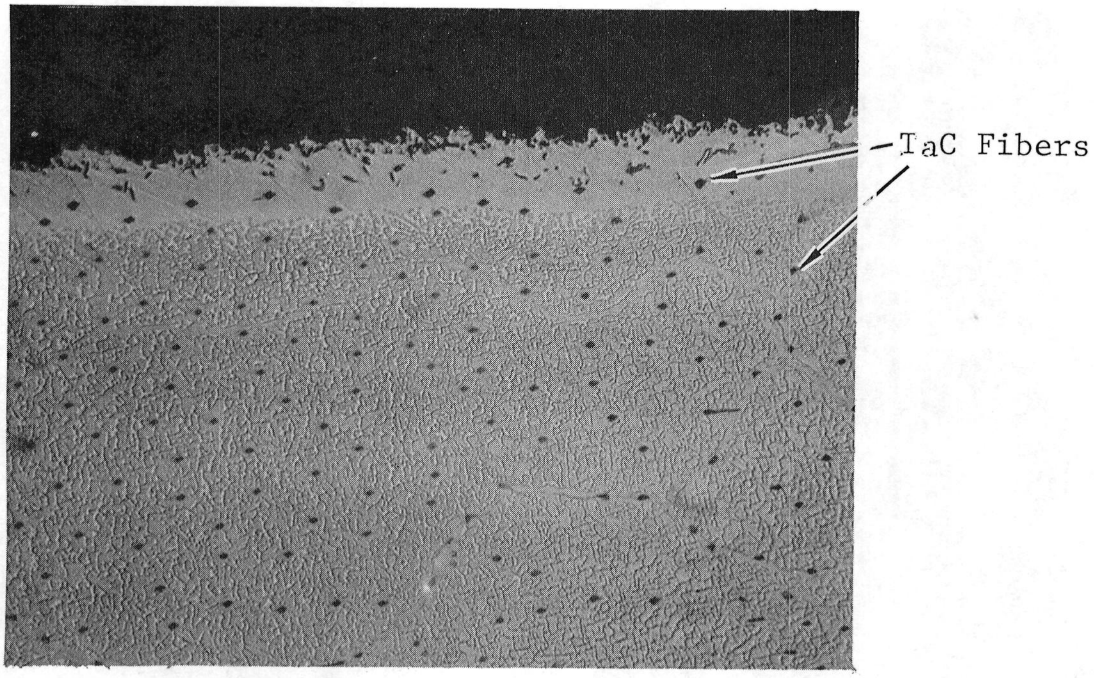
Surface Preparation	-	Chemical etch 30% H_2SO_4 - 60C (140F) until gasing starts
Temperature	-	300C (572F)
H_2 Gas	-	99.9% volume
DCC	-	0.08% volume
$\frac{DCC}{HCl}$	-	≈192
Coating Rate	-	≈.0007 cm/hr. (0.3 mil/hours)



500X Unetched

Figure 3

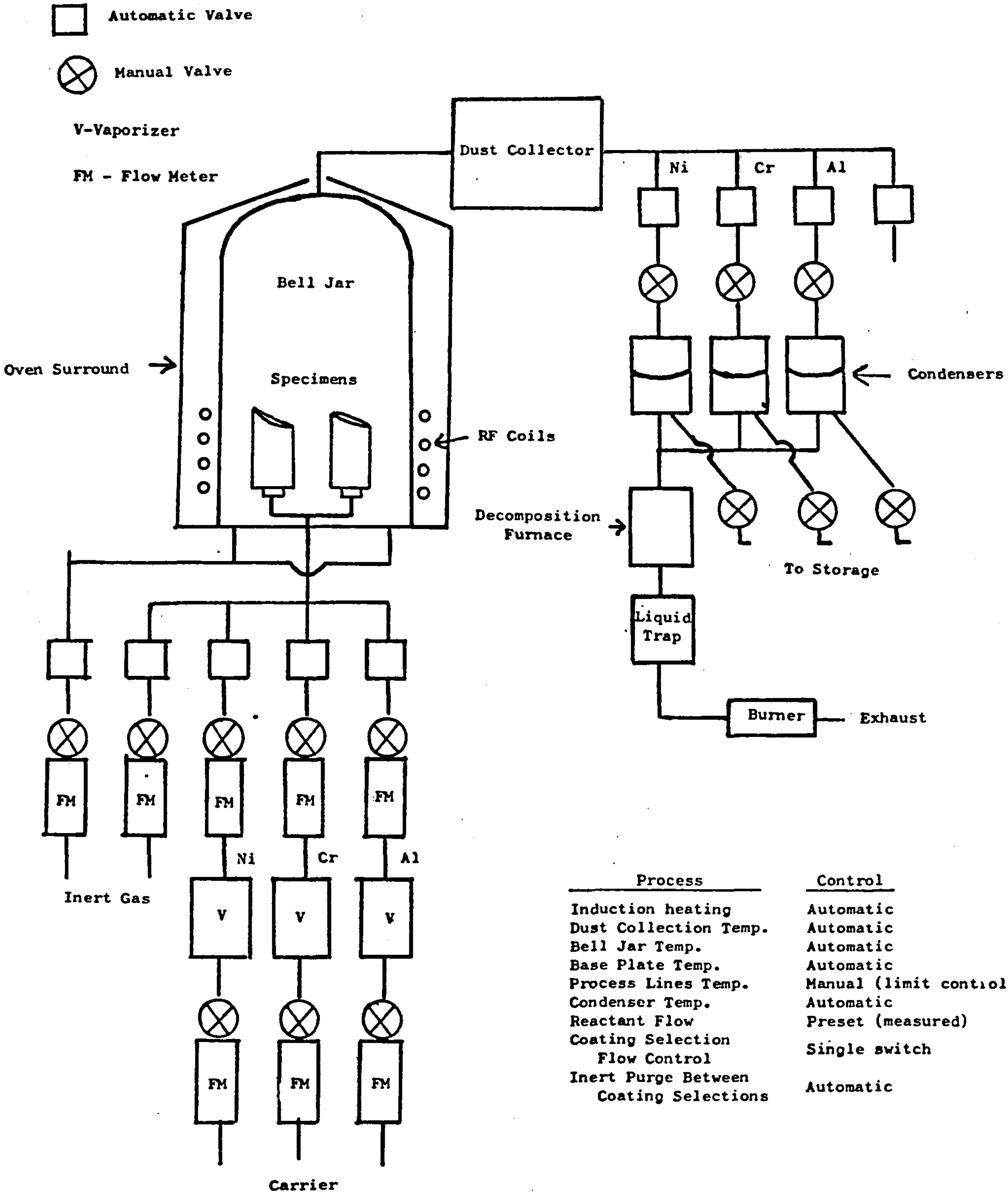
As Deposited CVD Cr on Rene' 125 Test Pin



500X
Phosphoric Acid Etch

Figure 4

CVD Cr Coated NiTaC Specimen After 300 Hours of Oxidation Testing at 982C (1800F)



Process	Control
Induction heating	Automatic
Dust Collection Temp.	Automatic
Bell Jar Temp.	Automatic
Base Plate Temp.	Automatic
Process Lines Temp.	Manual (limit control)
Condenser Temp.	Automatic
Reactant Flow	Preset (measured)
Coating Selection Flow Control	Single switch
Inert Purge Between Coating Selections	Automatic

Figure 5 Schematic of CVD Coater

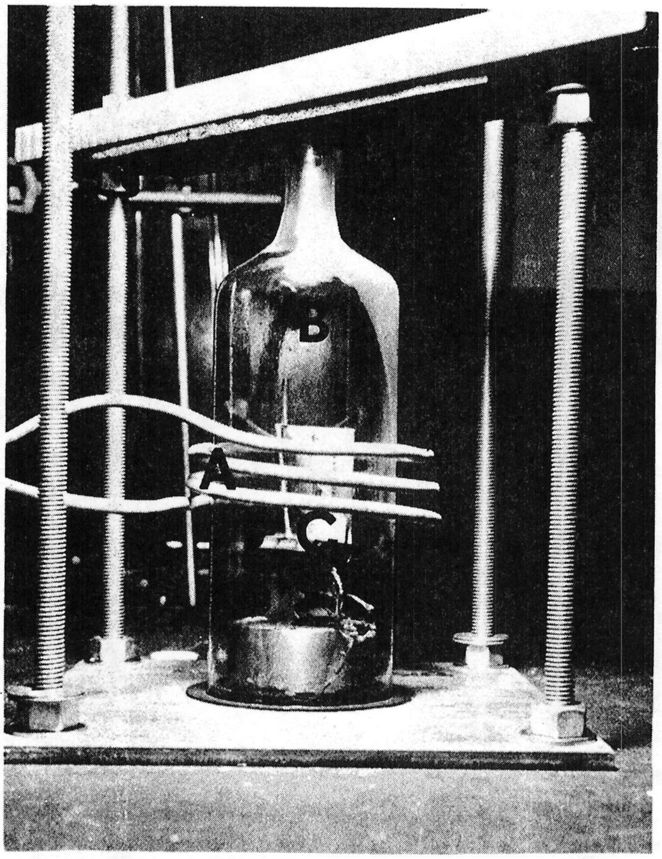


Figure 6

Chamber for CVD Coating of Blades

A: R. F. CORE
B: REACTOR
C: BLADE

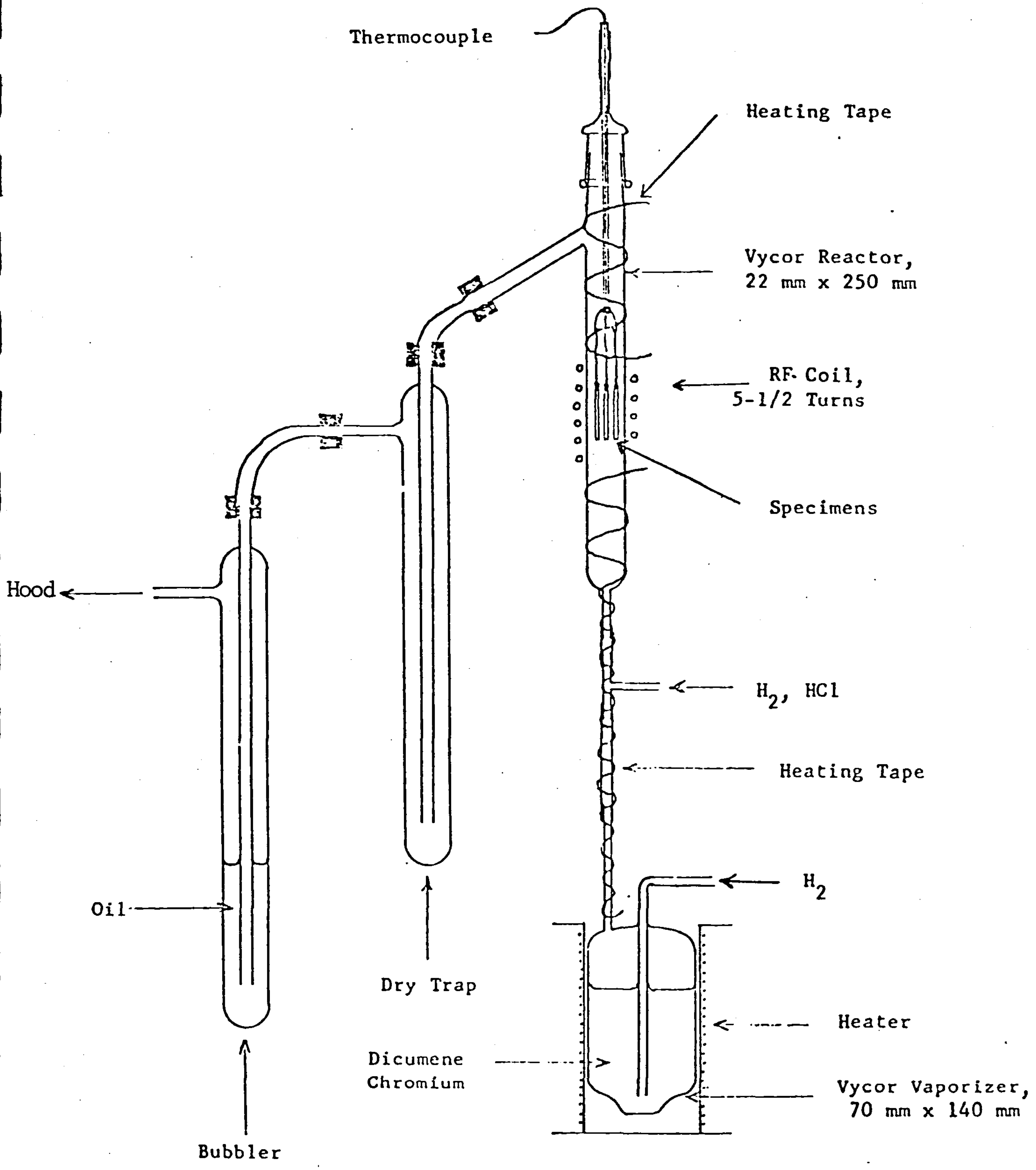


Figure 7 Schematic of Pin Coating System for CVD Cr

(iii) Cr By Slurry Injection Process

Applying coatings by the slurry method consists of blending the coating source material in powder form (CrF_3/CrF_2), suspending the powder in a liquid carrier and a binder to make a slurry and injecting the slurry into the blades. An injection device is shown in Figure 8. After the suspension is air dried, the blade is heated in an inert atmosphere or vacuum. The liquid carrier decomposes and Cr halide reacts with the metal surface and leaves a uniform internal chromide coating. The liquid carrier or suspending agent can be any liquid that will: (1) hold the coating particles in suspension, (2) not react with coating materials, (3) decompose upon heating and (4) leave no residual organics. In addition to holding the coating powder in suspension, a high viscosity binder is often added to the mixture to adjust the viscosity of the liquid.

The composition of the chromide coating can be adjusted by the slurry composition. The microstructure of the internal Cr coating of a CF6-50 high-pressure turbine blade is shown in Figure 9. Coating structure and chemical analysis by EDAX are shown in Figure 10. The coating was uniform and the coverage was excellent.

The experience to date has indicated that the success of the process is controlled by the following process parameters: (1) the pretreatment of the CrF_3 source; (2) the atmosphere and temperature of the blade during heat treatment; and, (3) the viscosity of the slurry and the amount of slurry injected into the blade.

(iv) CVD Al Technique

Although many aluminum alkyls have been used as sources of aluminum in CVD reactions, most workers have used tri-isobutyl aluminum,(6) (TIBA). An example of TIBA coating is shown in Figure 11. Comparison by Bazarre and Petriello(7) of deposition from tri-isobutyl and trinormalpropyl aluminum, and from di-isobutyl aluminum hydride and diethyl aluminum hydride showed that the purest coating (100 ppm max. impurities) with the lowest modulus come from the tri-isobutyl aluminum at deposition temperatures near 260C (500F). The dialkyl hydrides gave coatings with carbon contents up to 2 percent.

In view of the information and experience at Battelle with the deposition of aluminum alkyls, tri-isobutyl aluminum was selected as an aluminum source for this program.

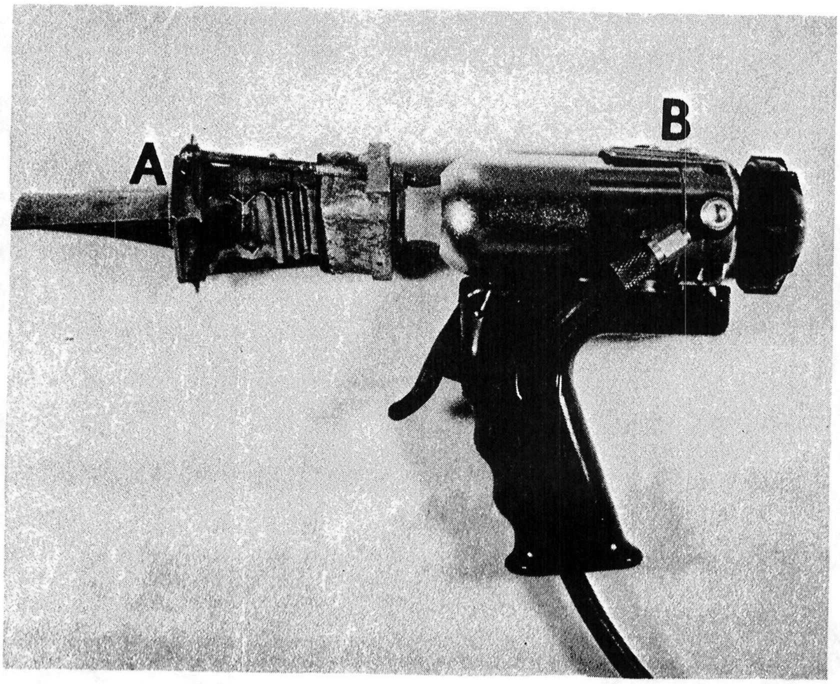
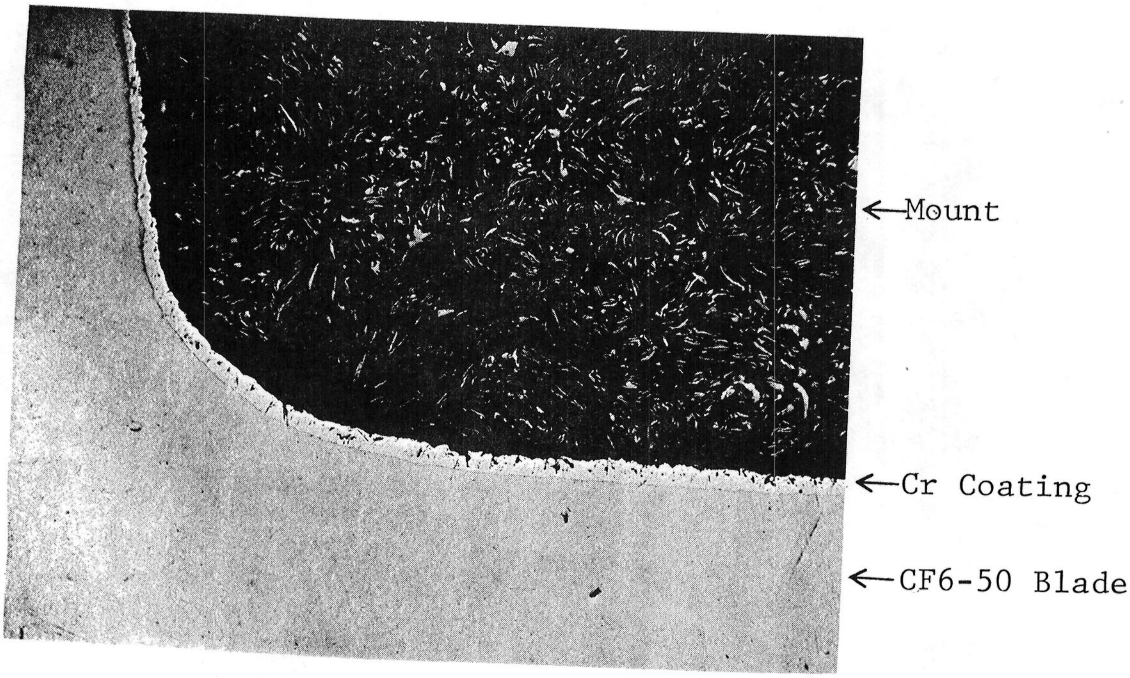


FIGURE 8

Slurry Injection Setup

A = BLADE
B = INJECTION DEVICE



500X, Unetched

Figure 9

Cr Deposited by the Slurry Injection Technique Inside a CF6-50 Blade

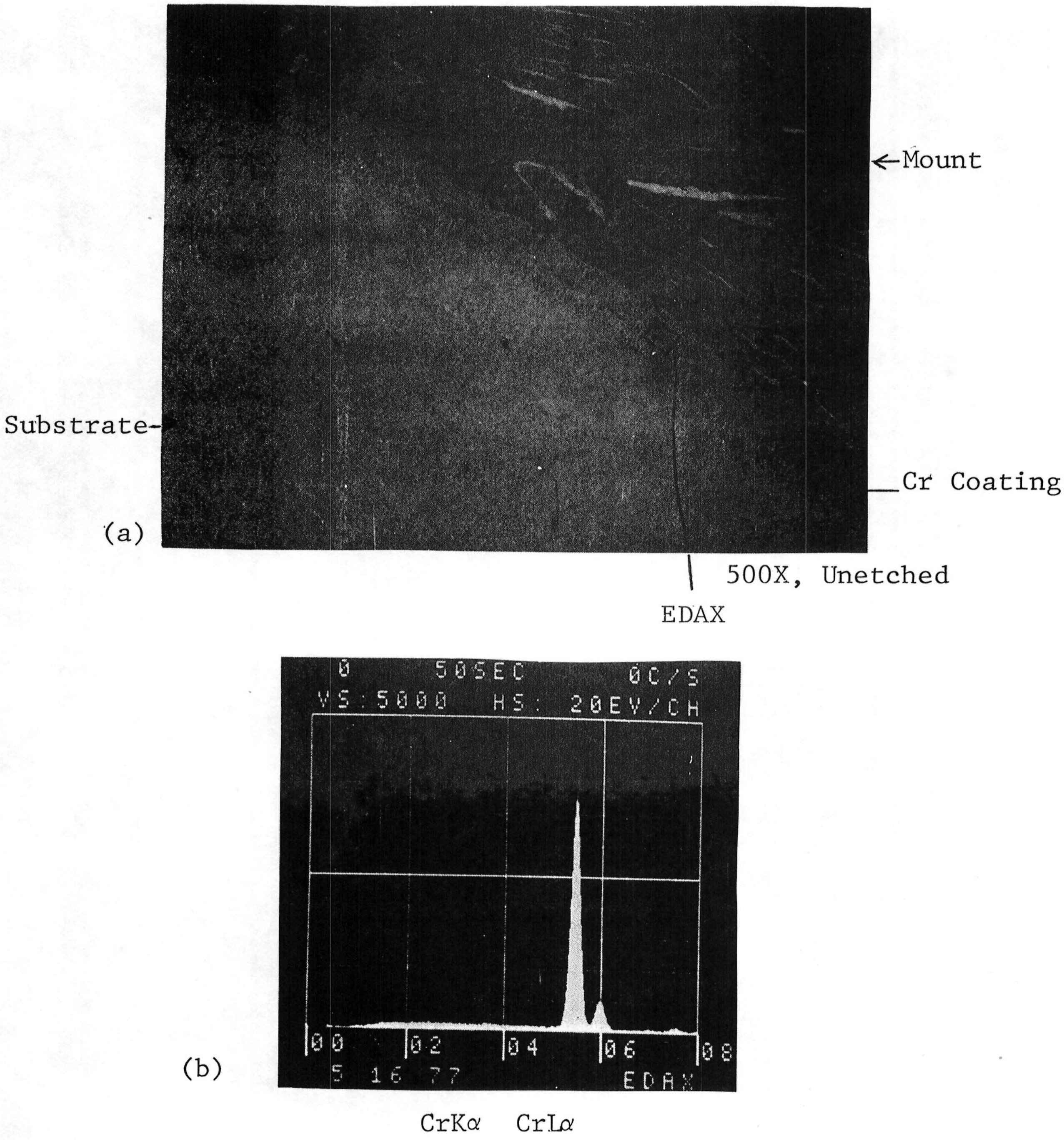
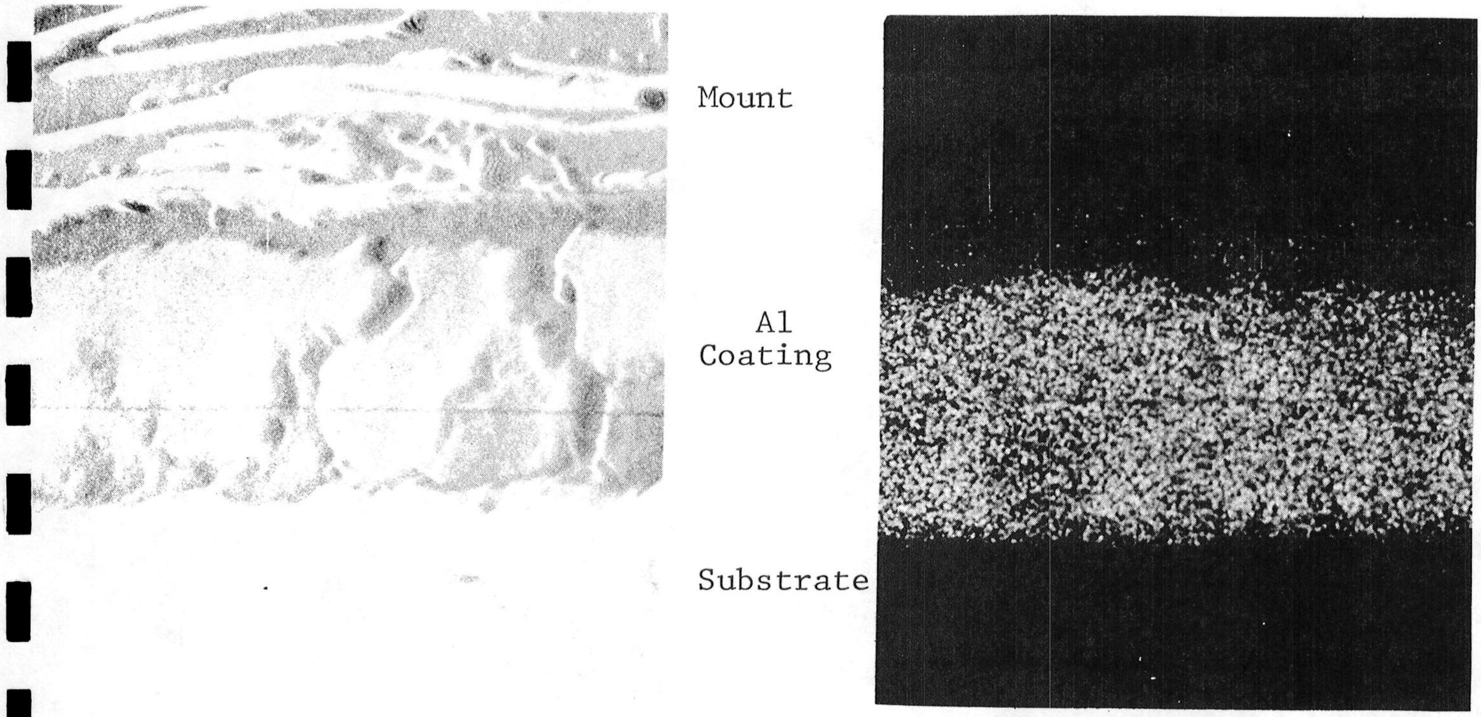


Figure 10

(a) As Deposited Cr by the Slurry Injection Technique.
(b) EDAX Analysis Confirmed the Deposit to be Cr



X2000 (SEM)

Al (x-ray scan)

Figure 11

CVD Al Deposit Using TIBA

Tri-isobutyl aluminum (TIBA) undergoes thermal decomposition in two distinct steps:

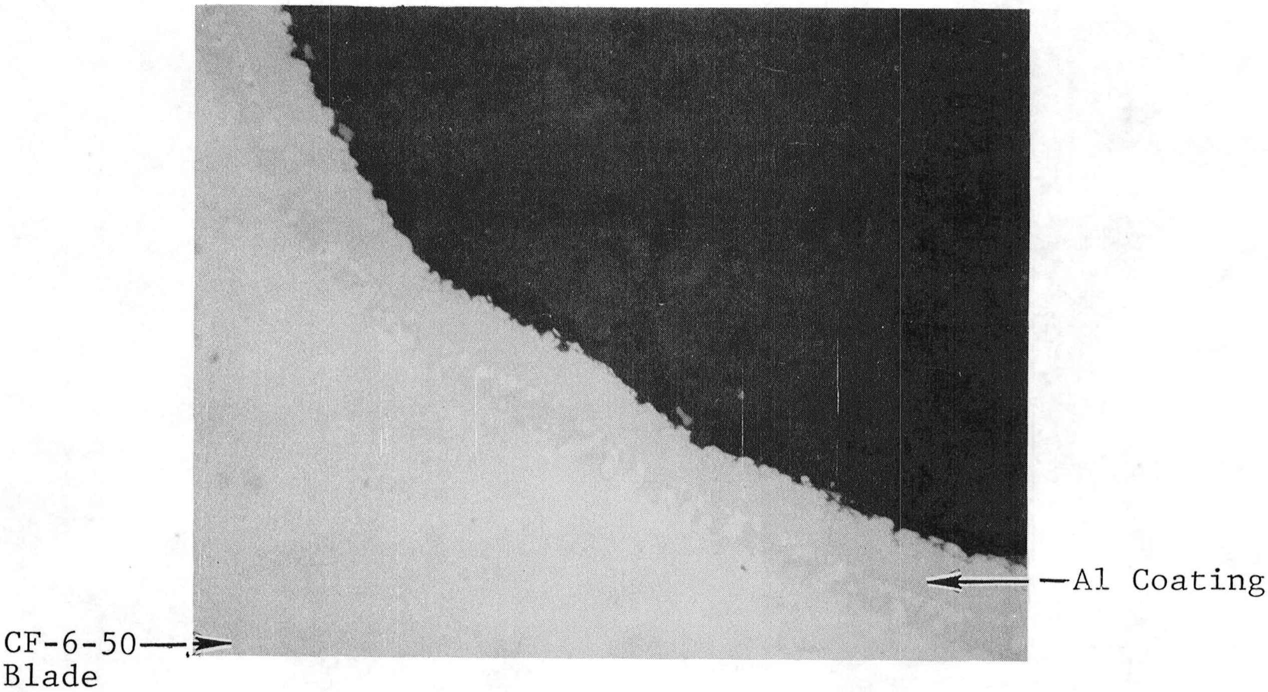
at 100-150C (212-302F) $[(CH_3)_2\ CH\ CH_2]_3\ Al \rightarrow [(CH_3)_2\ CH - CH_2]_2\ AlH + (CH_3)_2\ C{=}CH_2$

at 250C 482F $[(CH_3)_2\ CH{-}CH_2]_2\ AlH \rightarrow Al + 3/2\ H_2 + 2\ (CH_3)_2\ C{=}CH_2$

TIBA starts decomposing at about 71C (160F); the plating reaction must be carried out at low pressure (5 torr or less) or the premature decomposition must be suppressed by the addition of isobutylene to the carrier (Argon) gas. The high degree of reversibility makes this latter procedure quite effective. Bazzarre and Petriello showed that although isobutylene as a suppressant yielded columnar coatings from TIBA, the use of ethylene as a suppressant, presumably under otherwise identical conditions, gave a lamellar, smoother coating. Oxygen is added to the carrier gas in the amount of 0.1 vol. % to improve the quality of the deposit, possibly by scavenging the hydrogen released in the reaction.

(v) Al By Slurry Injection Technique

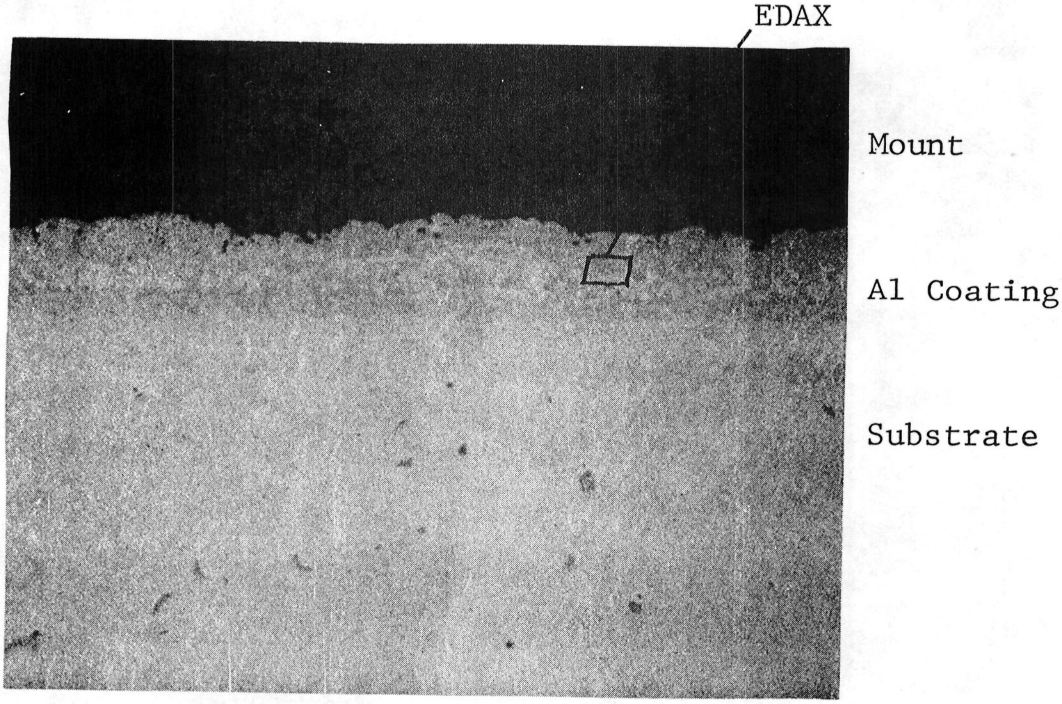
The principle of Al slurry injection is the same as the Cr injection technique discussed earlier. This work was started in 1976. Slurries of AlF_3 with a variety of organic reagents were tried for the purpose of obtaining a uniform suspension of particles which could be injected into the blade interior. A fixture which throws slurries at a controlled pressure and flow rate was designed and built. This enabled us to obtain a predetermined activity of the coating element, and therefore, the desired thickness of aluminum on the surface at a given temperature. The role of hydrogen in controlling the kinetics of the reaction was investigated. Uniform deposits of aluminum have been obtained over the entire cross section of CF6-50 blade airfoils (Figure 12). A SEM analysis of the coating structure is also given (Figure 13). The process is controlled by factors such as coating powder size, pretreatment, slurry viscosity, the amount of slurry injected, the coating temperature and time. Based on thermograviemetric and particle size analysis of the pack constituents, appropriate baking, grinding, and pack procedures have been optimized.



500X, Unetched

Figure 12

Al Coating Deposited on an Internal Surface of a CF-6-50-Blade Using Slurry Process



500X Unetched

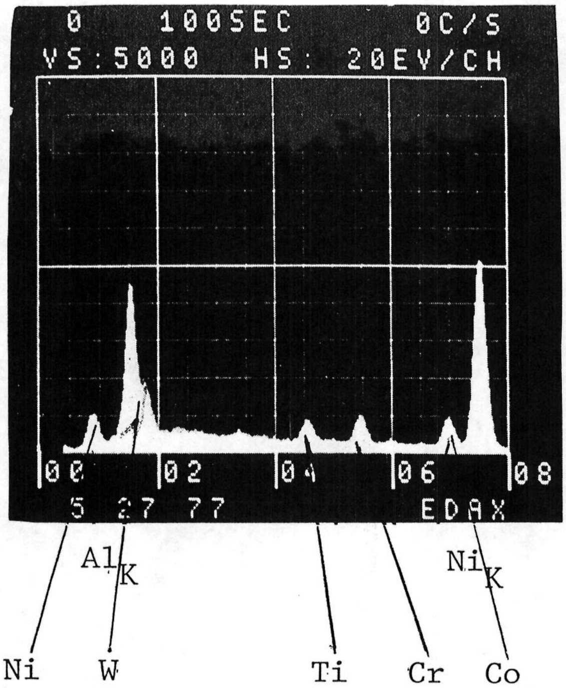


Figure 13

EDAX (SEM) Analysis of As Deposited Internal Al Coating On CF6-50 Blade (R'80).

(5) MECHANICAL PROPERTY EVALUATIONS

The protective coatings used on turbine alloys affect mechanical properties by three mechanisms:

(i) The added material produces a surface of different properties than the base alloys, e. g., the aluminide coatings typically are more brittle at low temperatures and more ductile at high temperatures.

(ii) Diffusion between the coating and bare alloy causes chemical and phase changes in the alloy itself for a distance below the coating that depends on the initial coating parameters and subsequent thermal exposure.

(iii) The heat treatment used in the coating process is frequently different from the normal treatment of the base alloy and may cause changes in the bulk properties.

Thus, the mechanical properties that need to be investigated for each alloy/coating system are: a) tensile strength and ductility; b) creep and stress rupture; c) high and low cycle fatigue; d) thermal fatigue; e) the ductile-brittle transition temperature of the coating; and f) the coating fracture strain.

After the coating thickness and composition were verified, the DBTT tests were carried out on test bars with 0.60 cm (0.16") diameter (Figure 14). The specimens were step-strained with an increment of .0025 cm/cm (0.001 in/in) elongation. The tests at each temperature were stopped when the coating cracking strain was identified (by first appearance of a crack at a magnification of 20X). The inspection of the coating crack was carried out by the Zyglo technique which picks up fine hairline cracks. If the coating was free from cracks, the specimen was reloaded and strained to a total of .50 cm/cm (0.2 in/in) strain and checked. The straining and inspection cycles were performed until coating cracks were observed. Up to five temperatures were tested for each coating process/combination. The plot of coating cracking strain vs. test temperature yielded the DBTT.

(6) RESULTS

The deposition sequence, layer thickness, and deposition techniques for this program are listed in Table V. The various processes selected are expected to provide compatibility between the intended internal and external coatings. Included in the process development are:

SI UNITS

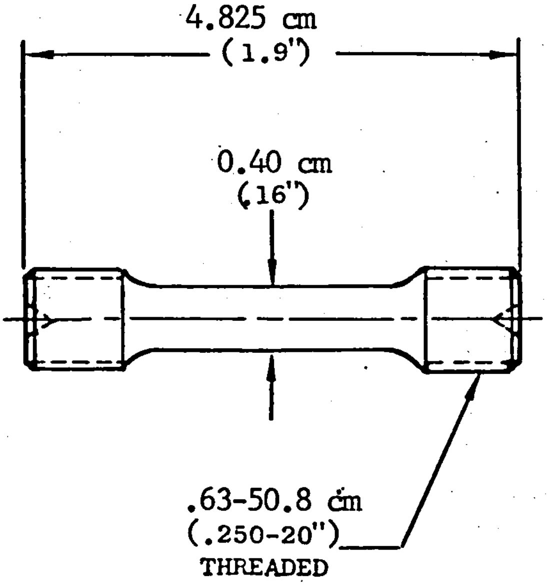


Figure 14. Specimen configuration used for ductile-brittle transformation testing - Not to scale

SI UNITS

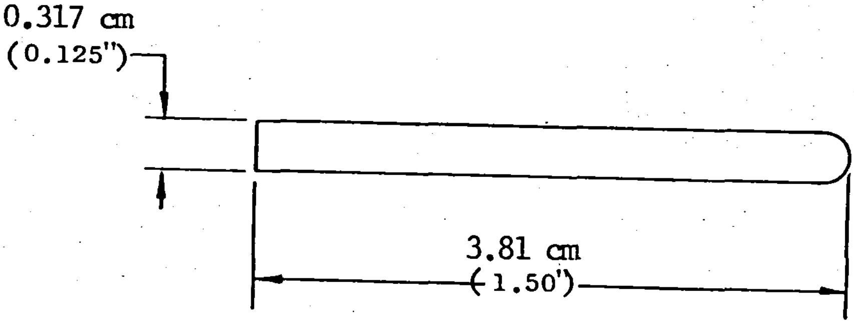


Figure 15. Pin Specimen Used for Coating Studies.

(i) Definition of heat treatment cycle used after element layer deposition, and

(ii) A definition of the mechanics and process parameters involved in applying elemental deposits.

The technical effort consisted of a single task, the goal being to screen and evaluate six coating/process combinations and select one coating system for use in coating blades for a process demonstration. Included in this task are verification of coating thickness, coating composition and measurement of DBTT.

A total of 19.8 Kg (40 lbs.) of AFNiTaC alloy designated 3116A2 (nominal composition) wt. % 6.25 Re, 4.05 Co, 1.75 Cr, 4.1 V, 9.1 Ta, 69 Ni, 6.2 Al, 0.26 C, was ordered from the General Electric Research Center at Schenectady. This alloy was used exclusively in the program.

Experiments with electroless Ni coating using the hydrazine process were started and a thickness of .001 cm (0.4 mil) of Ni was deposited on NiTaC pins. After heat treating at 1080C (1975F) for 4 hours, a ≈.0012 cm (0.5 mil) diffused coating was obtained. The Ni coating was found to adhere well to the substrate.

The three coating systems which did not require work at Battelle (namely electroless Ni, slurry Al, and slurry Cr) were applied in-house to NiTaC pins. The three coatings are identified as #2, #4 and #6 in the table. Elemental layers of Cr and Al were put down by a slurry injection technique and Ni layer was applied using the hydrazine process. After deposition of Ni, the specimens were heat treated for 4 hours at 1065C (1950F) in vacuum. The as-deposited coatings were evaluated with respect to coating thickness and composition are shown in Table VI.

TABLE V

INTERNAL COATING DEPOSITION SEQUENCE LAYER THICKNESS AND DEPOSITION TECHNIQUE

Coating System	Element/Target Thickness in M/CS/Deposition Technique*			
wt.%	1st Step	2nd Step	3rd Step	4th Step
#1 Ni 20 Cr	Ni/0.8/N	Cr/0.2/C		
#2 Ni 20 Cr	Ni/0.8/N	Cr/0.2/S		
#3 Ni 15 Cr 20 Al	Ni/0.8/N	Cr/0.2/C	Al/0.2/C	
#4 Ni 15 Cr 20 Al	Ni/0.8/N	Cr/0.2/S	Al/0.2/S	
#5 Ni 20 Cr 10 Al	Cr/0.2/C	Ni/0.8/N	Cr/0.2/C	Al/0.1/C
#6 Ni 20 Cr 10 Al	Cr/0.2/S	Ni/0.8/N	Cr/0.2/S	Al/0.1/S

* N - Hydrazine Electroless Ni

C - Chemical Vapor Deposition

S - Slurry Injection

TABLE VI

THICKNESS OF COATING #2, 4, 6 (1st Iteration)

Coating	Thickness Target (mils)	Actual (mils)
#2 Ni 20 Cr	1.5	1.2
#4 Ni 15 Cr 20 Al	2.0	2.5
#6 Ni 20 Cr 10 Al	2.0	1.8

The thickness for coatings #2 and #6 were within the required ± 20% limit whereas #4 was slightly over. The compositions of coatings #2 and #4 were within the range for Ni and Al, but were found to be low in Cr.

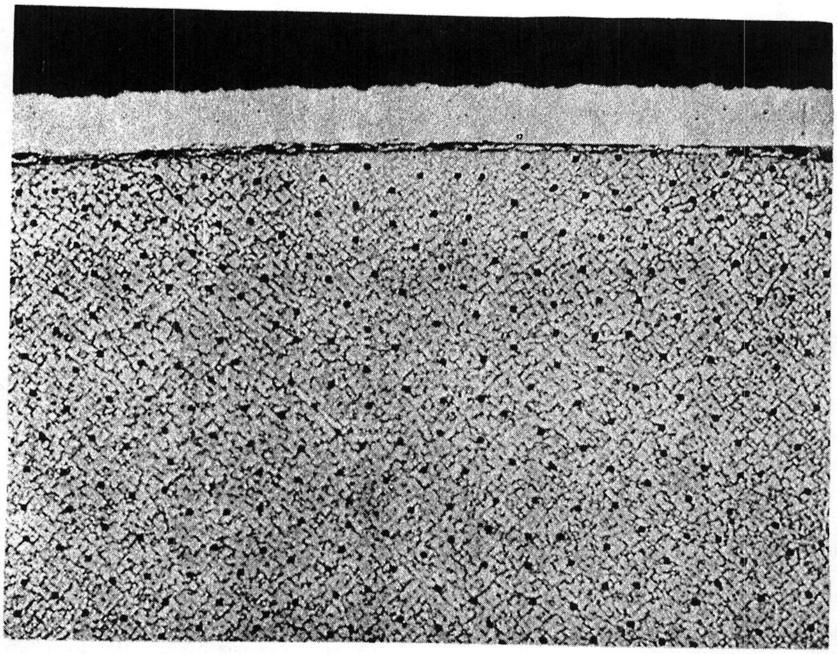
Metallographic analysis was performed on the three coating variations on NiTaC pins. Figures 16a and 16b show the electroless Ni coatings in the as-deposited and heat-treated condition respectively. The as-deposited structure shows good bonding, purity and structure. The heat treated electroless Ni coating also shows good structure with less than 0.2 mil of fiber denudation.

Figure 17a shows a Ni-Cr coating (coating #2, 1st iteration) on NiTaC. There were some oxide inclusions observed in the coating. A quantitative electron probe analysis was carried out on the coating. A computer plot of the microprobe data is shown in Figure 17b, where the results for Cr, Ni and Al from the substrate are presented. Additional microprobe data revealed that the diffusion zone also contained small amounts of other elements of the substrate.

The calculated averaged composition of the NiCr coating was 81% Ni, 10% Cr. The Cr level was low for this coating. A second iteration was attempted.

Figure 18a shows a NiCrAl coating, which is the first iteration of coating #4 on AF NiTaC test pin specimen. The coating exhibited a good structure with less than 1.0 mil of carbide fiber denudation. The quantitative electron microprobe results for the NiCrAl coating are presented in Figure 18b. The calculated averaged composition of this coating was approximately 67.5% Ni, 9% Cr, 14% Al. The diffusion zone contained small amounts of V, Re and Ta, while the additive layer contained less than 2 wt. % of substrate-elements. A second iteration for this coating was attempted to increase the Cr and Al levels.

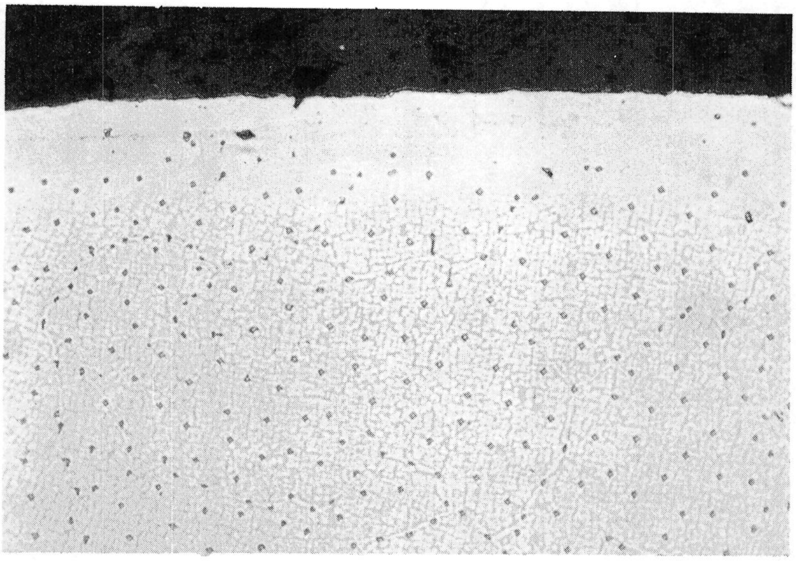
Figure 19a shows the NiCrAl coating #6 deposited on AF NiTaC pins using two chromizing steps. The quantitative electron microprobe results for this NiCrAl coating are presented in Figure 19b. The calculated averaged composition of this coating was approximately 63.5% Ni, 11.5% Cr and 19.5% Al. The diffusion zone was shown to contain small amounts of Re, Ta and V. The additive layer contained less than 2 wt. % of substrate alloy elements. The Al level and Cr level need to be decreased and increased respectively in the second iteration.



500X Etched
Phosphoric
Acid

Figure 16a

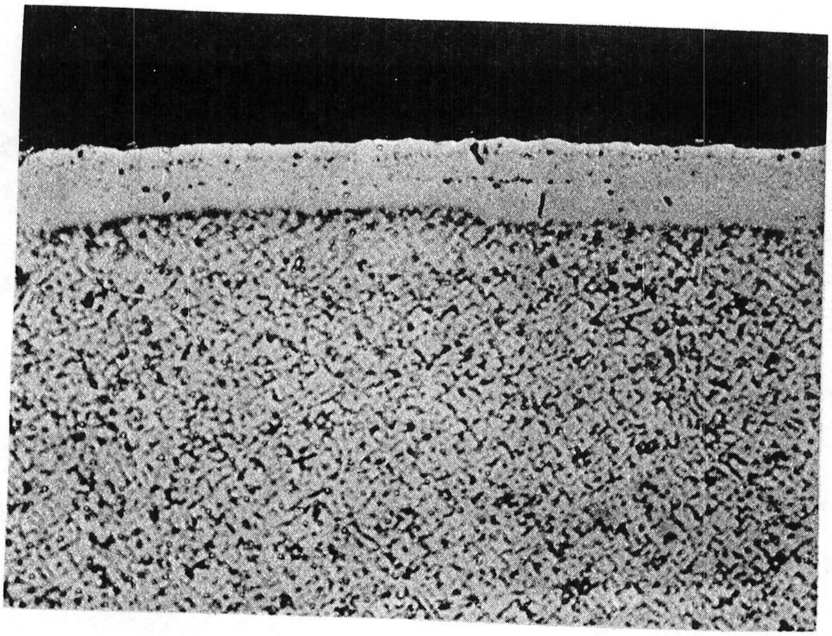
As deposited electroless Ni coating on NiTaC specimen.



500X, Etched
Phosphoric
Acid

Figure 16b

Hydrazine electroless Ni coating on NiTaC specimen after a 4 hour diffusion heat treatment at 1065C (1950F). A fiber denuded zone of less that .0005 cm (0.2 mil) can be observed.



500X, Etched

Figure 17a

A NiCr coating on NiTaC specimen. The deposition sequence consisted of hydrazine electroless Ni, a 4 hour diffusion heat treatment at 1065C (1925F), and slurry Cr at 1051C (1925F). Coating #2, 1st iteration)

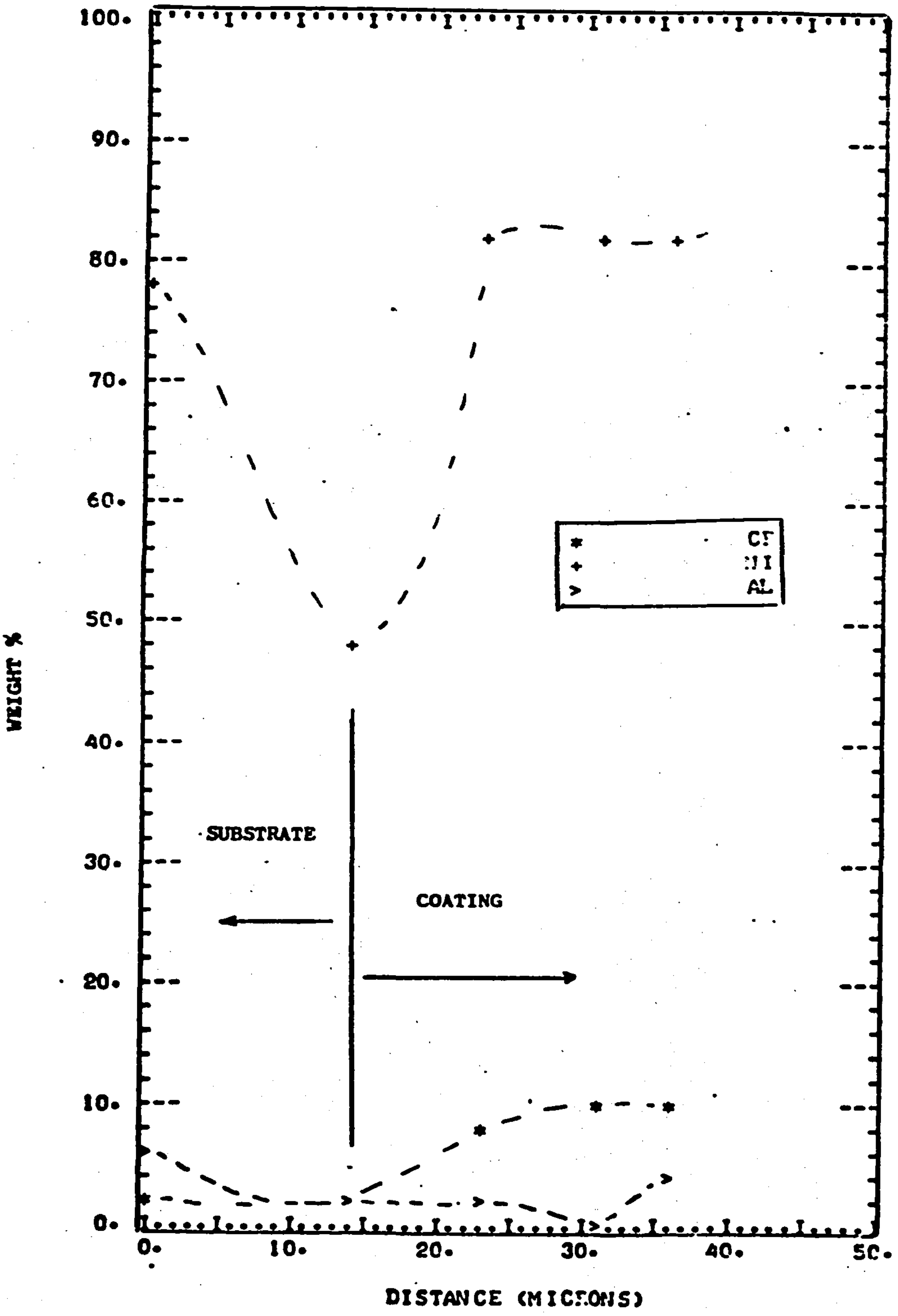
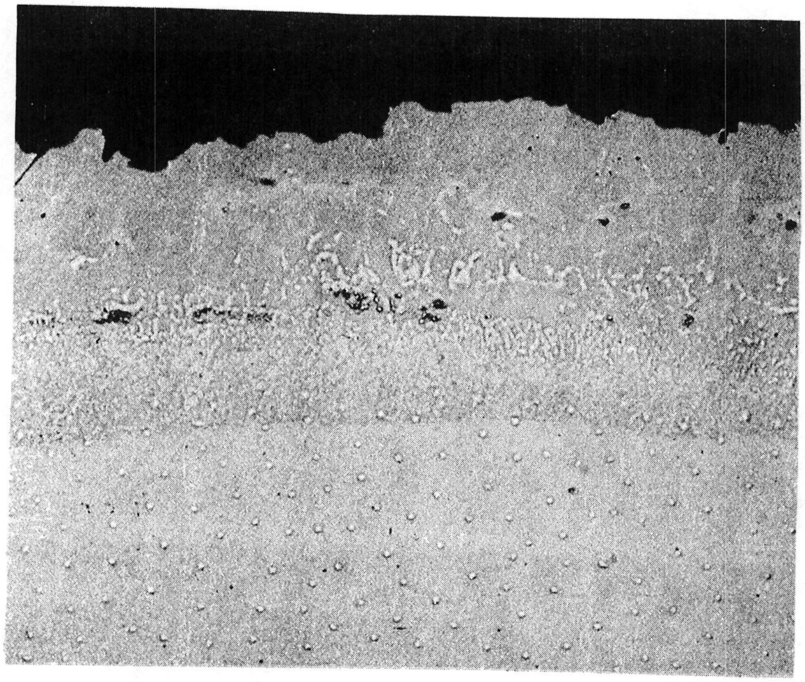


Figure 17b

A computer plot of electron microprobe data showing the distribution of Ni, Cr and Al in a NiCr coating on NiTaC. This coating represents the first iteration of coating #2 in Table 1.



500X Unetched

Figure 18a

A NiCrAl coating on NiTaC specimen. The deposition sequence consisted of electroless Ni, a four hour diffusion heat treatment at 1065 C (1950F), slurry Cr at 1051C (1925F), and slurry Al at 1051C (1925F). (Coating #4 1st iteration).

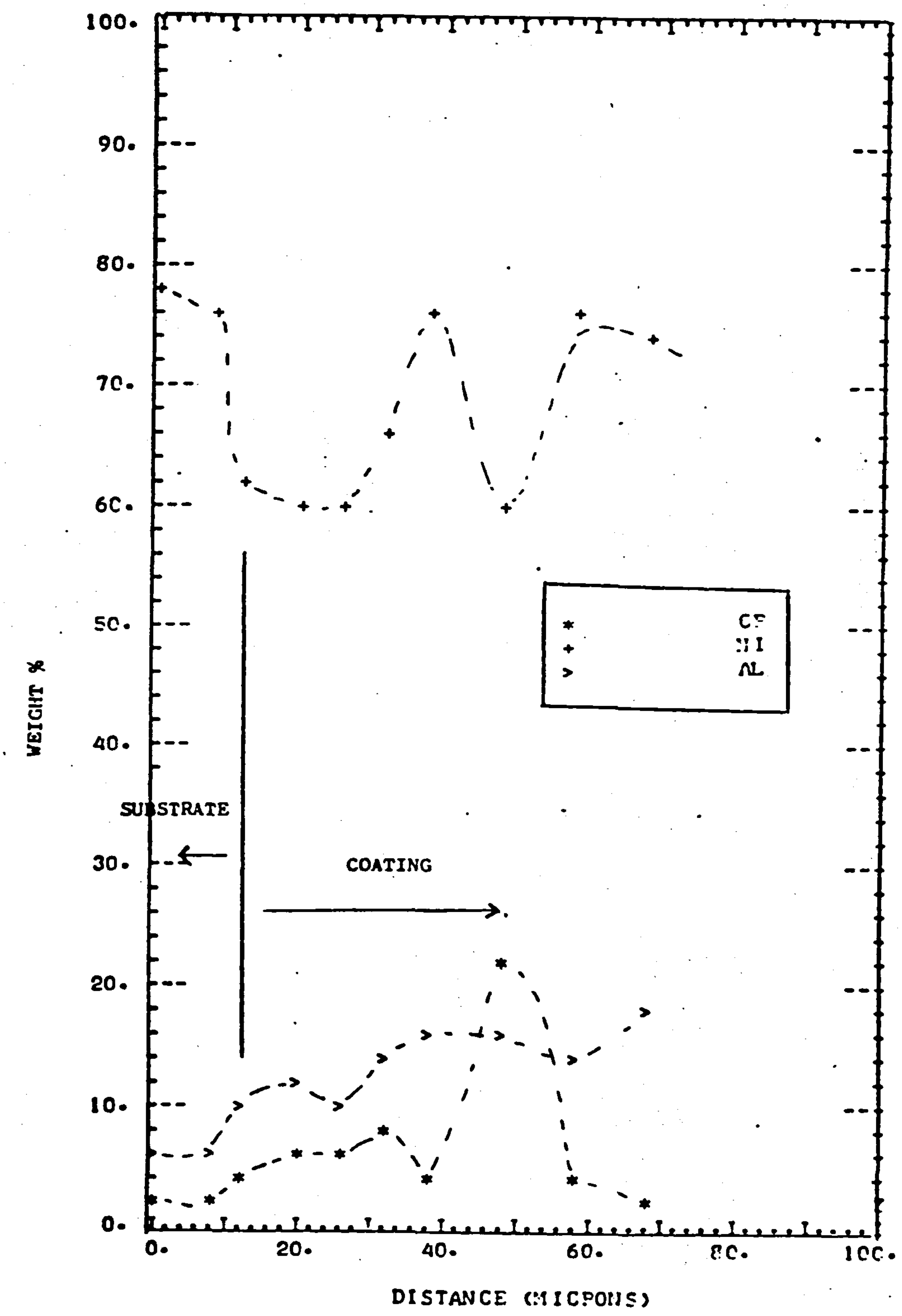
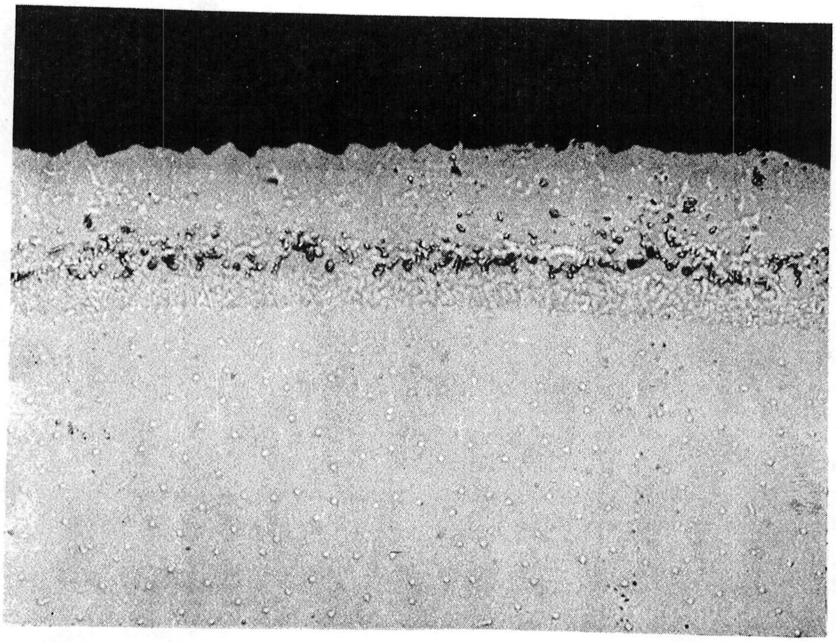


Figure 18b

A computer plot of electron microprobe data showing the distribution of Ni, Cr and Al in a NiCrAl coating on NiTaC. This coating represents the first iteration of coating #4 in Table 1.



500X, Unetched

Figure 19a

A NiCrAl coating on NiTaC specimen. The deposition sequence consisted of slurry Cr at 1051C (1925F), electroless Ni, a four hour diffision heat treatment at 1051C (1950F), a second slurry Cr at 1051C (1925F) and slurry Al at 1051C (1925F). (Coating #6 1st iteration).

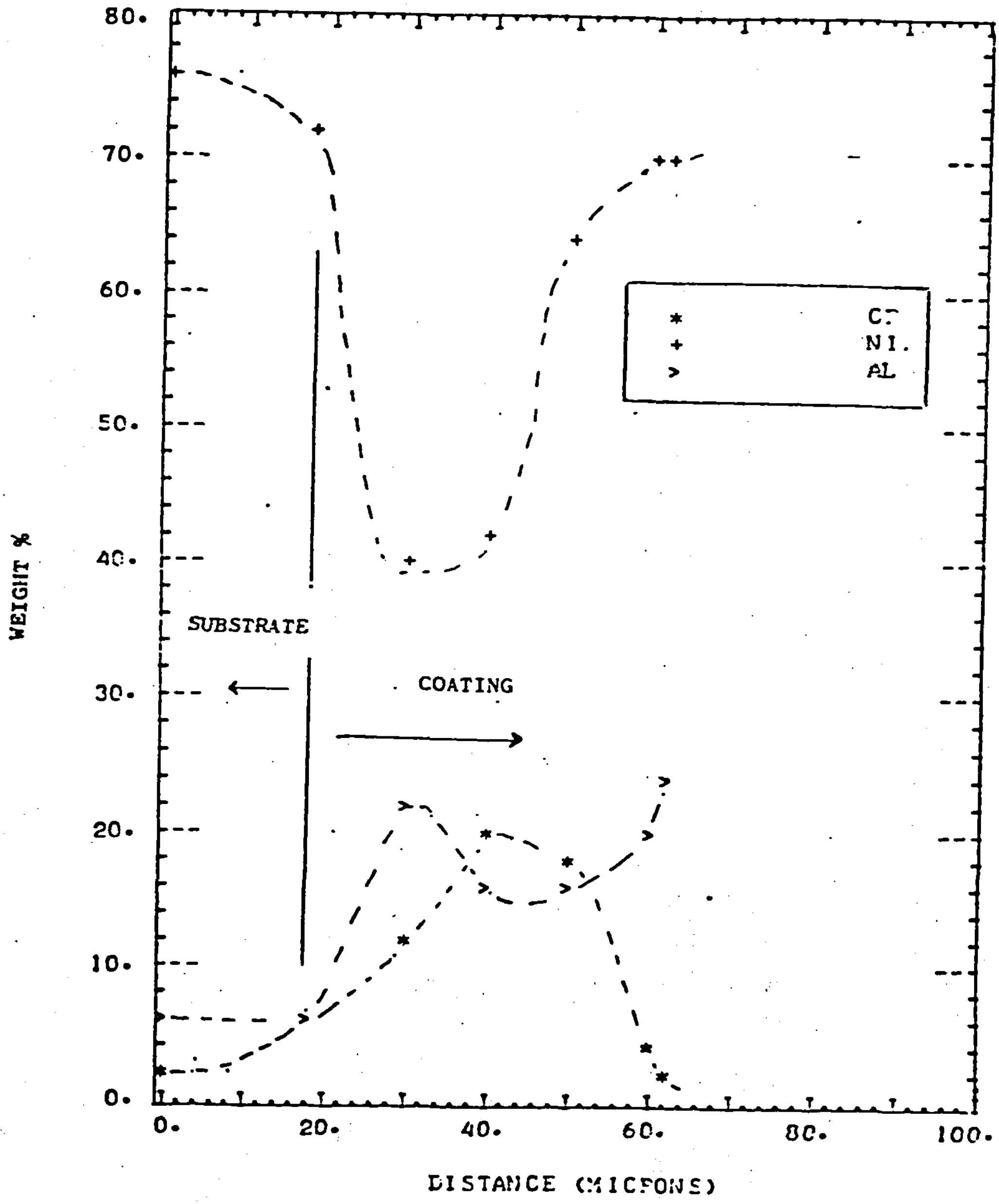


Figure 19b

A computer plot of electron microprobe data showing the distribution of Ni, Cr and Al in a NiCrAl coating on NiTaC. This coating represents the first iteration of coating #6 in Table 1.

The second iteration of candidate coatings #2, 4 and 6 were completed. Elemental layers of Cr and Al were deposited using a slurry injection technique and the Ni layer was deposited using electroless Ni. After deposition, samples were heat treated for four hours at 1065C (1950F) in hydrogen. A similar heat treatment was given to the samples after slurry injection.

The thickness and composition of the 2nd iterations of coating #2 and 4 were found to be within the required ± 20% range. Metallographic analysis of the second iteration of coating #2 revealed good bonding and structure. A quantitative electron microprobe analysis was carried out on this coating. A computer plot of the microprobe data is shown in Figure 20 where the results of Cr, Ni and Al coating are presented. Additional microprobe data, not shown, reveals that the diffusion zone also contained small amounts of some substrate elements - as expected. The calculated averaged composition of the NiCr coating, in terms of the major constituents was 82% Ni, 12% Cr and 2% Al. The target composition was 80% Ni, 20% Cr. The Cr level represents an improvement over the first iteration, but a substantial increase is still required. The Al was diffused from the substrate. A third iteration of this coating was planned in which a modified Cr slurry was used to increase the Cr level to the target composition.

Metallographic analysis of the second iteration of coating #4 revealed good bonding and structure. A quantitative electron microprobe analysis was carried out on this coating. A computer plot of the microprobe data is shown in Figure 21 where the results for Cr, Ni, and Al in the coating are presented. The calculated average composition of the NiCrAl coating, in terms of major constituents, was 65% Ni, 13% Cr and 18% Al. Thus, the coating has met the contract goal and achieved ± 20% of the target composition. The second iteration represents a major improvement over the first. A third iteration was planned to demonstrate reproducibility.

The electroless Ni coating did not adhere well to the prior chromide layer for the 2nd iteration of coating #6. Therefore, a 3rd iteration was planned.

The third iterations of candidate coatings #2, 4 and 6 were completed. The thickness of the as-deposited coatings were well within the required ± 20% range, Table VII. Metallographic

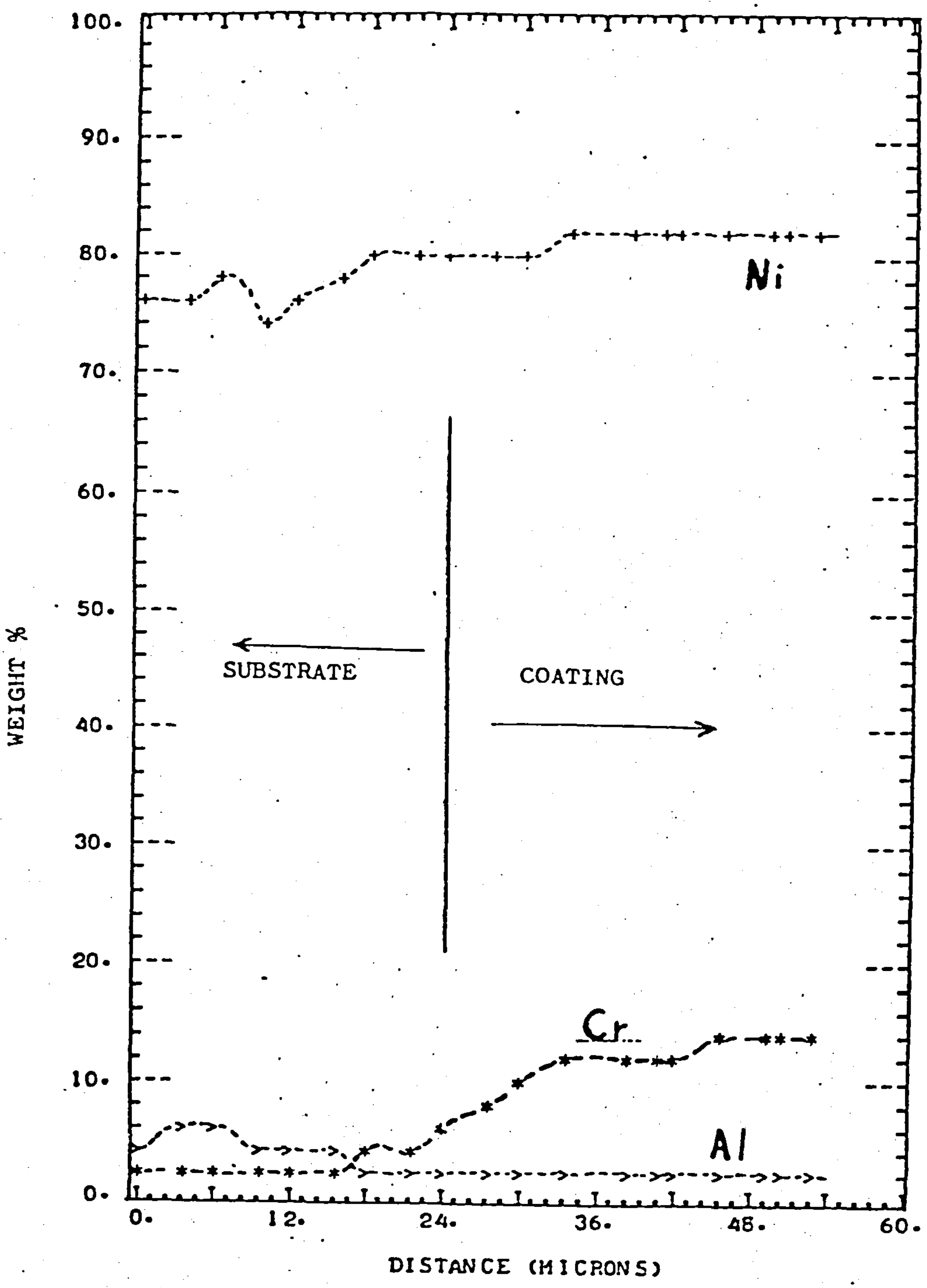


FIGURE 20

A computer plot of electron microprobe data showing the distribution of Ni, Cr and Al in a NiCr coating on NiTaC. This coating represents the second iteration of coating #2 in Table I.

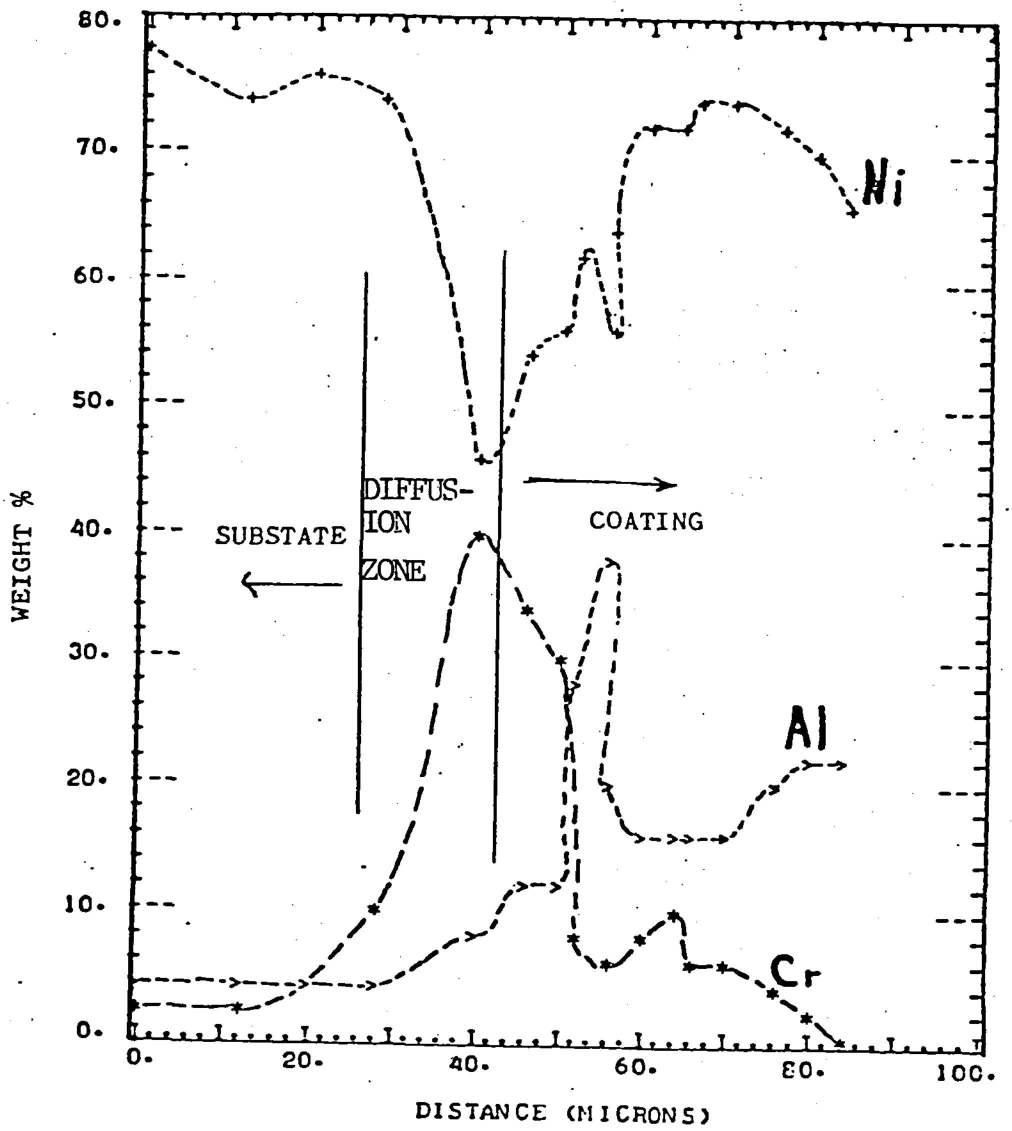


FIGURE 21

A computer plot of electron microprobe data showing the distribution of Ni, Cr and Al in a NiCrAl coating. This coating represents the second iteration of coating #4 in Table I.

analysis of the 3rd iteration of coating #2 revealed good bonding structure as shown in Figure 22a. A layer of NiCr with a Cr-enriched surface is observed. Below the NiCr layer, a diffusion zone consisting primarily of Cr enriched Ni was found. A quantitative electron microprobe analysis was carried out on this coating. A computer plot of the probe data is shown in Figure 22b, where the results of Cr, Ni and Al in the coating are presented. Additional microprobe data not shown, revealed that the diffusion zone also contained small amounts of other elements of the substrate, as expected. The calculated averaged composition of the NiCr coating was 75% Ni, 21% Cr. The target composition of 80% Ni, 20% Cr, therefore, achieved within ± 20%. The Cr level represents a substantial improvement over the second iteration. The Al was diffused from the base metal.

Metallographic analysis of the third iteration of coating #4 revealed good bonding and structure, as shown in Figure 23a. The outer layer has two phases, β-Ni(Cr)Al, and a secondary unidentified phase (probably α Cr). Below this layer is a diffusion zone showing α-Cr precipitation. A computer plot of the microprobe data is shown in Figure 23b, where the results of Cr, Ni and Al in the coating are presented. The calculated averaged composition of this coating, in terms of the major constituents, was 68% Ni, 12% Cr and 17% Al. The target composition is 65% Ni, 15% Cr and 20% Al. Thus, this coating has reproducibily met the contract goal and achieved ± 20% of the target composition.

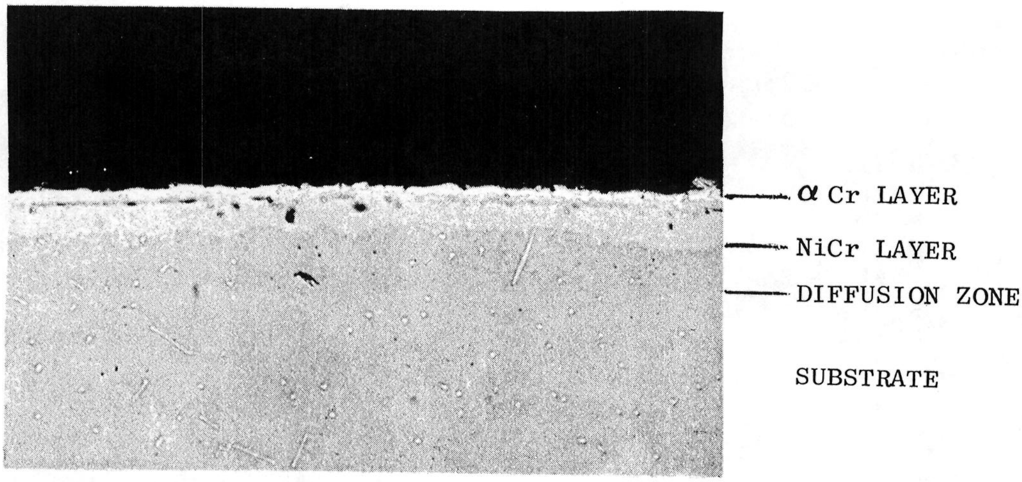
Microprobe analysis of the 3rd iteration of coating #6 (Figure 24) revealed that the averaged composition of this NiCrAl coating, in terms of the major constituents, was 13% Al, 15% Cr and 60% Ni. Therefore, a fourth iteration was tried to bring this coating composition to within the required limits.

Metallographic analysis of the fourth iteration of coating #6 revealed good bonding and structure as shown in Figure 25a. The outer layer consists of β-Ni(Cr)Al and a secondary unidentified phase (probably α Cr). Two zones of diffusion are present. Both diffusion zones show α-Cr precipitation and correspond to areas where the two separate layers were originally deposited. A computer plot of the microporbe data is shown in Figure 25b. The calculated averaged composition of the NiCrAl coating, in terms of the major constituents, was 12% Al, 19% Cr and 60% Ni.

TABLE VII

THICKNESS OF CANDIDATE COATINGS #2, 4, 6
(up to 3rd Iteration)

	Coating (wt.%)	Target Thickness (Mils)	First Iteration	Second Iteration	Third Iteration
#2	Ni-20Cr	1.5	1.2	1.4	1.4
#4	Ni-15Cr-20Al	2.0	2.5	2.0	2.0
#6	Ni-20Cr-10Al	2.0	1.8	-	1.8



500X, Unetched

Figure 22a

A NiCr coating on NiTaC pin specimen. The deposition sequence consisted of electroless Ni, and slurry Cr. (Coating #2, 3rd iteration)

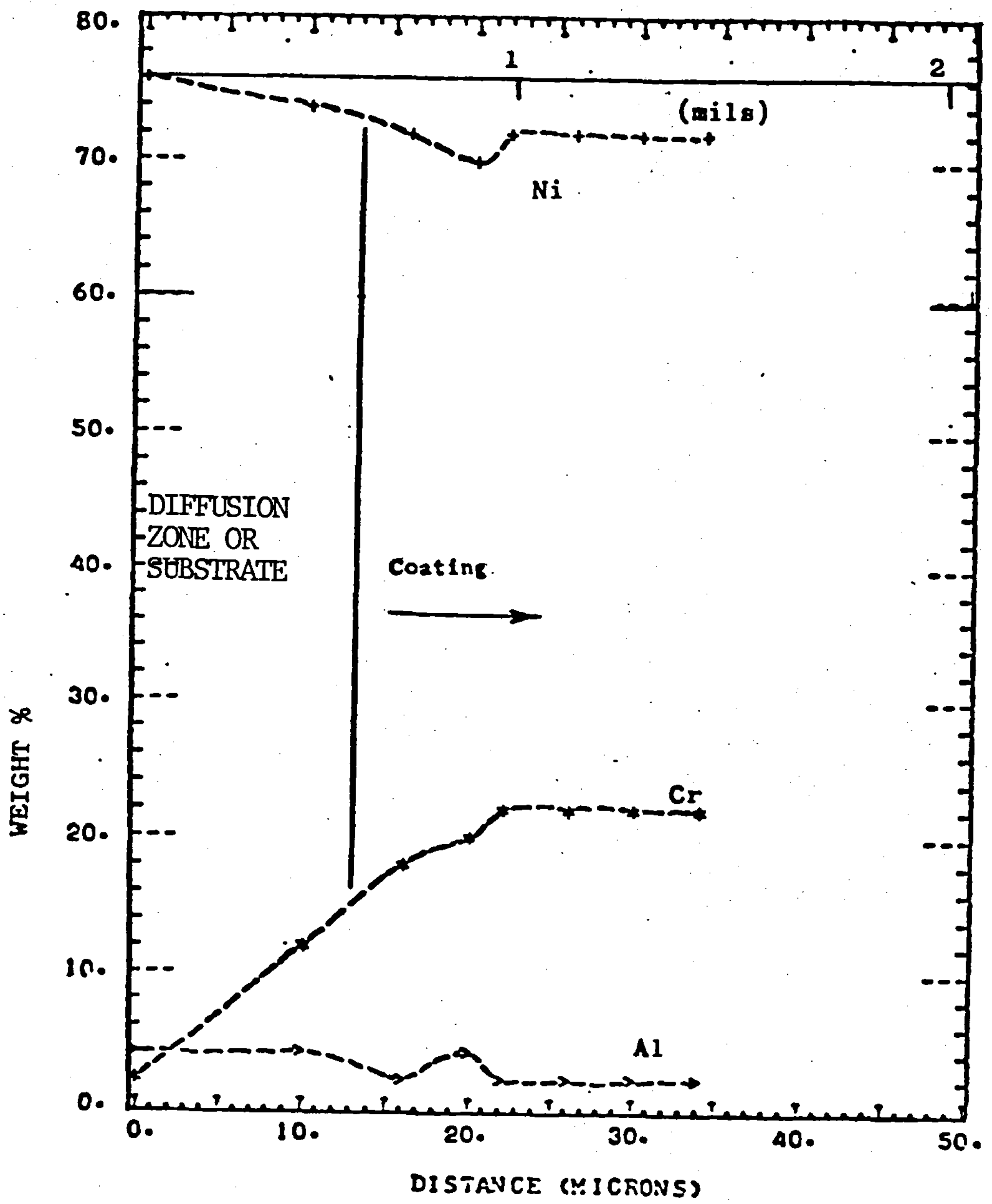
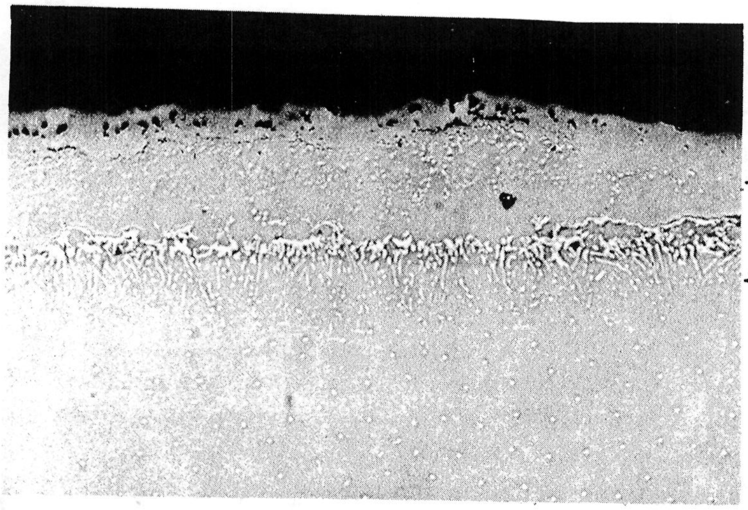


Figure 22b

A computer plot of electron microprobe data showing the distribution of Ni, Cr and Al in a NiCr coating on NiTaC. This coating represents the third iteration of coating #2 in Table I.



Cr enriched β NiAl layer

Diffusion zone with α Cr precipitates

Substrate

500X, Unetched

Figure 23a

A NiCrAl coating on NiTaC pin specimen. The deposition sequence consisted of electroless Ni, slurry Cr, and slurry Al. (Coating #4, 3rd iteration)

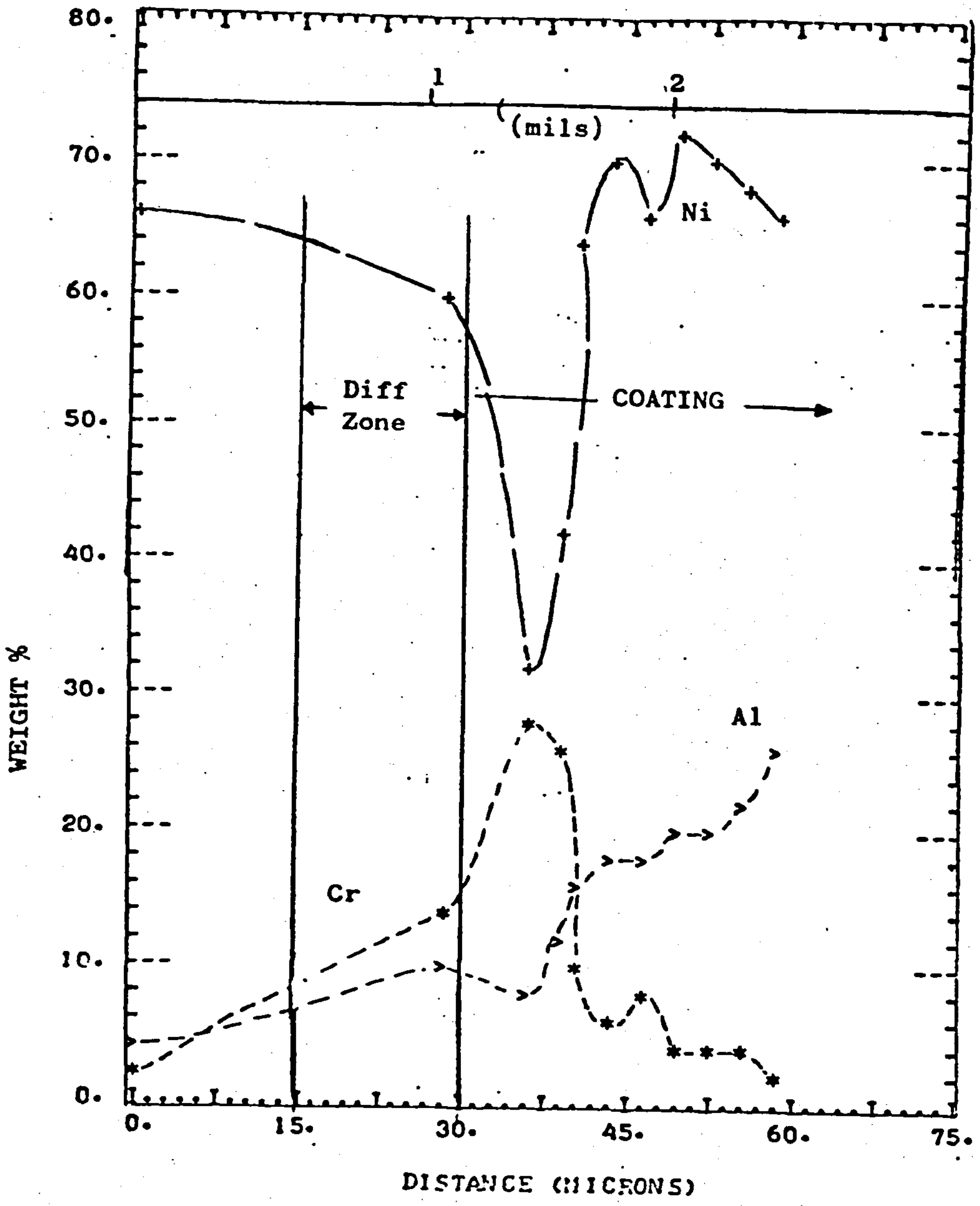


Figure 23b

A computer plot of electron microprobe data showing the distribution of Ni, Cr and Al in a NiCrAl coating on NiTaC. This coating represents the third iteration of coating #4 in Table I.

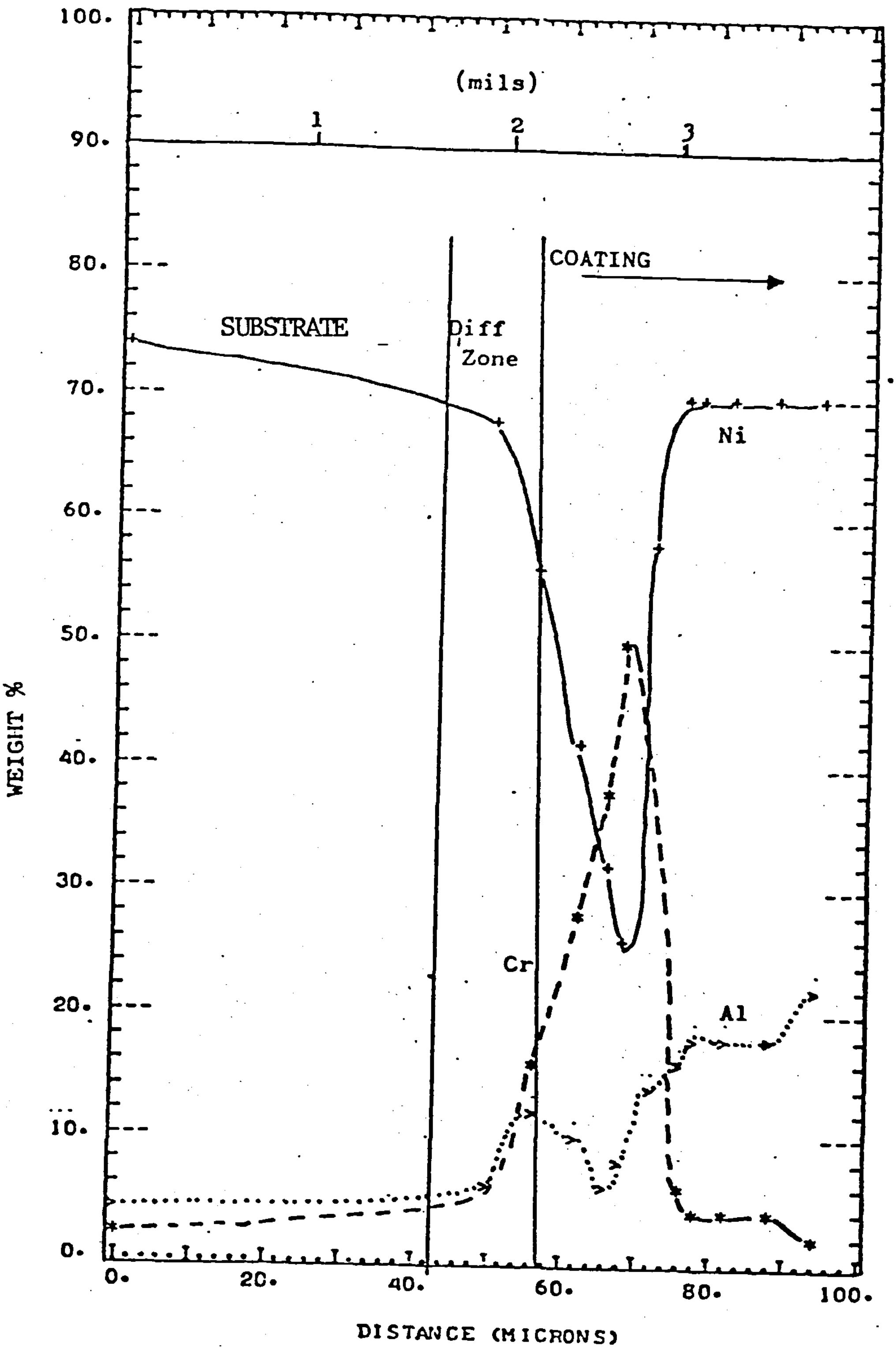
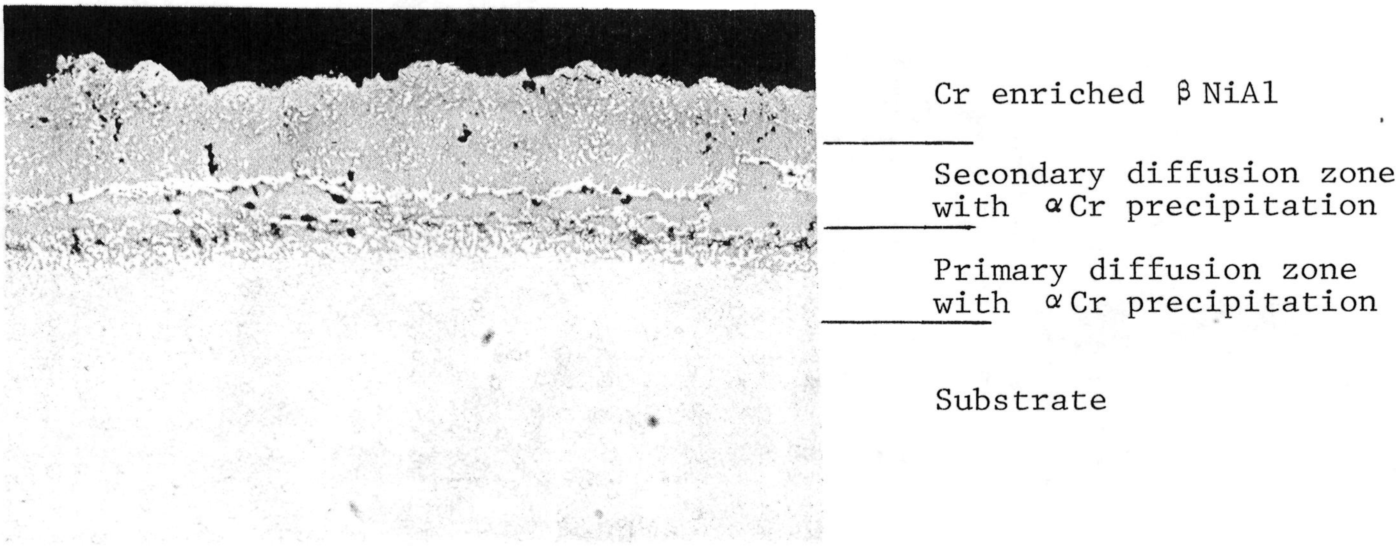


Figure 24

A computer plot of electron microprobe data showing the distribution of Ni, Cr and Al in a NiCrAl coating on NiTaC. This coating represents the third iteration of coating #6 in Table I.



500X, Unetched

Figure 25a

A NiCrAl coating on NiTaC pin specimen. The deposition sequence consisted of slurry Cr, electroless Ni, a second slurry Cr, and slurry Al. The specimen is unetched. (Coating #6, 4th iteration)

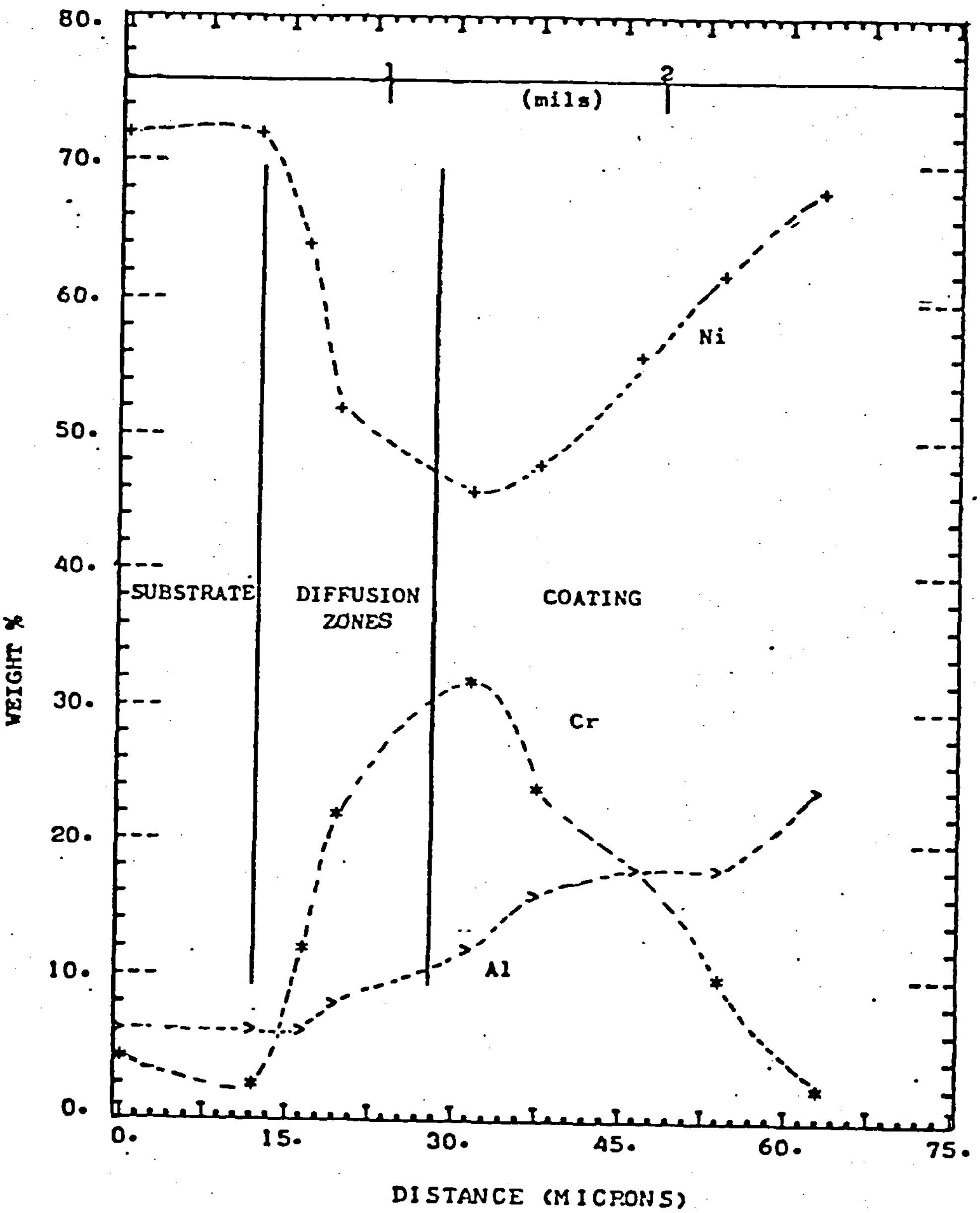


Figure 25b

A computer plot of electron microprobe data showing the distribution of Ni, Cr and Al in a NiCrAl coating on NiTaC. This coating represents the fourth iteration of coating #6 in Table 1.

This iteration is within ± 20% of the target composition of 70% Ni, 20% Cr and 10% Al and represents a significant improvement over previous attempts. Thus, the composition and thickness (Table III) goals have been achieved for all three General Electric applied coating/process candidates.

CVD Coating of Test Specimens:

A total of 15 AF NiTaC pin specimens were coated at Battelle Columbus Labs with CVD Cr. Five pins were bare and ten had an electroless Ni coating pre-applied at G. E.

The first iteration of coating #1 was applied using the CVD Cr process as the secondary step. The primary layer, Ni, was applied at General Electric using the electroless Ni process. After deposition of the elemental layers, samples were heat treated for several hours at 1065C (1950F) in vacuum.

Coating #1 was examined with respect to coating thickness (Table IX) and composition. The thickness range was within ± 20%. Metallographic analysis of the coating revealed unacceptable bonding and structure. Coverage was incomplete and coating spallation occurred in several places. A quantitative electron microprobe analysis was carried out (Figure 26) on a portion of the coating with acceptable bonding and structure. A computer plot of the microprobe data not shown revealed that the diffusion zone contained small amounts of substrate elements. The calculated averaged composition of this NiCr coating in terms of major constituents was 70% Ni, 16% Cr and 5% Al. The coating chemistry meets the target within the required ± 20%, but the coating structure and bonding were poor.

The first iteration of coating #3 was completed. This coating required CVD Cr and Al as two of the three sequential steps. The primary layer, Ni, was applied at G. E. by the electroless Ni process. After deposition, the elemental layers were heat-treated at 1065C (1950F) in vacuum. The coating was examined with respect to coating thickness (Table IX) and composition. The coating thickness was within the ± 20% range. Metallographic analysis of the coating revealed unacceptable bonding and structure (Figure 27). Coverage was incomplete and coating spallation occurred in several places.

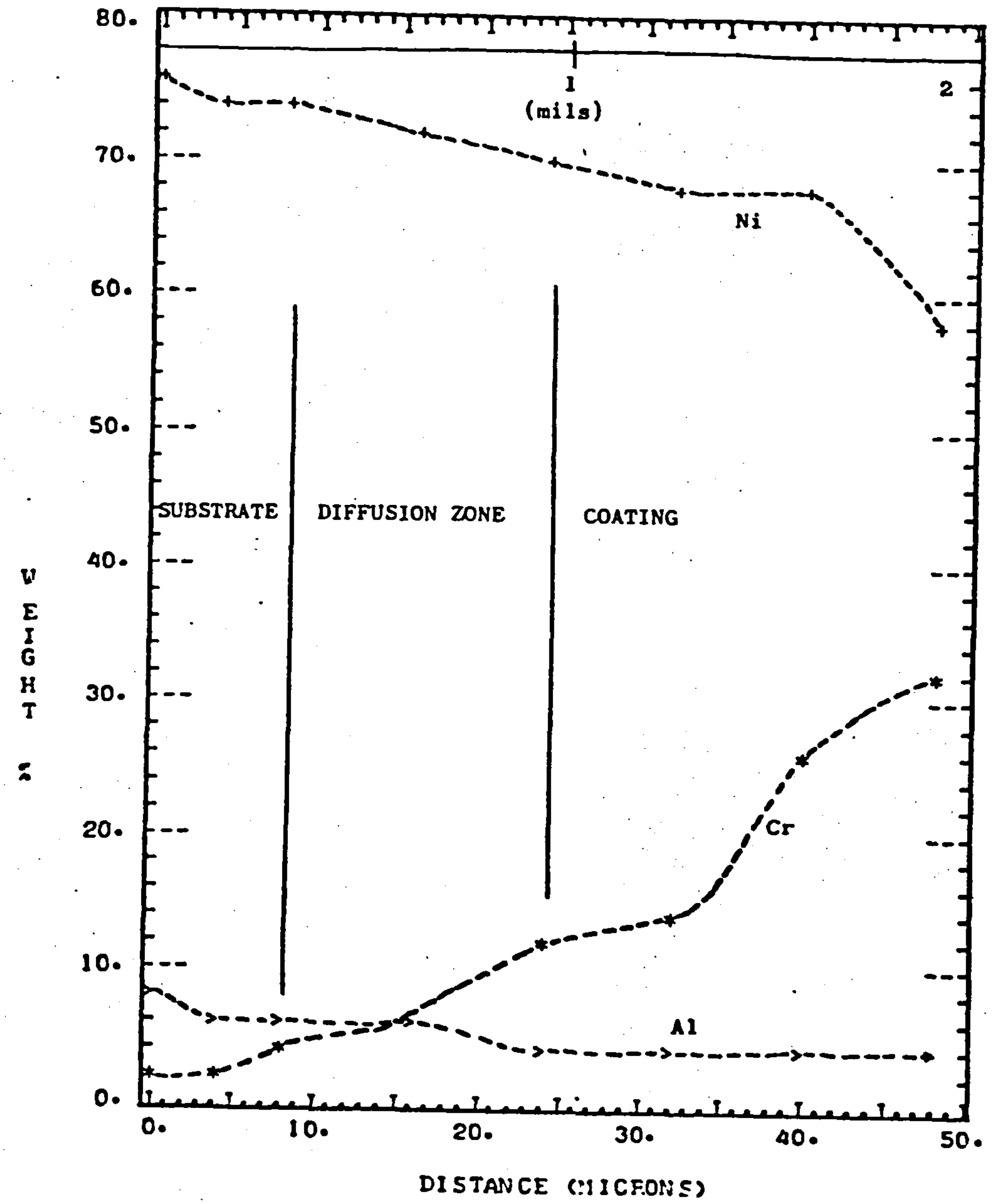


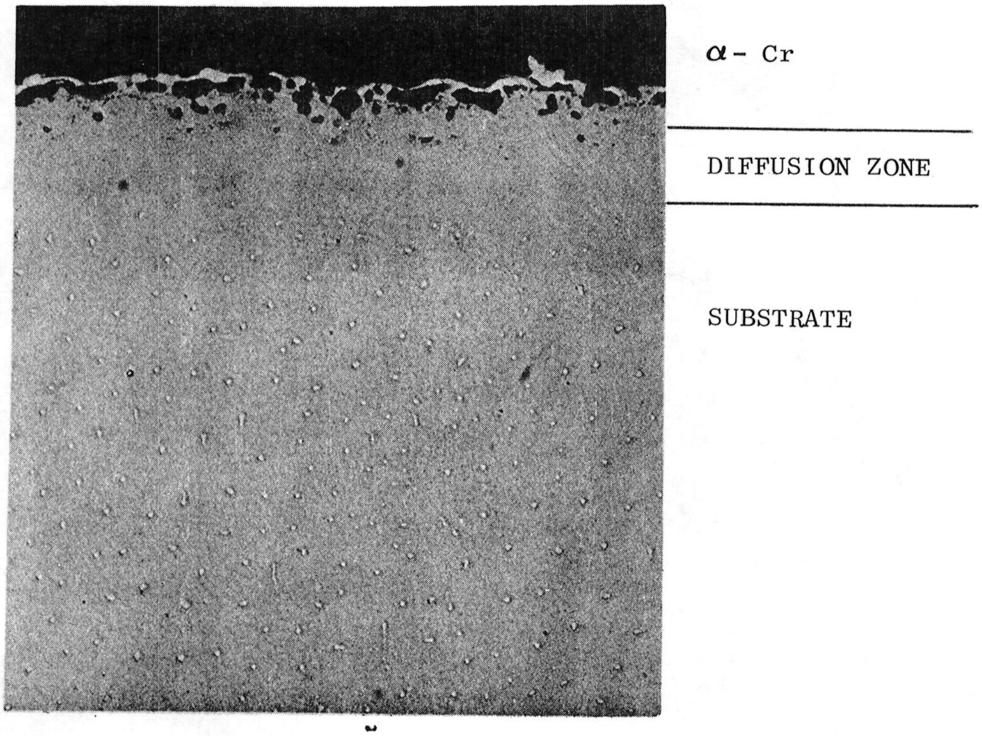
Figure 26

A computer plot of electron microprobe data showing the distribution of Ni, Cr, and Al in a NiCr coating on NiTaC. This coating represents the first iteration of coatingNo. 1 in Table I.

TABLE VIII

THICKNESS OF CANDIDATE COATINGS

	Coating	Target Thickness (Mils)	1st Iteration	2nd Iteration	3rd Iteration	4th Iteration
#1	NiCr	1.5	1.4	-	-	-
#2	NiCr	1.5	1.2	1.4	1.4	-
#3	Ni-15Cr-20Al	2.0	1.5	-	-	-
#4	Ni-15Cr-20Al	2.0	2.5	2.0	2.0	-
#6	Ni-20Cr-10Al	2.0	1.8	-	1.8	2.0



500X Unetched

Figure 27

A photomicrograph showing the unsuccessful attempt at coating #3. The deposition sequence consisted of electroless Ni, CVD Cr, a diffusion heat treatment CVD Al and a diffusion heat treatment. Note that no aluminiding was achieved. (Coating #3, 1st iteration)

Based on the observations made so far, it is highly doubtful that the CVD process could be used to produce internal NiCrAl coating, and, therefore, was not investigated further.

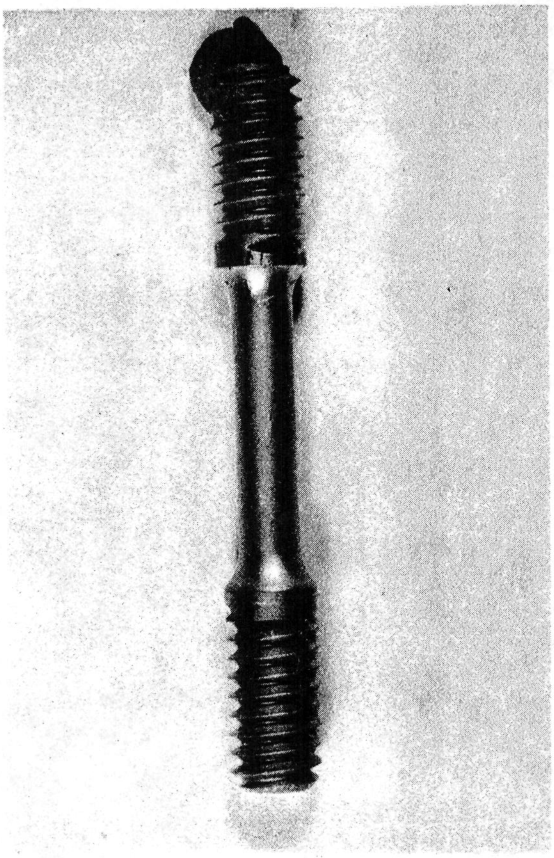
Coating of DBTT Specimens:

A NiCr coating #2 was successfully deposited on five DBTT specimens of NiTaC. The coating sequence consisted of electroless Ni, a diffusion heat-treat 1065C (1950F), slurry Cr deposition and final processing at 1038C (1900F). The macroscopic appearance of this coating on the DBTT specimen is shown in Figure 28. The coating has a smooth metallic appearance. The microstructure of the coating is shown in Figure 29. Good bonding and structure were observed, and a total coating thickness of 1.5 mil was achieved.

An evaluation of the coating #2 DBTT was carried out by progressively straining the samples at four different temperatures. Samples were examined for cracking optically using a fluorescent penetrant after each strain increment was applied. The results are presented in Figure 30. The finding was that the DBTT of coating #2 (NiCr) falls between 704C (1300F) and 760C (1400F) with a ductility of .0137 cm/cm (0.0054 in/in) at 760C (1400F). The poor performance of this coating is not understandable at this stage. It could possibly be due to an influence of substrate elements diffusing into the coating.

The determination of DBTT for coating #4 was performed at four temperatures. A plot of % strain vs. temperature (Figure 31) shows that the ternary NiCrAl coating (electroless Ni + slurry Al) is perfectly satisfactory to meet the requirements of a minimum of 0.6% coating strain capability and a ductile to brittle transition temperature of <760C (<1400F). Hence, the objective of this program in selecting a final coating system with desirable strain capability seems to have been met.

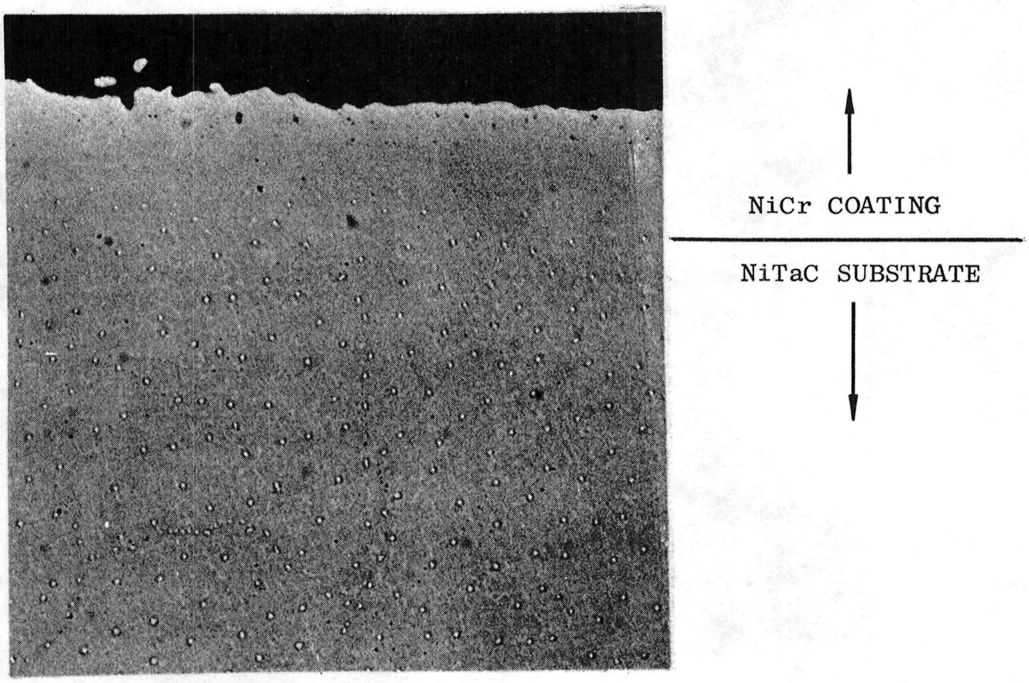
Based on the observations made so far, it was decided to delete three CVD coatings and continue with the three GE developed coating systems. Moreover, it became clear that AF 3116A (NiTaC) is no longer expected to be used in gas turbine airfoils primarily because of unacceptable transverse low cycle fatigue properties. NiTaC-14 has now been selected to replace AF 3116A.



2X

Figure 28

A NiCr coating on DBTT specimen of AF NiTaC. The coating sequence consisted of electroless Ni, a diffusion heat treatment 1065C (1950F) - 4 hrs. and slurry Cr (coating #2 in Table I).



500X Unetched

Figure 29

A NiCr coating deposited on NiTaC DBTT specimen. The deposition sequence consisted of electroless Ni, a diffusion heat treatment 1065C (1950F) - 4 hrs. and slurry Cr. This represents a successful attempt to coat a DBTT specimen with coating #2 in Table I.

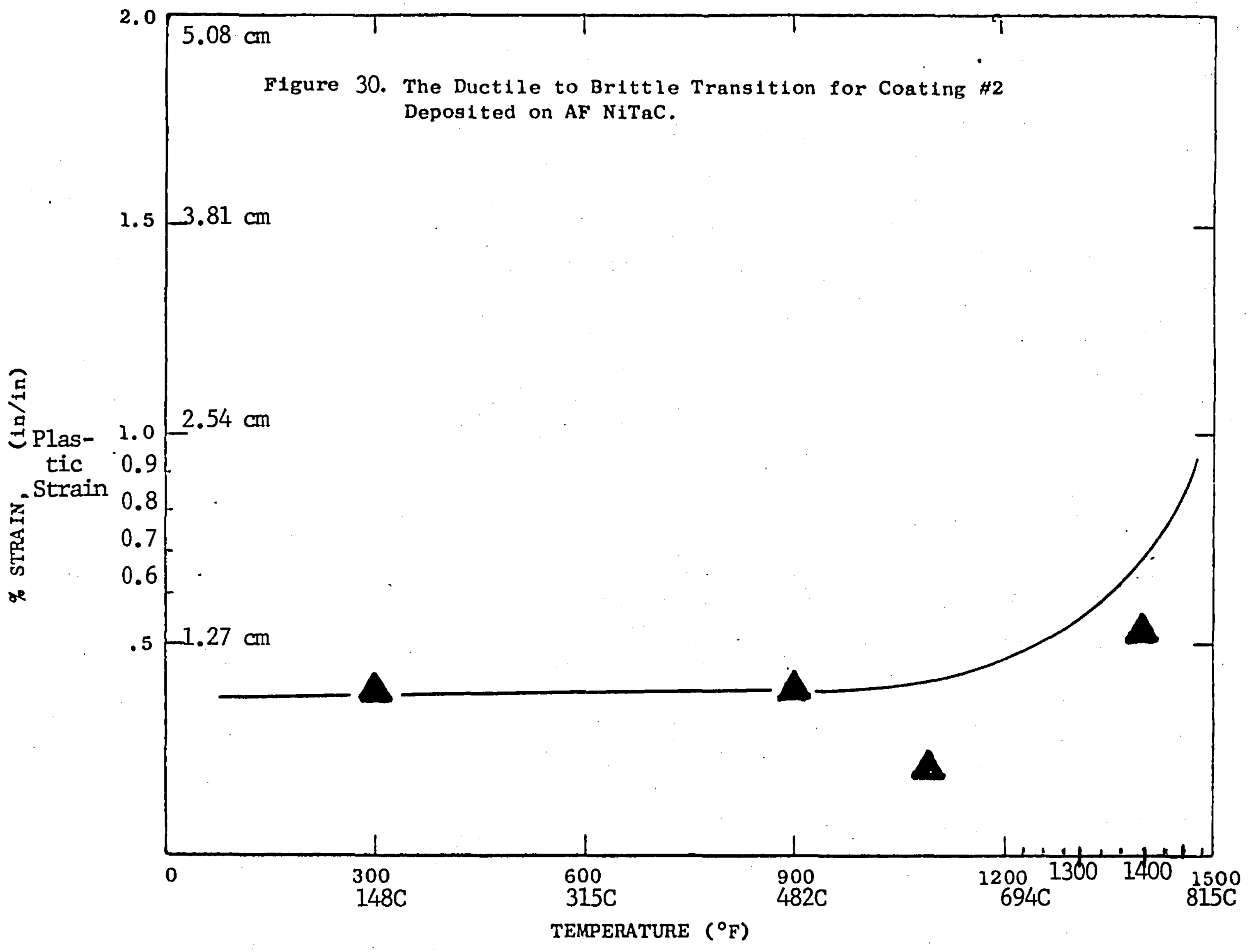


Figure 30. The Ductile to Brittle Transition for Coating #2 Deposited on AF NiTaC.

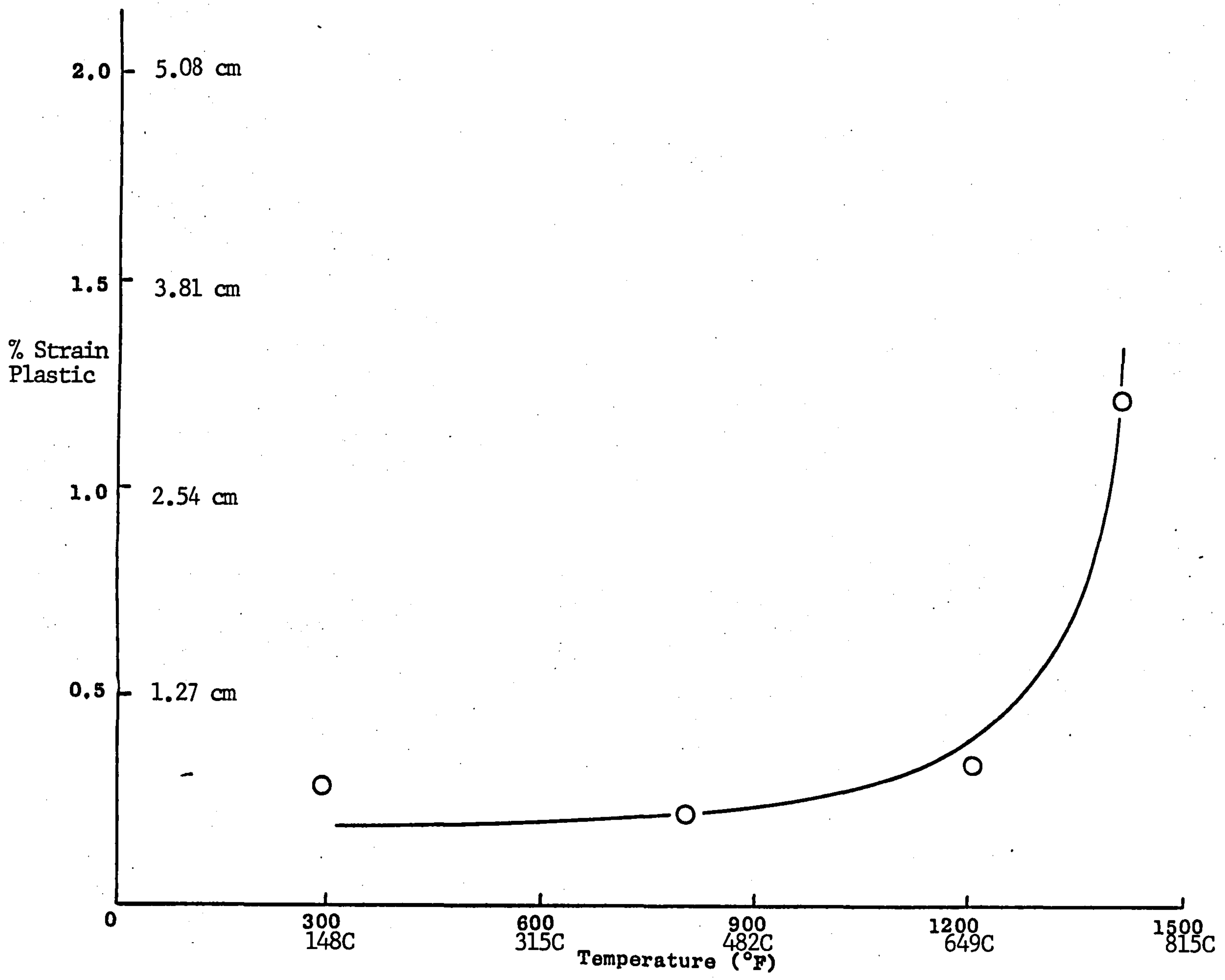


Figure 31 - **Ductile to Brittle Transition for Coating #4 Deposited on AF NiTaC**

It was also felt that, because of different coating behavior characteristics, it would be premature to initiate any effort at this time on NiTaC-14 until further alloy efforts are completed. As a result of these circumstances, the Contract NAS3-21038 was redirected to analyze, and report on the technical work generated so far in the program. The data provides base technology information which could be utilized by the commercial aviation industry now or in the future with other alloys and with other engines.

(7) DISCUSSION

Currently, the best opportunity for development of internal coatings exists in the well studied metallic coating compositions of the MCrAl (M = Ni, Co or Fe) type. The phase diagrams, oxidation and corrosion behavior of MCrAl type coatings have been well documented (8-10). In addition, substantial engine experience is available on these coatings applied externally to turbine parts, and the results to date have demonstrated superior oxidation and corrosion resistance.

The key feature which provides the excellent oxidation and corrosion resistance of MCrAl coatings is the ability to generate a dense, adherent Al_2O_3 protective scale. The function of Cr is to promote the activity of the Al in the MCrAl. It also improves the material ductility which is needed for application to advanced DS alloys. For internal coatings, because of the lower gas stream velocity, lower metal temperature and less thermal cycling effects, the NiCrAl system should be adequate for our engines.

Ductility of coatings is an important consideration since cracking of a coating at blade operating strains can lead to propagation of the cracks into the substrate. Internal coatings must have adequate ductility over the entire range of operating strains and temperatures, which may be as low as 750C (1400F) in some locations. For instance, at some internal surface locations of an advanced DS blade, a strain as high as 0.6% can be reached. In particular, DS eutectic blades have a lower longitudinal modulus than conventionally cast alloy blades under given stress conditions, and this will produce larger blade strains. The coatings, internal and external, must have a ductility that accomodates the higher strain, or it will crack and concentrate stresses for crack propagation into the DS blade alloy. For advanced engine applications, aluminide type coatings do not have sufficient ductility for all areas of DS eutectic blades, i.e., they crack with less than 0.3% strain at 750C (1400F) and this is considered to be quite inadequate. Moreover, there is additional room for the super-position of thermal strains on top of the mechanical strains. Figure 32 is a comparison of coating ductility of NiAl (Codep) and NiCrAl (EA) type coatings at various temperatures. The superior ductility of NiCrAl coating has been demonstrated in recent F101 engine tests.

Compositional compatibility of the internal coating with the substrate alloy is necessary since deleterious phases can be formed by interdiffusion of the coating and substrate elements. Examples of this are the single aluminide diffusional coatings which form small amounts of sigma intermetallic phases with standard nickel base superalloys (such as Rene' 80 and Rene' 125). With more advanced turbine blade materials, such as the AF NiTaC alloy, compatibility is even more important. Interdiffusion of coating elements with the substrate may cause dissolution of the aligned TAC structure resulting in loss of strength. Past experience has indicated that the NiCr or NiCrAl type coatings have the capability to meet the stated environmental requirement.

(8) CONCLUSIONS

(1) A process for internal coating of DS NiTaC aircooled blades has been identified. It is based on the use of electroless (Ni hydrazine process), slurry Cr and slurry Al. Parameters for thickness and composition control were also optimized.

(2) Chemical vapor deposition techniques for Cr and Ni did not prove satisfactory.

(3) Results of DBTT tests indicated that NiCrAl coating #4 (Ni-15Cr-20Al) performed best of six coatings investigated and met the minimum strain and transition temperature requirements, (min. 0.6% strain at 760°F (1400°F)).

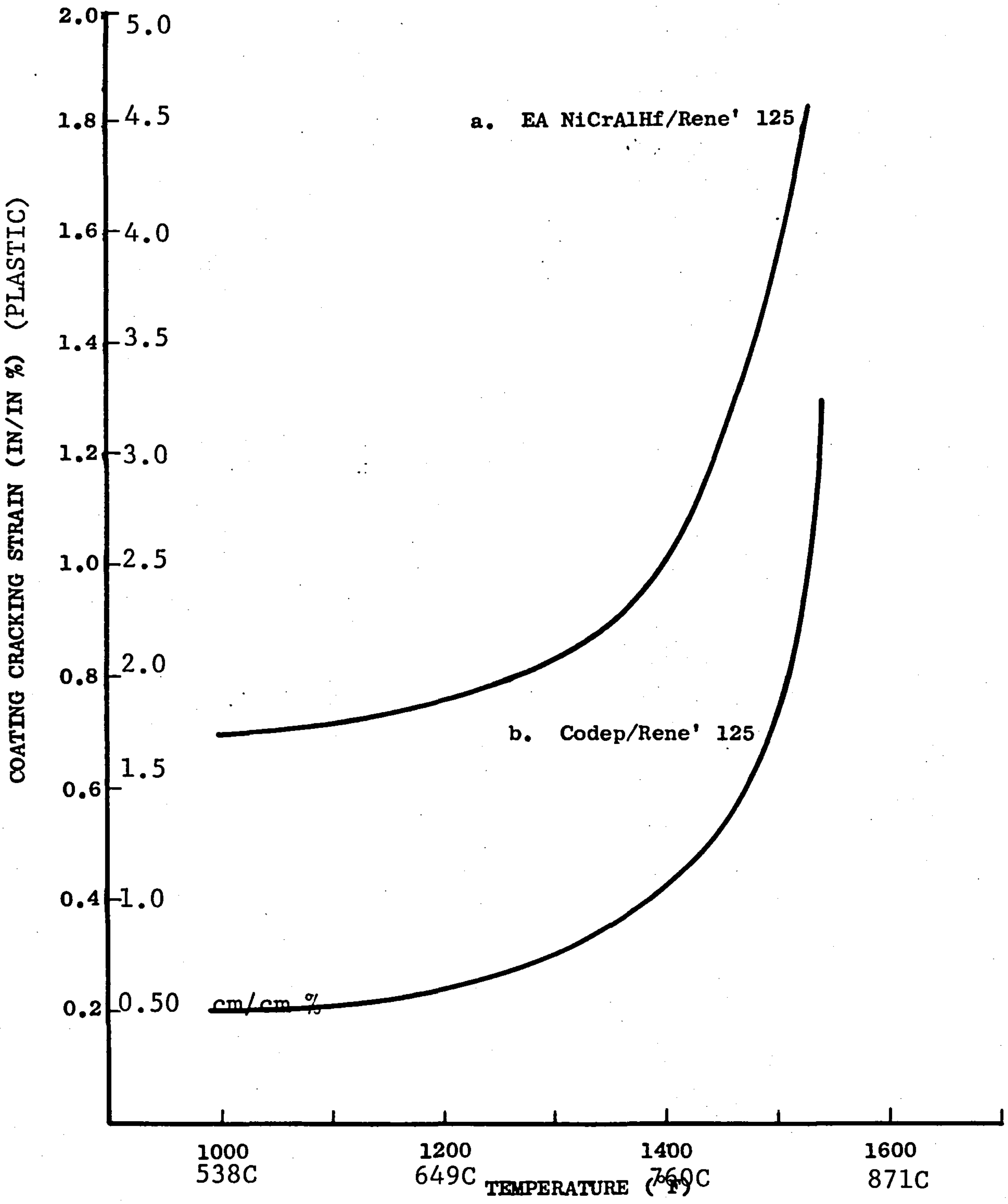


Figure 32 Coating Strain Capability as a Function of Temperature and Type of Coating System.

(9) REFERENCES

(1) Gorbunova, K. M. Ivanov M. V. & Moiseev, V.P. "Electroless Deposition of Nickel-Boron Alloys" J. Electrochem. Soc: Vol 120, 5 p. 613-618. May, 1973.

(2) Dini, J. R. & Coronado, P. R. "Thick Nickel Deposits of High Purity by Electroless Methods", Plating (54) p. 385, 1967.

(3) Levy, D. J. "Thin Nickel Films by Hydrazine Autocatalytic Reduction", Electrochemical Tech. (1) p. 38, 1963.

(4) Blocher, Jr., J.M. Hinterman, H.E. & Hall, L.H. Proc. Fifth Intern. Conf. on Chemical Vapor Deposition, Fulmer, England. Sept. 21-26, 1963.

(5) Rairden, J.R. & Jackson, M. R. "Coatings for DS Eutectics", NASA Cr-135050, 1976

(6) Powell, C.F., Oxley, J.H. & Blocher, Jr., J.M. "Vapor Deposition", John Wiley & Sons, New York, 1966

(7) Bazzarre, D. F. & Petriello, J. "Plating", Oct. 1970, pp. 1025-30

(8) Taylor, A. and Floyd, R. W. "The Constitution of Nickel-Rich Alloys of the Ni-CrAl System:, J. Inst. Metc. 80, 1952, p. 451

(9) Tumerarev, A. & Panyushin, L. "Izvestiaya Vysshkh Uchbnykh Zavedeniz Chernaya Metallurgiys", 9, 1959, p. 105

(10) Pettit, F. S. "The Oxidation Mechanism of Ni-Al Alloys at Temperatures Between 900 and 1300C" Trans AIME 239, 1967, p. 1296

DISTRIBUTION LIST

MR. G. C. DEUTSCH/RW
NASA HEADQUARTERS
600 INDEPENDENCE AVE
WASHINGTON, DC 20546

ADM. & TECH. SERVICES
MS 500-312
NASA LEWIS RESEARCH CTR
21000 BROOKPARK ROAD
CLEVELAND, OH 44135

MR. S.J. GRISAFFE
MS 49-1
NASA LEWIS RESEARCH CTR
21000 BROOKPARK ROAD
CLEVELAND, OH 44135

M&SD FILE
MS 49-1
NASA LEWIS RESEARCH CTR
21000 BROOKPARK ROAD
CLEVELAND, OH 44135

DR. S.R. LEVINE
M.S. 49-1
NASA LEWIS RESEARCH CTR
21000 BROOKPARK ROAD
CLEVELAND, OH 44135

LIBRARY
NASA
GODDARD SPACE FLIGHT CT
GREENBELT, MARYLAND 20771

MR. J. GANGLER/RWM
NASA HEADQUARTERS
600 INDEPENDENCE AVENUE
WASHINGTON, DC 20546

LIBRARY (2)
MS 60-3
NASA LEWIS RESEARCH CTR
21000 BROOKPARK ROAD
CLEVELAND, OH 44135

MR. J.P. MERUTKA (BAL)
MS 49-1
NASA LEWIS RESEARCH CTR
21000 BROOKPARK ROAD
CLEVELAND, OH 44135

MR. N.T. SAUNDERS
MS 301-4
NASA LEWIS RESEARCH CTR
21000 BROOKPARK ROAD
CLEVELAND, OH 44135

DR. D. POFERL
MS 500-202
NASA LEWIS RESEARCH CTR
21000 BROOKPARK ROAD
CLEVELAND, OH 44135

DR. J. BUCKLEY MS219
NASA
LANGLEY RESEARCH CTR.
LANGLEY FIELD,VA 23665

LIBRARY,ATTN: J. JENKINS
NASA FLIGHT RESEARCH CTR
P.O. BOX 273
EDWARDS, CALIFORNIA 93523

MR. L. HARRIS/RW
NASA HEADQUARTERS
600 INDEPENDENCE AVENUE
WASHINGTON, D.C. 20540

REPORT CONTROL OFFICE
MS 5-5
NASA LEWIS RESEARCH CTR
21000 BROOKPARK ROAD
CLEVELAND, OH 44135

DR. H.B. PROBST
MS 49-3
NASA LEWIS RESEARCH CTR
21000 BROOKPARK ROAD
CLEVELAND, OH 44135

MR. J. ZIEMIANSKI
MS 301-4
NASA LEWIS RESEARCH CTR
21000 BROOKPARK ROAD
CLEVELAND, OH 44135

LIBRARY/ACQUISITIONS
JET PROPULSION LAB.
4800 OAK GROVE DRIVE
PASADENA,CA 91103

NATIONAL TECHNICAL (2)
INFORMATION SERVICE
SPRINGFIELD, VA 22151

TECHNOLOGY UTILIZATION
MS 3-19
NASA LEWIS RESEARCH CTR
21000 BROOKPARK ROAD
CLEVELAND, OH 44135

MR. C.P. BLANKENSHIP
MS105-1
NASA LEWIS RESEARCH CTR
21000 BROOKPARK ROAD
CLEVELAND, OH 44135

LIBRARY M.S.185
NASA
LANGLEY RESEARCH CTR.
LANGLEY FIELD,VA 23365

TECHNICAL LIBRARY,CODE JM6
NASA
MANNED SPACE CRAFT CTR.
HOUSTON, TX 77058

DR. R.E. JAFFEE
E.P.R.I.
3412 HILLVIEW AVE.
PALO ALTO, CA 94304

MR.G.A. WACKER, CODE 2812
HEAD,METAL PHYSICS BRANCH
NAVAL SHIP R&D CTR.
ANNAPOLIS, MA
21402

MR.A.L.BALDI V.P. R&D
ALLOY SURFACES CO.INC.
100 S.JUSTISON ST.
WILMINGTON DE 19899

MR. D. CLINGMAN
GENERAL MOTORS CORP.
DETROIT DIESEL ALLISON
P.O. BOX 894-W5
INDIANAPOLIS,IN 46206

LIBRARY
NASA
MARSHALL SPACE FLIGHT
CENTER
HUNTSVILLE, ALABAMA 35812

DIRECTORATE, AMRDL
(SAVDL-EU-TAP)
ATTN: J. LANE
FT. EUSTIS, VA 23604

MR.W.R. FREEMAN
HOWMET CORPORATION
500 TERRACE PLAZA
699 BENSTON ROAD
WHITEHALL, MI 49461

MR. CHARLES AMMANN
TECH.DIR.,COATED PRODUCTS
CHROMALLOY R&T DIV.
BLAISDELL RD
ORANGEBURG, NJ 10962

DR. PAUL SIEMERS K1,4A21
GENERAL ELECTRIC CO
R & D CENTER
P.O. BOX 8
SCHENECTADY, N.Y. 12341

MR. C.J. SPENGLER
MET. ENGR., MAT.& MET.
WESTINGHOUSE ELEC. CORP
R & D CENTER
PITTSBURGH , PA 15235

MR. P. GOODWIN AIR-5203
NAVAL AIR SYSTEMS COMMAND
NAVY DEPARTMENT
WASHINGTON, D.C. 20360

LIBRARY
UNIVERSITY OF DAYTON
RESEARCH INSTITUTE
300 COLLEGE PARK AVE
DAYTON, OHIO 45409

DR.J. WURST
U.OF DAYTON RES.INST.
DAYTON, OH 45409

REPORTS ACQUISITION
AEROSPACE CORPORATION
P.O. BOX 92957
LOS ANGELES, CALIFORNIA
90009

MR. TCM ROSEBERRY
MATL.COAT. & TECH.SEC.
BATTELLE MEMORIAL INST.
505 KING STREET
COLUMBUS, OH 43201

MR.D. HANINK
ENGINEERING OPERATIONS
DETROIT DIESEL ALLISON
GENERAL MOTORS CORP.
INDIANAPOLIS,IN 46206

MR. A.R. STETSON
SOLAR TURBINES INT'L
2200 PACIFIC HWY.
P.O. BOX 80966
SAN DIEGO, CAL. 92138

MR. T.E. STRANGMAN
AIRESEARCH MFG. CO.
111 S. 34TH ST.
PHOENIX, AZ.
85034

TECHNICAL REPORTS LIBRARY
OAK RIDGE NATIONAL LAB.
OAK RIDGE, TENN. 37830

LIBRARY
RESEARCH & DELV. CENTER
GENERAL ELECTRIC COMPAN
P.O. BOX 8
SCHENECTADY, N.Y. 12301

UTC LIBRARY,M.DONNELLY
UNITED TECH. CORP
400 MAIN STREET
EAST HARTFORD CT 06108

E.R.BARRETT-T/M3417
MATERIALS TECHNOLOGY
TRW EQUIPMENT GROUP
23555 EUCLID AVENUE
CLEVELAND,OH 44117

DR. JOHN D. GADD
TRW INC-AECR
1400 N. CAMERON ST.
HARRISBURG, PA 17105

MR. J.W. GLATZ,MAT.ENGR.
EXPLOR. DEV. BRANCH
NAPTC R&D DIV.
NAVAL AIR PROP. TEST CTR.
TRENTON, N.J. 08628

LIBRARY
AVCO SYSTEMS DIVISION
201 LOWELL STREET
LOWELL, MASSACHUSETTS
01851

LIBRARY
PRATT & WHITNEY AIRCRAFT
UNITED TECH. CORP
WEST PALM BEACH, FLORIDA
33402

MR. N. GEYER
AFML/LLM
WRIGHT PATTERSON AFB.
OHIO 45433

DR. J. BERKOWITZ
ARTHUR D. LITTLE,INC.
20 ACORN PARK
CAMBRIDGE, MASSACHUSETTS
02140

DR. D.K. GUPTA
J BUILD. (MERL)
PRATT & WHITNEY AIRCRAF
400 MAIN STREET
EAST HARTFORD CONN 06108

DR. J. WERT
MATLS.ENGR.DEPT
BOX 1621 STATION B
VANDERBILT UNIVERSITY
NASHVILLE TENN 37235

MCIC
BATTELLE MEMORIAL INST.
505 KING AVENUE
COLUMBUS, OHIO 43201

MR. VERN ANDERSON
PWA GROUP
GOVERNMENT PROD. DIV.
P.O. BOX 2691
WEST PALM BEACH, FL 33402

MR. J.K. ELBAUM
ASML/LTM
WRIGHT-PATTERSON AFB.
OHIO 45433

MR.G. PERKINS
LOCKHEED PALO ALTO R.LAB.
DEPT.,52-31, B204
3251 HANOVER STREET
PALO ALTO,CA 94062

TECHNICAL REPORTS LIBRARY
DEPARTMENT OF ENERGY
WASHINGTON D.C. 20545

MR. I. MACHLIN
CODE AIR-52031B
DEPARTMENT OF THE NAVY
NAVAL AIR SYS. COMMAND
WASHINGTON DC 20361

MR. ROBERT BECK
MGR. MAT'LS ENGR.
TELEDYNE CAE
1330 LASKEY ROAD
TOLEDO, OH 43612

MR. A.R. CIUFFREDA
EXXON RESEARCH & ENG.CO.
P.O. BOX 101 02
FLORHAM PARK, NJ 07932

MR. M. GOLD
FOSSIL POWER GEN. DIV.
BABCOCK AND WILCOX CO.
20 S. VAN BUREN AVE.
BARBERTON, OH 44203

DR. M.A.H. HOWES
METALS DIVISION
ITT RESEARCH INST.
10 W. 35TH STREET
CHICAGO,IL 60616

MR. WILSON LEEMING
SUNDSTRAND AVIATION
4747 HARRISON
ROCKFORD, IL 61101

MR. J. MOGUL
DIR., MATL'S ENGR.
CURTISS-WRIGHT CORP.
1 PASSAIC ST.
WOOD RIDGE, NJ 07075

MR. P.S. GIUPTON
MONSANTO CO.
P.O. BOX 1311
TEXAS CITY, TX 77590

DR. D. J. MAYKUTH
BATTELLE LABS.
505 KING AVE.
COLUMBUS, OH 43201

MR. E.H. SCHMIDT
AIRESEARCH IND. DIV.
P.O. BOX 92992
LOS ANGELES, CA 90009

MR. D.E. LEVSTER
BABCOCK AND WILCOX CO.
BOX 1260
LYNCHBURGH, VA 24505

MR. H. DOFRING BLD 53-316
GAS TURBINE PROD. DIV.
GENERAL ELECTRIC CO.
SCHENECTADY, NY 12345

PROF. A.J. MCEVILY
METALLURGY DEPT. U-136
UNIVERSITY OF CONN.
STORRS, CT 06268

MR. P. J. VALDEZ
CHIEF MET. ENG.
SOLAR TURBINES INT'L.
P. O. BOX 80966
SAN DIEGO, CA 92138

MR. C.F. CHENG
SCIENCE APPLICATIONS INC.
1211 W. 22ND STREET
OAKBROOK, IL 60521

DR. J.A. FRIEDERICY 93031
AIRESEARCH MFG. CO.
2525 W. 190TH ST.
TORRANCE, CA 90509

MR. F.P. NITZ
ROCKETDYNE AC37
6633 CANOGA AVE.
CANOGA PARK, CA 91304

PROF. A.L. KAYE
PURDUE UNIV.
CALUMET CAMPUS
2233 171ST STREET
HAMMOND, IN 46323

MR. C.F. MUENCH (36802)
GENERAL ELECTRIC CO.
1000WESTERN AVE.
LYNN, MA 01910

MR. F.M. ANTHONY (B-81)
BELL AEROSPACE CO.
P.O. BOX ONE
BUFFALO, NY 14240

DR. JOHN H. GERSTLE
THE BOEING CO.
P.O. BOX 3707
SEATTLE, WA 98124

MR. J. NEWHART(PE62)
NAPTC
TRENTON, NJ
08628

MR. LESTER B. ENGEL JR.
CHIEF METALLURGIST
BROWN BOVERI TURBO. INC
711 ANDERSON AVE.
ST. CLOUD MN 56301

ACQUISITION DEPT. (25)
NASA S&T INFO. FACILITY
P.O. BOX 8757
BALT-WASH INT AIRPORT
MARYLAND 21240

METCO INC.
MR.D.C. COLTER MGR,SP.MKT
1101 PROSPECT AVE.
WESTBURY, L.I., NY
11590

PRATT AND WHITNEY AIRCRAFT
ATTN: D. SCOTT DUVALL
400 MAIN STREET
E. HARTFORD, CT 06108

MR. DONALD MCGRATH
MATERIALS ENGINEERING
AIRESEARCH MFG. CO.
2525 WEST 190 TH STREET
TORRENCE, CA 90509

MR. SYLVESTER LEE
AFML/LTM
WRIGHT-PATTERSON AFB
OH 45433

MR. ROBERT BECK
MAT. DEV.&MANUF. ENGR.
TELEDYNE CAE
1330 LASKEY RD.
TOLEDO, OH 43612

AIRESEARCH MFG. CO.
ATTN:DR. T.E. STRANGMAN
402 S. 36TH.
PHOENIX, AZ 85010

NASA
ATTN: LIBRARY
AMES RESEARCH CENTER
MOFFETT FIELD, CA 94035

UNITED TECHNOLOGIES, INC.
ATTN: MR. F. S. KEMP
POWER SYSTEMS DIVISION
SOUTH WINDSOR, CT 06074

MR. C. A. PRATT,JR.
AFML/MXE
WRIGHT-PATTERSON AFB
OH 45433

MR. MACHALA DRDTA-RGR
USA TARADOOM
PROP. SYS. DIVISION
WARREN, MI 48090

METCO, INC.-SUITE 809
ATTN: MARC F. LIPINSKI
21010 CENTER RIDGE RD
CLEVELAND, OH 44106

NASA
ATTN: MR. GENE CATALDO
GEO. C. MARSHALL SPC CT
MARSHAL SFC, AL 358121

MR. R.E. ENGDAHL, PRES.
DEPOSITS&COMPOSITES INC.
318 VICTORY DRIVE
HERNDON VA 22070

DR. DONALD H. BOONE
DEPT.MECH.ENGR.,CODE 69BL
NAVAL POSTGRADUATE SCHO
MONTEREY CA 93940

MR. MURRAY
ARMY RESEARCH OFFICE
PO BOX 12211
RESEARCH TRIANGLE PARK
NC 27709

ELECTRIC POWER REA INSTIT
ATTN: VANCE COOPER
P. O. BOX 10412
PALO ALTO, CA 94303

METCO INC.
DR. P.C. WOLF DIR.OF ENGR
1101 PROSPECT AVE.
WESTBURY, L.I., NY
11590

NAVAL SEA SYSTEMS COMMAND
ATTN: S.B. SHEPARD
CODE 5231
WASHINGTON, DC 20362

MR. B. GOLDBLATT
AVCO LYCOMING DIV.
550 S.MAIN STREET
STRATFORD, CT 06497

DR. G.W. GOWARD
PRATT & WHITNEY AIRCRAFT
UNITED TECH. CORP
400 MAIN STREET
EAST HARTFORD CONN 06108

MR. N.B. ELSNER,
MGR.,ADV.MAT'LS BR.
GENERAL ATOMIC CO.
P.O. BOX 81608
SAN DIEGO, CA 92138

DR. J. M. DAVIDSON
INT. NICKEL CO. INC.
STERLING FOREST
SEELEY W. MUDD BLUIDING
NEW YORK, NY 10027

DR. LOUIS DANIS
WILLIAMS RESEARCH CORP.
2280 WEST MAPLE ROAD
WALLED LAKE, MI
48088

MR. R. GREKILA
WESTINGHOUSE ELECTRIC
RESEARCH LABS
BEULAH RD.,CHURCHILL BLD
PITTSBURGH, PA 15235

PROF. R.A.RAPP
116 WEST 19TH AVE.
OHIO STATE UNIVERSITY
COLUMBUS, OH 43220

PROF. L.SEIGLE
DEPT. OF MAT'LS SCIENCE
STATE UNIV. OF NEW YORK
STONYBROOK, LI NY 11794

DR. EARL R. THOMPSON
MGR. MATERIAL SCIENCE
UNITED TECH. RES.LAB.
EAST HARTFORD CO. 06108

COMMANDING OFFICER
ARMY MAT.&MECH. RES. CTR.
ATTN:M. LEVY AMXMR-RM2
WATERTOWN,MA.02192

MR. R.F. KIRBY,SUPV.
MATERIALS ENGR.DEPT.93-39
AIRESEARCH COMPANY
111 S. 34TH STREET
PHOENIX,ARIZONA 85010

DR. R.C. TUCKER JR.
LINDE DIV.
UNION CARBIDE CORP.
1500 POLCO STREET
INDIANAPOLIS, IN 46224

PROF. H. HERMAN
DEPT. OF MAT'LS SCIENCE
STATE UNIV. OF NEW YORK
STONYBROOK, LI NY 11794

DR. R. BRATTON,MGR
CERAMIC SCIENCE
WESTINGHOUSE RES. LABS.
BEULAH ROAD
PITTSBURG, PA 15235

MR. G.J. WILE
POLYMET CORPORATION
1597 CHESTER ROAD
CINCINNATI, OH 45215

MR. G.R. SIPPEL
SECTION CHIEF -DEV. LAB.
D. D. ALLISON DIV. GMC
DEPT 5827-W8, PO BOX 894
INDIANAPOLIS, IN 46206

MR. R.STUEBER
CHROMALLOY R&T
BLAISPELL ROAD
ORANGEBURG NY 10901

DR. R.F. BUNSHAH
MATLS. DEPT.
6532 BOELTER HALL
U. OF CALIFORNIA
LOS ANGELES, CA 90024

DO NOT DETACH FROM REPORT
PLEASE LINE THROUGH YOUR NAME
BEFORE RETURNING TO THE LIBRARY

Name	Mail Stop
D. Carter	441

NASA Langley (May 1979) MSD-TLB N-7