AD-A032 554 SOLAR SAN DIEGO CALIF F/G 11/3
CONTROLLED COMPOSITION REACTION SINTERING PROCESS FOR PRODUCTIO--ETC(U)
AUG 76 W G STEVENS, A R STETSON F33615-75-C-5268
UNCLASSIFIED RDR-1802-6 AFML-TR-76-91 NL

1 OF 1
AD A032554

END
DATE
FILMED
1-77

AFML-TR-76-91

(12)
NW

CONTROLLED COMPOSITION REACTION SINTERING PROCESS FOR PRODUCTION OF MCrAlY COATINGS

SOLAR DIVISION OF INTERNATIONAL HARVESTER COMPANY
SAN DIEGO, CALIFORNIA 92138

August 1976

TECHNICAL REPORT AFML-TR-76-91
FINAL REPORT FOR PERIOD 11 JULY 1975 - 15 DECEMBER 1975

Approved for public release; distribution unlimited.

D D C
RECEIVED
NOV 26 1976
B

AIR FORCE MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio 45433

NOTICE

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

This technical report has been reviewed and is approved.

J. Jay Crosby
J. JAY CROSBY
Project Engineer

Norman M. Geyer
NORMAN M. GEYER
Technical Manager for High Temperature Materials Processing and High Temperature Materials Branch
Metals and Ceramics Division

FOR THE COMMANDER

Norman M Tallan
NORMAN M. TALLAN
Acting Chief, Processing and High Temperature Materials Branch
Metals and Ceramics Division
Air Force Materials Laboratory

AIR FORCE - 16 NOVEMBER 76 - 200

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

⑲ REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ⑱ AFML-TR-76-91	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER ⑨
4. TITLE (and Subtitle) ⑥ CONTROLLED COMPOSITION REACTION SINTERING PROCESS FOR PRODUCTION OF MCrAlY COATINGS. (letter)		5. TYPE OF REPORT & PERIOD COVERED Final Report, 11 July [illegible]-15 Dec. [illegible]75, 6. PERFORMING ORG. REPORT NUMBER RDR 1802-6
7. AUTHOR(s) ⑩ W. G. Stevens and A. R. Stetson		8. CONTRACT OR GRANT NUMBER(s) ⑮ F33615-75-C-5268
9. PERFORMING ORGANIZATION NAME AND ADDRESS Solar Division of International Harvester Company 2200 Pacific Highway, P. O. Box 80966 San Diego, California 92138		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 62102F 73120139
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Materials Laboratory Air Force Systems Command Wright-Patterson Air Force Base, Ohio 45433		12. REPORT DATE ⑪ Aug[illegible]t [illegible]76 13. NUMBER OF PAGES 48
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) ⑭ RDR-1802-6		15. SECURITY CLASS. (of this report) UNCLASSIFIED 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		⑫ 60p.
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) ⑯ 7312 ⑰ 01		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Superalloy Coatings Fluidized Beds Hot Corrosion		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The feasibility of the fluidized bed-controlled composition reaction sintering process for depositing sulfidation resistant and ductile CoNiCrAlY coatings on simple blade shapes of nickel-based superalloys has been demonstrated. Critical process parameters of all steps in the process have been identified. Methods were developed for adjusting the coating composition to emphasize either the chemical or mechanical properties of these coatings.		

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

326550

1B

PREFACE

The work described herein was performed by the Solar Division of International Harvester Company Research Laboratory, San Diego, California under sponsorship of the Air Force Materials Laboratory under Contract Number F33615-75-C-5268, Project Number 7312.

This report covers the period of work from 11 July to 15 December 1975. Mr. A. R. Stetson was Program Director and Dr. W. G. Stevens was the Principal Investigator. Mr. Jesse J. Crosby, AFML/LLM, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio was Technical Manager for the Air Force.

We wish to recognize Mr. Harold Cook, Research Engineer, for his contributions to the program. He was responsible for fluidized bed operation and modification and for the majority of coating and testing activity.

TABLE OF CONTENTS

Section Page

I INTRODUCTION 1

1. Background 1
2. Objective 1
3. Process Feasibility 2
4. Coating/Process Development 3
5. Coating Process Evaluation 3
6. Scale-up and Cost Analysis 4

II EXPERIMENTAL 5

A. MATERIALS 5

1. Bonding Resins 5
2. Modifier Metal Powders 5
3. Alloy 6
4. Aluminizing Pack Materials 7
5. Miscellaneous Materials 7

B. PROCESSES 8

1. Precleaning 8
2. Bonding Resin Application 8
3. Modifier Application 11
4. Aluminizing 12
5. Post Coating Heat Treatments 15

C. DIAGNOSTIC TESTS 16

1. Oxidation 16
2. Sulfidation 16
3. Bend Ductility 17
4. Coating Composition 17

III RESULTS AND DISCUSSION 19

A. PRECLEANING PROCEDURE 19
B. BONDING RESIN SELECTION AND MODIFIER APPLICATION 20

TABLE OF CONTENTS (Cont.)

Section Page

1. Duplex Process 20
2. Single Cycle Process 24
3. Slurry-Spray Process 28

C. MODIFIER SELECTION AND ALUMINUM DEPOSITION CONDITIONS 28

1. Modifiers 30
2. Aluminizing Packs 33

IV CONCLUSIONS 41

V RECOMMENDATIONS 42

VI REFERENCES 43

APPENDIX - Results of Furnace Oxidation and Sulfidation Testing of the CCRS CoCrAlY and CoNiCrAlY Coating 44

LIST OF ILLUSTRATIONS

Figure		Page
1	Single cycle fluidized bed application of the MCrY modifier	xi
2	Line sight limitation of PVD process	2
3	Inconel 713C alloy turbine blade used for coating development work	6
4	Fluidized bed coating facility	9
5	Porous diffuser for fluidized bed	10
6	Schematic of fluidized bed coating process	12
7	Aluminum-cobalt phase system	14
8	Temperature time profile of slow heat aluminizing process	15
9	Specimen appearance after furnace and crucible sulfidation	17
10	Bend transition temperature test setup	18
11	Etched appearance of IN-713C	19
12	Infra-spectrum of surfactant washed from the U. S. I. Microthene FN-500 and FE-532 powders	21
13	Polyethylene coating on IN-713C	23
14	Polyethylene bonded CoCrY alloy powder coating on IN-713C duplex process	23
15	Bonding problem with duplex process for applying CCRS modifier	24
16	Effect of modifier resin content on coating porosity and thickness	26
17	Mechanism of porosity formation	27
18	CoNiCrAlY coating deposited by single cycle CCRS process	29
19	Typical sprayed-slurry of Co-20Ni-15Cr coating (added as elemental powders) on IN-713C	30
20	MCrY modifier composition calculated from CCRS MCrAlY coating analyses	31
21	Surface roughness of CCRS MCrAlY coatings	32

LIST OF ILLUSTRATIONS (Cont.)

Figure		Page
22	Aluminum content of CCRS coating as function of pack and modifier chemistry at 1038°C	32
23	Failure lifetimes of CCRS coatings in crucible sulfidation test at 955°C	34
24	Aluminum deposition as function of time for Co-20Ni-25Cr-0.5Y coated substrates	37
25	Aluminum deposition as function of aluminum pack composition for Co-20Ni-25Cr-0.5Y coated substrates	38
26	Al-Co-Ni phase diagram	39
27	Furnace oxidation behavior of CCRS coatings	46
28	Furnace sulfidation behavior of CCRS coatings	47
29	CCRS CoCrAlY coating after 72 hours at 1093°C in air	48
30	CCRS CoCrAlY coating after 72 hours furance sulfidation at 937°C	48

LIST OF TABLES

Table		Page
1	Bonding Resins for CCRS Coatings	5
2	Modifier Metal Powders for CCRS Coatings	6
3	Materials Used in Aluminizing Packs and Slurry	7
4	Miscellaneous Materials	7
5	Etchants for IN-713C Coating Substrates	8
6	Operating Parameters for Fluidizing Bonding Resins	10
7	Operating Parameters of Fluidized Modifier Beds	13
8	Prototype Aluminizing Pack Compositions	13
9	MCrY Deposition Reproducibility as Function of MCrY Fluidized Bed Temperature	22
10	Co-20Ni-25Cr-0.5Y Deposition on IN-713 Blade Section by Single Cycle Fluidized Bed Process	28
11	Aluminum Content as Function of Nickel Content of the Modifier and Pack Aluminum Activity	33
12	Crucible Sulfidation Lifetime Data for CCRS MCrAlY Coatings	35
13	Conditioned Aluminizing Pack Compositions	36
14	Aluminum Deposition on Co-20Ni-25Cr-0.5Y Coated IN-713C Specimens as a Function of Time and Pack Activity	37
15	Hardness and Bend Ductility of CCRS MCrAlY Coatings	40

UNIT CONVERSION

This report is presented in SI units only. Common conversions to English units are presented below:

Modern Metric (SI)	English
204° C	400° F
230° C	450° F
537° C	1000° F
815° C	1500° F
927° C	1700° F
955° C	1750° F
983° C	1800° F
1038° C	1900° F
1093° C	2000° F
1149° C	2100° F
133 mm	5.25 inch
197 mm	7.75 inch
1 Kg	2.2 lbs.
2.26 m^3/hr	80 cu ft/hr

SUMMARY

The feasibility of the controlled composition reaction sintering process for producing MCrAlY (M is Co and/or Ni) coatings on nickel-base superalloys was demonstrated. The single-cycle fluidized bed application of the prealloyed modifier to simple blade shapes was also demonstrated. These two accomplishments constitute a successful completion of Task I of the program.

The critical process parameters identified in the single-cycle fluidized bed application, shown schematically in Figure 1, of the prealloyed modifier are:

- Uniformity of modifier particle size
- Minimum part preheat temperature of 204° C
- Bed immersion time of 1 to 2 seconds
- Bisque hardening at 204° C
- At least 4 weight percent resin (polymethyl methacrylate) deposited on modifier particles required to minimize coating porosity.

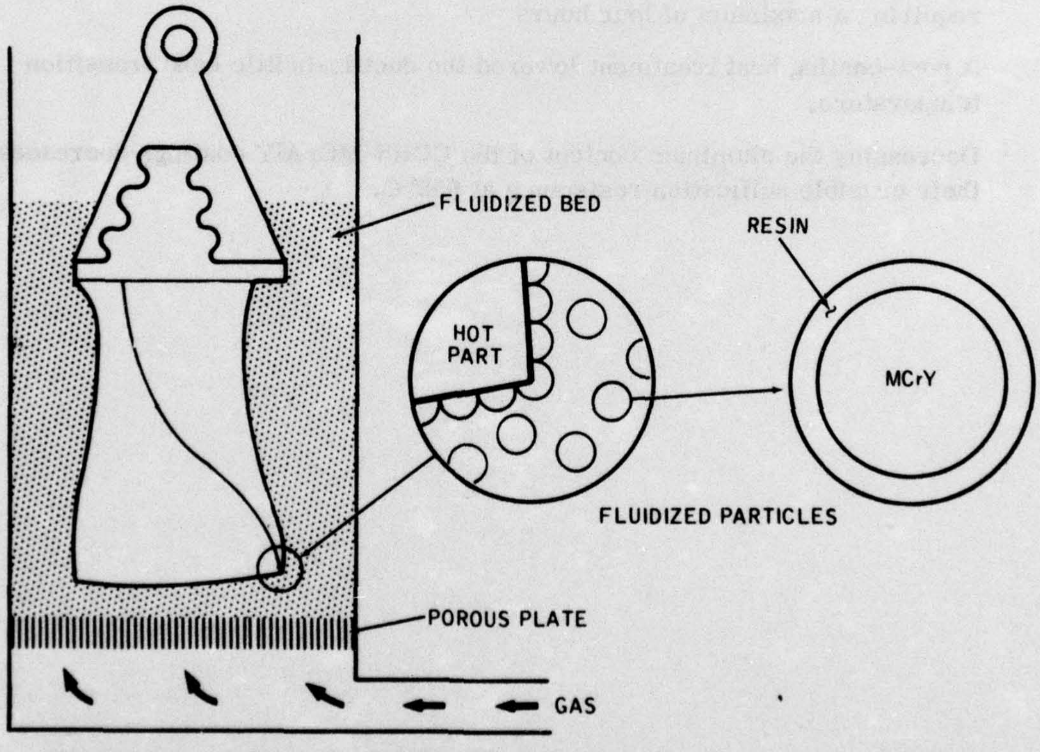


Figure 1. Single cycle fluidized bed application of the MCrY modifier.

The required properties of the modifier to produce controlled composition reaction sintered MCrAlY coatings are:

- Prealloyed as opposed to elemental powders
- Atomized powders of $< 37 \mu m$ particle diameter (Surface finish of the coating is governed by modifier particle size.)
- Co-20Ni-25Cr-0.5Y as opposed to Co-25Cr-0.5Y

The critical process parameters involved in the reaction sintering process were identified as:

- Aluminum deposition at a minimum temperature of 1037° C to ensure metallurgical bonding of the coating to the substrate
- A slow pack heat-up rate to allow depolymerization of bonding resin
- An aluminizing pack composition of 16Co-5Cr-4Al-Balance Al_2O_3 for the Co-20Ni-25Cr-0.5Y modifier.

Diagnostic testing of the CCRS-MCrAlY coatings identified the following effects:

- The controlled composition reaction sintering process is relatively rapid requiring a maximum of four hours
- A post-coating heat treatment lowered the ductile-brittle bend transition temperature.
- Decreasing the aluminum content of the CCRS-MCrAlY coatings decreases their crucible sulfidation resistance at 955° C.

INTRODUCTION

1. Background

Advanced gas turbine engines require higher turbine inlet temperatures to produce greater thrust and greater fuel efficiency. These turbine engine components require coatings that significantly increase their resistance to oxidation and hot corrosion without compromising their strength or ductility. The dual requirements of oxidation-corrosion resistance and high temperature strength and ductility places serious restraints on permissible coating base-metal interaction and dictates the use of a highly compatible protective coating. Recent studies(1, 2) have shown that the MCrAlY coatings applied by physical vapor deposition, PVD, are effective in protecting a variety of advanced nickel and cobalt-base superalloys, directionally solidified alloys, and oxide dispersion strengthened alloys over a range of critical environmental conditions while retaining substrate mechanical properties.

Although the PVD-MCrAlY coatings have mitigated many of the high temperature corrosion problems associated with gas turbine materials, the PVD deposition process has a severe limitation. This limitation is illustrated by the diagram in Figure 2. The multivane segment has to have extensive manipulation (rotation in the figure) to ensure even coating of its outer surfaces because the deposition thickness is proportional to the cosine of the angle between the line-of-sight to the vapor source and the surface normal. Any shadowed surface will receive a thinner coating due to the inability to make this angle small and internal air cooling passages are left with virtually no coating in the PVD process.

2. Objective

The objective of this program is the development of the controlled composition reaction sintering, CCRS, process for depositing MCrAlY coatings. This process has been described in detail(3, 4) and is summarized briefly in the following steps:

- Precleaning
- Application of the particulate modifier MCrY
- Reaction sintering in a controlled activity aluminizing pack.

The latter step produces interparticulate growth, coating densification and metallurgical bonding of the coating to the substrate. The vapor phase deposition of aluminum may also partially aluminize air cooling passages as well as react with the modifier powder to produce the MCrAlY coating.

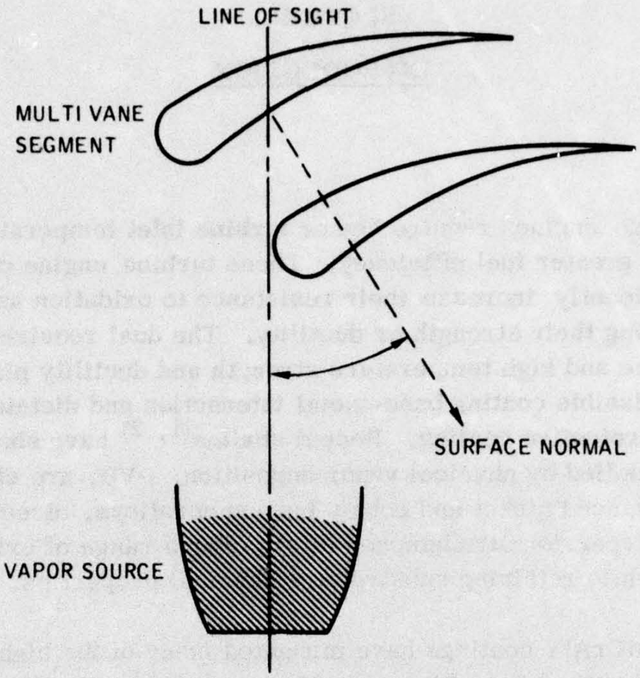


Figure 2. Line sight limitation of PVD process.

When fully developed, the CCRS process will offer the prospect of coating complex configured parts. The process is inherently favorable to scale-up, will require low cost facilities and offer significant cost reductions relative to the present physical vapor deposition processes. This program is divided into the following four tasks: (1) process feasibility; (2) coating/process development; (3) coating/process evaluation; and (4) scale-up and cost analysis.

3. Process Feasibility

The major effort in Task I was demonstrating that the CCRS coating process can be uniformly applied to simple turbine blade shapes. The process variables investigated were: techniques for uniform application of the modifier to blade shapes; modifier composition and use of elemental versus prealloyed powders; modifier particle size; activity of aluminizing packs; and thermal treatments needed to obtain low aluminum content ductile MCrAlY coatings.

Fluidized bed application of the modifier metal powders was the principal technique investigated. Processing variables included cleaning procedures, preheat temperatures, bonding resin type, bonding resin coating thickness, need for resin glazing, metal modifier bed fluidizing conditions and the need for post-coating bisque hardening.

This is a final summary report on Task I and covers all the activities from July 11 to December 15, 1975. Details are presented on the fluidized bed and slurry-spray processes for applying the modifier powders as well as CCRS process for producing CoCrAlY and CoNiCrAlY coatings on a nickel-base superalloy, IN-713C. A description of the performance tests (furnace oxidation and sulfidation, crucible sulfidation, bend ductility and surface finish) and diagnostic tests used to characterize these coatings and the results therefrom are also included. These data clearly demonstrate the feasibility of the combined fluidized bed-CCRS processes for depositing MCrAlY coatings on simple blade shapes. The goals of Task I have thus been met. The remainder of this program will be directed toward successful completion of the Tasks II, III and IV which are described in the following sections.

4. Coating/Process Development

The results of Task I have shown that the single-cycle fluidized bed method of modifier application is the preferred modifier application technique. In Task II this method combined with the CCRS process will be employed to apply the (Co-20Ni-25Cr-0.5Y) 12-17Al coating to the alloy, IN-100. Adjustments to the process (modifier composition and pack deposition conditions) will be made to produce a CoNiCrAlY coating whose performance is independent of the substrate alloy.

Further development of this coating process will involve changing the compositions to improve the oxidation and hot corrosion resistance or thermal expansion properties of the coating. Diganostic evaluation of these CCRS-CoNiCrAlY coatings will be used to verify the attainment of the desired composition and the effect of the compositional changes on coating morphology, grain size, oxide content, microcracking, internal oxidation, ductility and other critical coating characteristics. It will also be demonstrated that the CCRS process for producing CoNiCrAlY can be applied to single blades and assembled vane segments which cannot be uniformly coated by the electron beam-physical vapor deposition process (EB-PVD).

5. Coating Process Evaluation

In Task III the performance of the CCRS processed specimens will be evaluated; also, specimens of MA-754 (an oxide dispersion strengthened nickel-base alloy) will be coated. The testing program will compare the performance of EB-PVD (Co-25Cr-12.5Al-0.5Y) and CCRS coated specimens on IN-100. The program will include hot corrosion burner rig, oxidation-erosion, stress rupture, low-cycle fatigue and impact testing. The results of this testing program will demonstrate the effectiveness of the CCRS process in providing oxidation and corrosion resistance at least equivalent to EB-PVD coatings without loss in mechanical properties.

6. Scale-up and Cost Analysis

The final task of this program shall be the preparation of a production plan for applying the CCRS-(Co-20Ni-25Cr-0.5Y) 12-17Al coating to gas turbine components. This plan will include a survey of the capital equipment, labor, energy, and material required for production level coating of both new and used turbine blades and vanes. A survey of equipment manufacturers will be made to determine the cost and availability of suitable facilities for producing these coatings.

SECTION II

EXPERIMENTAL

Experimental effort was concentrated on Task I, Process Feasibility, whose dual goal was the demonstration of the feasibility of the fluidized bed coating and controlled composition reaction sintering processes for producing MCrAlY coatings. The following subsections provide the details of the materials and processes employed in producing these coatings.

A. MATERIALS

1. Bonding Resins

Four bonding resins (polyethylene, polymethylmethacrylate, polyvinyl acetate and ethyl-cellulose) were investigated in this program. Polyethylene, polymethylmethacrylate and polyvinyl acetate are linear, non-aromatic thermoplastic polymers, which depolymerize with minimal char formation(5). Ethyl-cellulose is also a linear polymer which was used as the binder in the metal slurries investigated. The critical properties of these bonding resins are listed in Table 1.

TABLE 1. BONDING RESINS FOR CCRS COATINGS

Resin Type	Trade Name and Manufacture	Particle Size	Characteristic Shape	Glass Transition Temperature (Ref. 5)	Decomposition Temperature (Ref. 5)
Polyethylene	High Molecular Weight - 1222 Allied Chemical	74μm	Blocky	-18° C	450° C
Polyethylene	*Microthene FN-500* U.S.I. Chemicals	*<20μm*	*Spherical*	-18° C	450° C
Polymethylmethacrylate	Elvacite 2008 E. I. DuPont	<149μm	Spherical	121° C	350° C
Polyvinyl Acetate	Microthene FE-532 U.S.I. Chemicals	30-40μm	Spherical	-	-
Ethyl-Cellulose	N-22 Hercules Powder Company	-	-	200-210° C*	-

*Melting Range

2. Modifier Metal Powders

Two modifier compositions were investigated in this program:

1. M1 Co-25Cr-0.5 to 0.7Y
2. M2 Co-20Ni-25Cr-0.5 to 0.7Y

These compositions were prepared in various particle size ranges from the alloys and elements listed in Table 2.

TABLE 2. MODIFIER METAL POWDERS FOR CCRS COATINGS

Alloy or Element	Manufacture	Analysis	Particle Size
CoCrY	Alloy Metals	Co-25.99Cr-0.59Y-0.23Fe	9 w/o >105μm, 43 w/o 105-44μm, 20 w/o 44-37μm, 28 w/o <37μm
CoNiCrY	Alloy Metals	Co-19.33Ni-24.8Cr-0.54Y	16 w/o >105μm, 41 w/o 105-44μm, 20 w/o 44-37μm, 23 w/o <37μm
Cobalt	African Metals	Co-0.32Ni-0.08Fe-0.09Ca-0.06Si-0.022Mn-0.022C-0.015S-0.01Cu	1.4 w/o >62μm, 1 w/o 62-44μm, 2.9 w/o 44-37μm, 94.7 <37μm
Nickel	Glidden Metals	99.59Ni+Co-0.005C	3.7 w/o >44μm, 96.3 w/o <44μm
Chromium	Alcan	99⁺Cr	<149μm
Cobalt-Yttrium	Alloy Metals	Co-75Y	Ingot

3. Alloy

All the CCRS coatings studied in Task I of this program were deposited on IN-713C alloy. The nominal composition of the alloy is:

Ni-13Cr-6Al-4.5Mo-2.3Cb-0.7Ti-0.1C-0.05Zr-0.012B.

This alloy was obtained from surplus third-stage turbine blades from Solar's Saturn and Centaur gas turbine engines. Figure 3 shows such a blade cut to provide coating development test specimens.

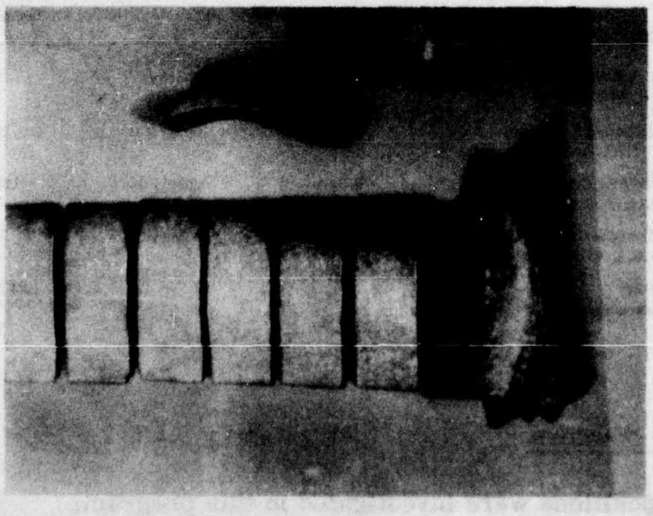


Figure 3. Inconel 713C alloy turbine blade used for coating development work.

4. Aluminizing Pack Materials

Six different aluminizing packs were used in the investigation of the CCRS process for producing MCrAlY coatings. These packs were prepared from the materials listed in Table 3.

TABLE 3. MATERIALS USED IN ALUMINIZING PACKS AND SLURRY

Material	Manufacturer	Analysis - Trade Name	Particle Characteristics
Cobalt	African Metals	Co-0.32Ni-0.08Fe-0.08Ca-0.06Si-0.022Mn-0.022C-0.015S-0.01Cu	1.4 w/o >62μm, 1 w/o 62-44μm, 2.9 w/o 44-37μm, 94.7 w/o <37μm
Nickel	Glidden Metals	99.59 Ni+Co-0.005C, AN-325	3.7 w/o >44μm, 96.3 w/o <44μm
Chromium	Alcan	99+, MD 101	<149μm
	Union Carbide	Cr-0.23Fe-0.04N-0.03Al-0.035-0.01C-0.01Si-0.006P	--
Aluminum	Alcoa	201	--
Aluminum Oxide	Alcoa	Al	--
	Norton	E1	105μm, blocky
Ammonium Chloride	J. T. Baker	"Analyzed Reagent" 5-0660	Granular

5. Miscellaneous Materials

The various other materials used in the investigation of the CCRS process for producing MCrAlY coatings are listed in Table 4.

TABLE 4. MISCELLANEOUS MATERIALS

Material	Manufacturer	Grade
Acetone	MCB	Reagent AX120
Methanol	MCB	Reagent MX485
Xylene	MCB	Reagent XX55
48% Hydrofluoric Acid	MCB	Reagent HX620
Concentrated Hydrochloric Acid	MCB	Reagent HX603
30% Hydrogen Peroxide	MCB	Reagent HX635
Chloroform	MCB	Reagent CX1055
1,1,1 Trichloroethane	MCB	Tech TX1075
Sodium Sulfate	J. T. Baker	Anhydrous Granular, Analyzed Reagent
Sodium Chloride	J. T. Baker	Crystal, Analyzed Reagent
Al_2O_3 Crucibles	Degussa-Ventron	A1-23
Inconel Sheet Stock	Ducommun Metals	IN-600

B. PROCESSES

Numerous processes were investigated during the course of this program. They are described in the following subsections and tables. The applicability of each of these processes to the production of MCrAlY coatings will be clarified in the Results and Discussion section (Sec. III).

1. Precleaning

The precleaning process employed in this program consisted of the following steps:

- Degrease
- Etch
- Rinse.

Degreasing agents consisted of either chloroform or 1,1,1 trichloroethane. After the parts were degreased and air dried, they were etched using one of the two etchants listed in Table 5 for fifteen minutes. Then the parts were rinsed in distilled water, rinsed in acetone, air dried and weighed.

TABLE 5. ETCHANTS FOR IN-713C COATING SUBSTRATES

	Composition (w/o)			
Etch Number	HCl	HF	H_2O_2	H_2O
1	3.5-3.6	2.2	2-2.3	Balance
2	13.5-14.0	1-1.1	3.5-4.8	Balance

2. Bonding Resin Application

Several processes for applying the bonding resin to the precleaned parts and modifier metal powders were investigated. A fluidized bed process was used to apply the bonding resins, listed in Table 1, to the simple blade shapes shown in Figure 3 while spray drying and solvent precipitation processes were employed to coat the modifier metal powders with the bonding resin. In several experiments a slurry of the modifier metal powder was sprayed directly into the precleaned substrate. The details of all these processes are discussed in the following paragraphs.

Parts, precleaned and weighed, were coated with the polyethylene; polymethylmethacrylate (PMMA) or polyvinyl acetate (Table 1) bonding resins by a fluidized bed technique. This technique, referred to in Figure 1, consisted of heating the part to 204 to 230° C and then dipping it into a fluidized bed of the bonding resin for one to two seconds. Figures 4 and 5 show the assembled fluidized bed and the details of the gas diffuser. The operating parameters of the resin fluidized bed (bed on left in Fig. 4) are presented in Table 6.

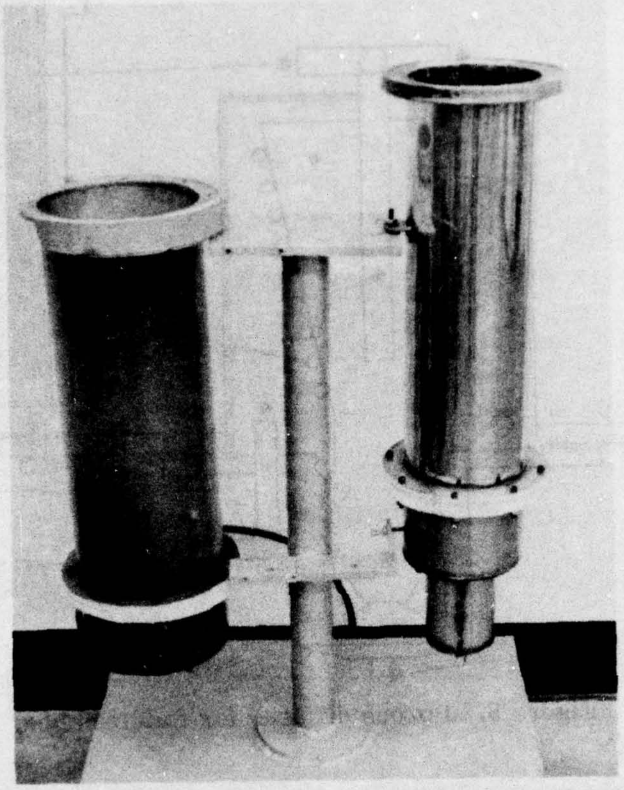


Figure 4. Fluidized bed coating facility.

Powders of the metal modifiers were coated with PMMA by a spray drying process and also by a solvent precipitation process. In the spraying process a slurry of the metal modifier in an acetone solution of PMMA was sprayed through a TGA-502 series DeVilbiss spray gun. The powder was collected and passed through a 200-mesh screen to remove the large particles. The ratio of weights of PMMA and metal powder adjusted to control the amount of polymer deposition.

In the solvent precipitation process for coating the modifier powders with PMMA, a slurry of the modifier powder and an acetone solution of PMMA was also employed. The process consisted of pouring this slurry into a "Waring blender". A quantity of distilled water or methanol was then added to precipitate the resin. Both of these

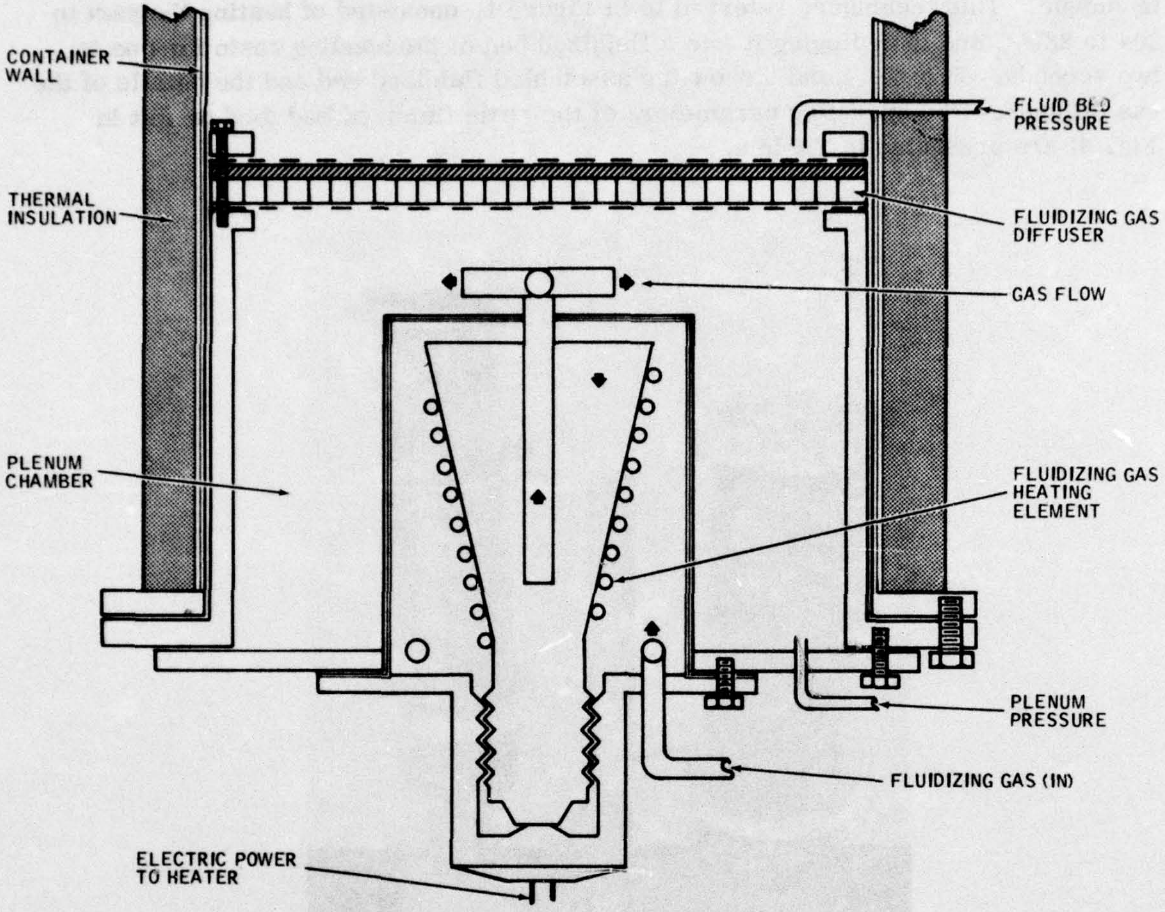


Figure 5. Porous diffuser for fluidized bed.

TABLE 6. OPERATING PARAMETERS FOR FLUIDIZING BONDING RESINS

Bed Diameter:	**197 mm**
Bonding Resin Charge:	**1 Kg**
Air Flow:	**2.26 m^3/hr**
Bed Depth:	**133 mm**
Bed Solids Fraction:	**0.41 (Ref. 6)**
Diffuser Pore Diameter:	**10 μm**

liquids are non-solvents for PMMA. The partitioning of the acetone into the water or methanol causes the precipitation of the PMMA on the metal particles. As in the spray drying process, the ratio of the weights of PMMA to metal is adjusted to control the amount of polymer deposited. After drying, this powder was separated on 200 or finer mesh sieves to remove the agglomerates and large particles.

The amount of PMMA deposited on the metal powders by the above procedures was determined by the following process. A weighed sample of the PMMA coated metal was stirred in an aliquot of hot acetone and poured through a tared filter having pores of 4 to 5.5 μm. After several additional rinses with hot acetone, the filter and washed metal were dried and reweighed. The amount of PMMA was calculated from the difference in weights of the coated and washed powder.

3. Modifier Application

Three processes were used to apply the modifier metal powders to the IN-713C substrates and were investigated in Task I of this program. Two of them involved fluidized beds and one employed a slurry-spray technique. The details of each of these processes for applying the modifier powders are described in the following subsection.

Fluidized beds of both PMMA coated and uncoated modifier metal powders were investigated in the demonstration of the feasibility of the CCRS process for producing MCrAlY coatings. A duplex (two-step) process, illustrated in Figure 6, involving a fluidized bed of the bonding resin and a heated bed of the modifier powder was investigated. This process involves reheating the bonding resin coated substrate to 204-230° C to soften the resin and render it tacky. This tacky, resin coated substrate was then dipped into a heated 149° C fluidized bed of modifier metal powder for 2 to 3 seconds.

Another fluidized bed technique, single-cycle, was also investigated. In this process (Fig. 1) a precleaned and weighed substrate was heated to 204-230° C and was dipped into a fluidized bed of PMMA coated modifier powder for 1 to 2 seconds. Then the coated substrate was reheated to 204-230° C to harden the bisque prior to pack aluminizing. Typical operating parameters for each type of fluidized modifier bed are described in Table 7.

Slurries of several of the metal powders or mixtures thereof were prepared using an ethyl-cellulose thickened vehicle to suspend the powders. A 0.5 weight percent of yttrium was added by adding the corresponding weights of CoY_2 to this mixture, then these mixtures were ball milled for one hour prior to being loaded into a TGA 502 Series DeVilbiss spray gun for application to precleaned and preweighed substrates.

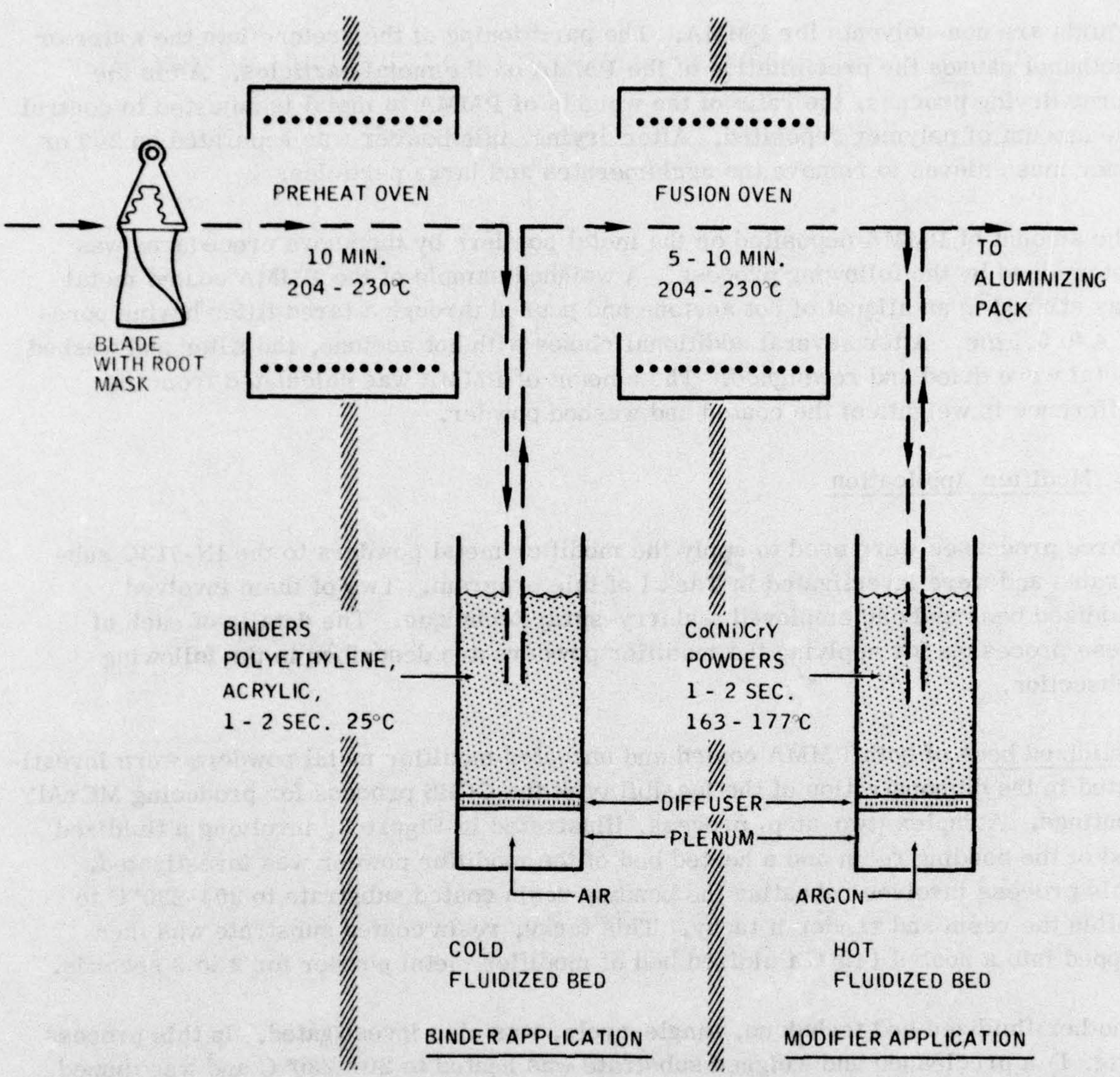


Figure 6. Schematic of fluidized bed coating process.

4. Aluminizing

As stated in a preceding subsection, six different aluminizing packs were investigated in Task I of this program. The packs were derived from three basic compositions which are listed in Table 8. The actual compositions of the aluminizing pack were determined by atomic absorption analysis of the aqua regia soluble portion of each pack after the pack had been conditioned. Conditioning in this case means raising the activated pack to a temperature equal to or greater than its deposition temperature for a period of at least 16 hours.

TABLE 7. OPERATING PARAMETERS OF FLUIDIZED MODIFIER BEDS

	Duplex Process	Single Cycle Process
Bed Diameter	152 mm	60 mm
Modifier Metal Charge	3.2 Kg	0.2 Kg
Fluidizing Gas	Air	Argon
Flow Rate	3.4 m^3/hr	0.34 m^3/hr
Expansion	27 v/o	25 v/o
Bed Solids Fraction (Ref. 6)	0.46	0.43
Bed Temperature	149° C	R.T.
Diffuser Pore Diameter	10 μm	10 μm

TABLE 8. PROTOTYPE ALUMINIZING PACK COMPOSITIONS

	Composition (w/o)				
Prototype Pack Number	Co	Cr	Al	Al_2O_3	NH_4Cl
1	14.4	5	5.6	74.75	0.25
2	16	5	4	74.75	0.25
4	--	24	11	64.75	0.25

The compositions were initially selected to provide an aluminum activity which would produce an all β-NiAl coating, Pack 1, and a $\beta+\gamma$ coating, Pack 2. The compositions of these prototype packs, 1 and 2, are indicated on the cobalt-aluminum phase diagram shown in Figure 7. Both packs were expected to form β-NiAl at the aluminizing temperature, however, a post-coating heat treatment at 815° C from Pack 2 was expected to produce a coating of 87 percent β-NiAl and 13 percent γ-Ni(Al) solid solution alloy. Pack 4 was introduced into the program to test the effect of a high activity aluminum deposition on the formation of the CCRS MCrAlY coatings. The chromium activity of all of the packs other than Number 4 was chosen to be equal to the activity of chromium in the modifier alloy, i.e., the modifier alloy contained 25 percent chromium and the soluble portion of prototype Packs 1 and 2 also contain 25 percent chromium.

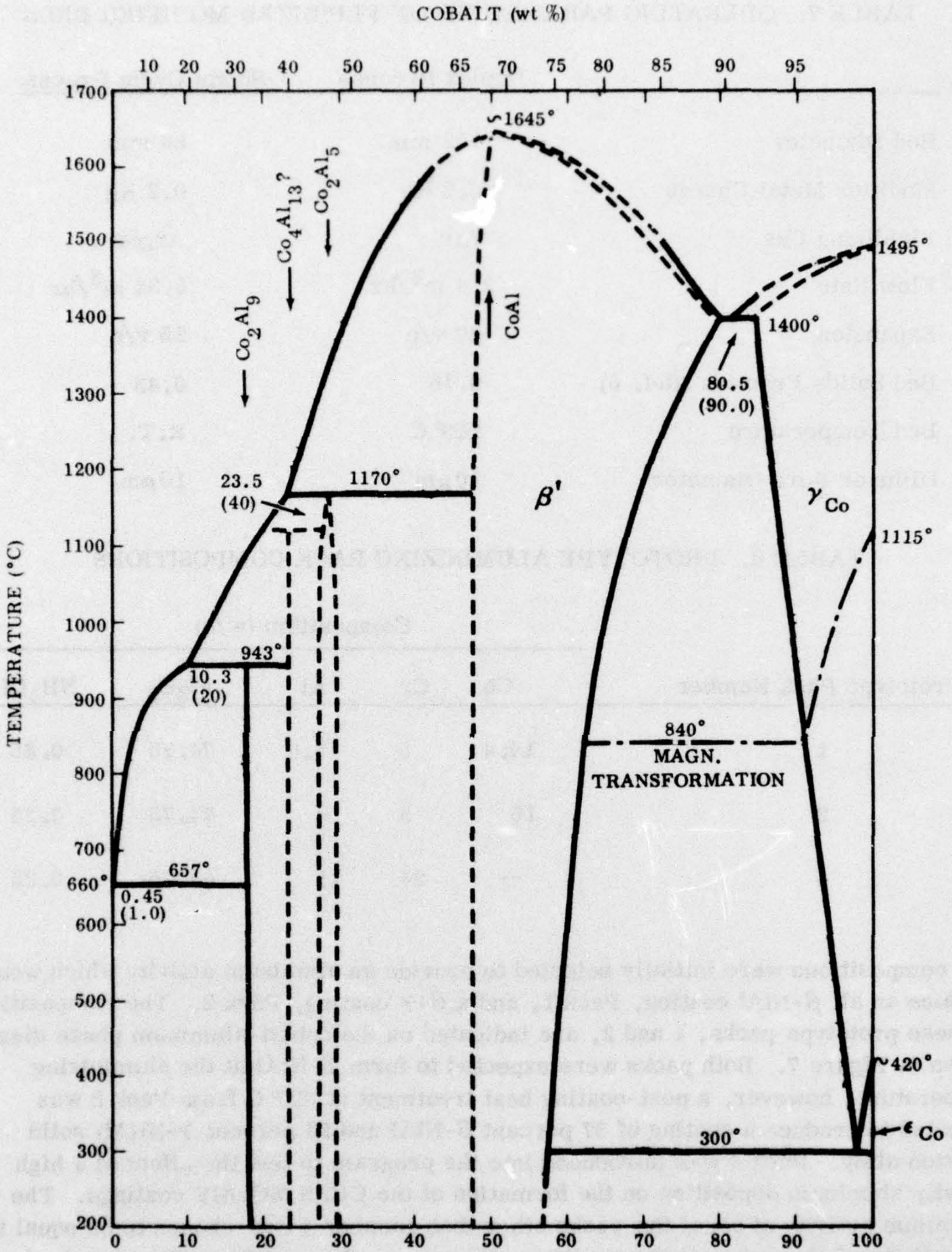


Figure 7. Aluminum-cobalt phase system (7).

Aluminizing of the modifier coated substrates was performed by imbedding them in condition packs, reactivated with 0.25 weight percent NH_4Cl. The packs were enclosed in a cold rolled steel liner which in turn was enclosed in a weld-sealed Inconel retort. The sealed retort was cycle purged three times by evacuating and backfilling with argon, then left under a slight positive pressure of argon.

Two procedures were investigated for bringing the retort and its contents to the desired aluminum deposition temperature. The first procedure consisted of placing the sealed, cycle purged retort into a furnace at the desired deposition temperature for the required deposition time and then removing the retort from the furnace.

The second process involved placing the sealed, cycle-purged retort in the furnace at a temperature such that the bonding resin would not depolymerize more rapidly than approximately one milligram per second(5). After one hour of elapsed furnace time the temperature was increased to the desired aluminum deposition temperature. Figure 8 shows a temperature time profile of a sealed retort recorded for this slow heat aluminizing process.

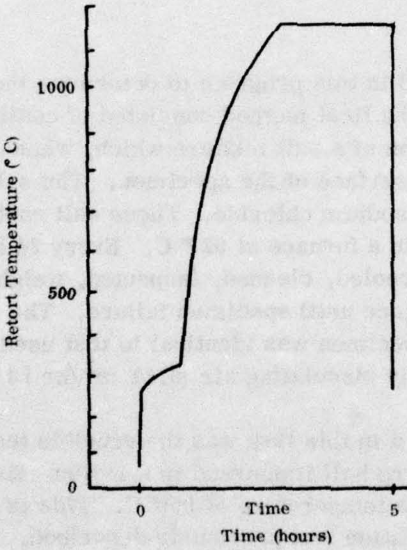


Figure 8. Temperature time profile of slow heat aluminizing process.

5. Post Coating Heat Treatments

This treatment consists of solution aging CCRS coatings at two temperatures and times. The process involves placing the coated specimens in an argon atmosphere, re-exposing the coating to the deposition temperature for at least 15 minutes, and then lowering the temperature to either 818 or 955° C for 24 or 64 hours.

C. DIAGNOSTIC TESTS

Extensive use of the diagnostic tests, metallography, chemical analysis, oxidation and sulfidation characteristics, bend ductility and surface roughness was employed in the demonstration of the feasibility of the fluidized bed-CCRS process for producing MCrAlY coatings. The determination of oxidation, sulfidation and bend ductility characteristics are not yet standardized and will be described in this subsection.

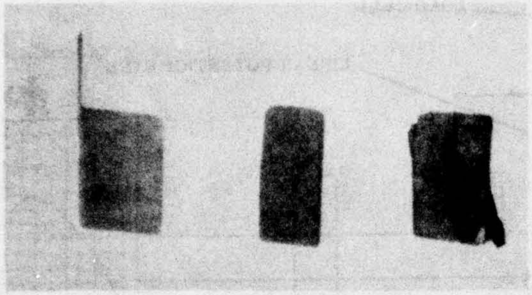
1. Oxidation

The oxidation resistance of a portion of the CCRS coatings investigated was determined by the technique of furnace oxidation. The test consists of monitoring the weight of the coated specimen as a function of time at 1093° C. The specimens were supported on alumina boats in the furnace and the furnace atmosphere was slowly circulating air (0.11 m^3/hr [4 cu ft/hr]). The specimens were removed every 24 hours, 72 hours over weekends, cooled, inspected, weighed and replaced in the furnace until an obvious coating failure occurred. The criteria for coating failure was a large decrease in weight caused by the spalling of the coating.

2. Sulfidation

Two different tests were employed in this program to determine the sulfidation resistance of the CCRS coatings. The first method consisted of coating a weighed specimen with a 20 percent solution of a salt mixture which, when dried, left a deposit of about 1 mg/cm^2 on the surface of the specimen. The salt mixture was 95 percent sodium sulfate-5 percent sodium chloride. These salt coated specimens were supported on alumina boats in a furnace at 927° C. Every 24 hours the specimens were removed from the furnace, cooled, cleaned, inspected, weighed, recoated with fresh salt and replaced in the furnace until specimen failure. The criteria for specimen failure of a coating on this specimen was identical to that used in oxidation test. The furnace atmosphere was slowly circulating air (0.11 m^3/hr [4 cu ft/hr]).

The other sulfidation test employed in this task was the crucible test. In the test, weighed CCRS coated specimens are half immersed in a molten mixture of 95 percent sodium sulfate-5 percent NaCl at a temperature of 955° C. This is a much more severe test than the furnace sulfidation test previously described. Every 24 hours the crucibles and specimens are removed, cooled, cleaned, inspected and the specimens weighed, replaced in fresh salt and replaced in the furnace until specimens fail. The appearance of specimens from both types of sulfidation tests are compared in Figure 9. The specimen on the right shows a mild failure of a crucible sulfidation tested CCRS coating. This type of failure is typified by a large decrease in weight and large spallation or blistering of the coating.



Specimen on left in as-coated condition.

Specimen in middle was sulfidation tested in furnace at 927° C with 1 mg/cm^2 of $Na_2SO_4/NaCl$ on the surface for 223 hours.

Specimen at right failed after being sulfidation tested in crucible containing molten $Na_2SO_4/NaCl$ at 955° C for 72 hours.

Figure 9. Specimen appearance after furnace and crucible sulfidation.

3. Bend Ductility

The ductility in bending of the CCRS coatings developed during this program was measured by controlled bending of a three-point loaded beam at elevated temperature. A schematic of the bend test fixture is shown in Figure 10. A typical test sequence consisted of soaking the specimen and test fixture at 538° C for 15 minutes then bending the specimen 10 degrees at a strain rate of 6.8×10^{-3} mm/mm/min.

The strain rate was estimated from the following equation$^{(8)}$

$$\epsilon_{max} = \frac{6hY_L}{L^2} \qquad (1)$$

where Y_L is the crosshead speed of the test machine, h is specimen thickness, L is the length of the specimen between the outer knife edges, and ϵ_{max} is the strain rate. Inspection of the output of the load cell and audio monitoring during the bend of 10 degrees reveals whether the coating or specimen bar cracked. If it has not cracked, the load is removed, the temperature of the specimen and fixture is lowered 30° C, soaked for 15 minutes and the test repeated. By repeating the sequence until the specimen cracks, a good estimation of bend transition temperature may be obtained with a minimum number of test specimens. The procedure is called the progressive bend test$^{(9)}$.

4. Coating Composition

The elemental composition of the several CCRS MCrAlY coatings was determined by X-ray fluorescent spectrometry and also by electron microprobe analysis. These data were compared with the aluminum activity of the packs. These data were also used in correlating the performance of these CCRS coatings with their composition.

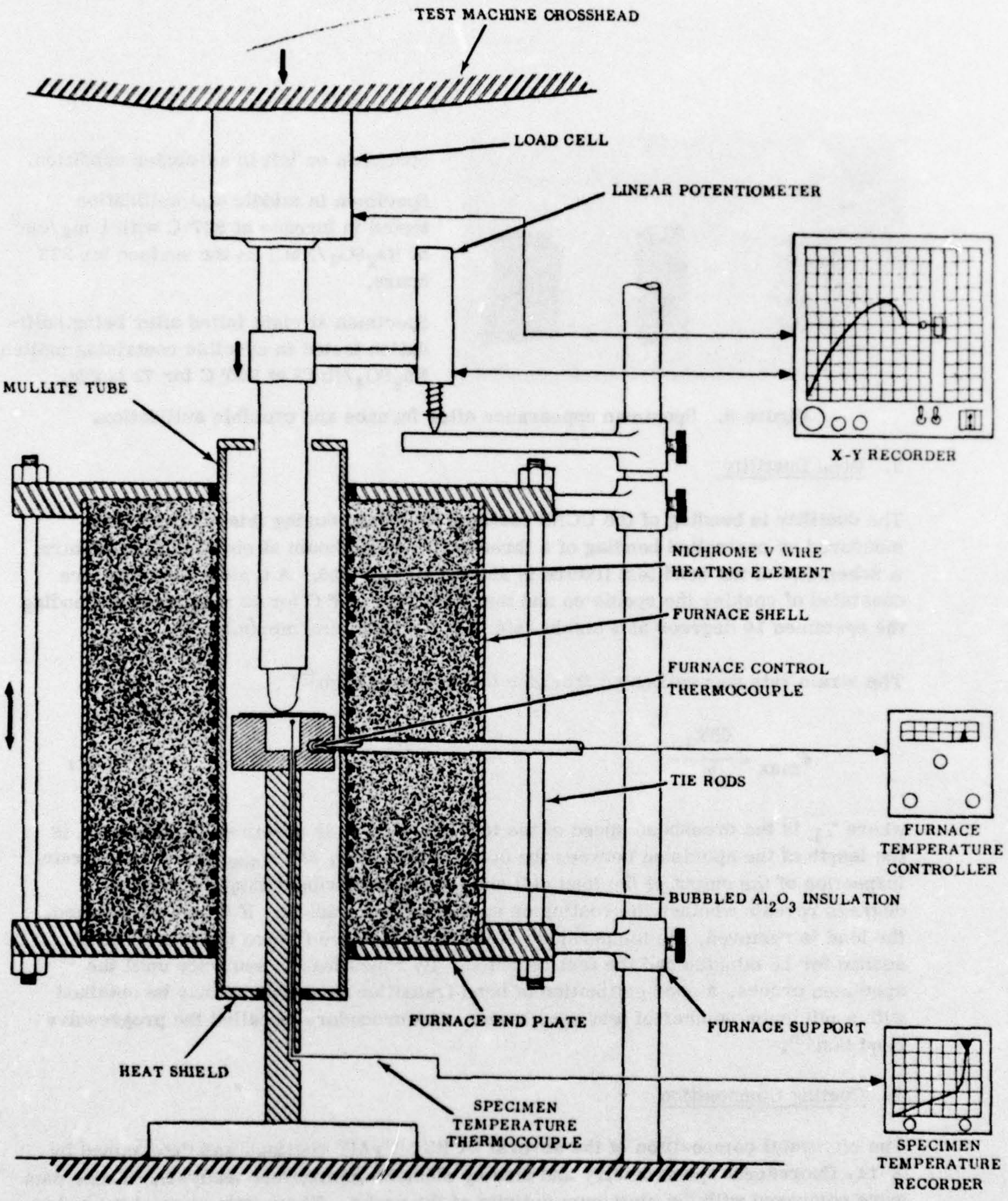


Figure 10. Bend transition temperature test setup.

SECTION III

RESULTS AND DISCUSSION

The dual goal of Task I of this program was the demonstration of the feasibility of a fluidized bed process for applying the modifier powder to simple blade shapes, and the controlled composition reaction sintering process for producing a MCrAlY coating on a nickel-base superalloy. The results presented in this section demonstrate that this combination of processes is a feasible approach for the production of MCrAlY coatings. The results of this program are presented and discussed in the order of their occurrence in the combined fluidized bed-CCRS process. As previously stated, this process consists of three steps:

1. Precleaning of the nickel-base superalloy to be coated with MCrAlY
2. Application of the particulate modifier, MCrY, to this part using a fluidized bed technique
3. Reaction sintering of this MCrY coated part in a controlled activity aluminizing pack to produce the MCrAlY coated nickel-base superalloy part.

A. PRECLEANING PROCEDURE

The precleaning procedure described in the Experimental section was used to clean the IN-713C substrates. Etch No. 2 at ambient temperature leaves the surface with a high grain boundary defined surface (Fig. 11). The composition of the etching solution will probably require adjustment to produce such surfaces on the two remaining alloys, IN-100 and MA-754, to be investigated in the remainder of this program.

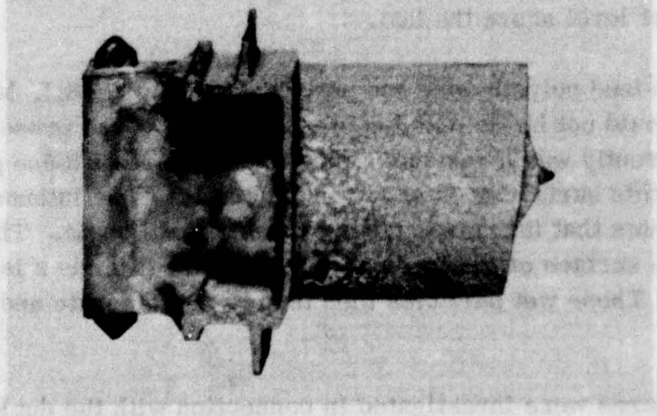


Figure 11. Etched appearance of IN-713C.

B. BONDING RESIN SELECTION AND MODIFIER APPLICATION

In selecting the optimum method for applying the MCrAlY modifiers to the IN-713C substrates, four different bonding resins and three different methods of application were investigated in the program. The bonding resins and application processes have been described in the Experimental section. The paragraphs to follow will describe the results varying the process parameters of the three application processes.

1. Duplex Process

In the duplex process the following process operations were performed:

- Fluidizing the resin
- Preheating the part
- Immersing part to bond resin
- Glazing resin (reheating to soften resin)
- Immersing resin coated specimen in fluidized bed of MCrY modifier
- Pack aluminizing (reaction sintering).

The progress and problems associated with each of these operations are presented below.

The bonding resins investigated in the duplex process of modifier application were polyethylene, polymethylmethacrylate and polyvinyl acetate (properties are noted in Table 1). Of these resins only the large particle sized materials, Allied Chemical's high molecular weight polyethylene and the Elvacite 2008 PMMA were fluidizable. Fluidizing of these two resins using the conditions specified in Table 6 produced a gently boiling bed and doubling the air flow rate to produce a turbulent, spouting bed only increased the dust level above the bed.

The smaller particle sized polyethylene and polyvinyl acetate (U.S.I. Microthene FN 500 and FE 532) could not be fluidized reproducibly due to the presence of a surfactant which apparently was added during the manufacture of these powders. The infrared spectrum of this surfactant is shown in Figure 12. The intense bond at 1100 Kaysers (cm^{-1}) indicates that this material is probably a sulfonate. The surfactant slowly migrates to the surface of the resin particles where it binds a layer of water by hydrogen bonding. These wet particles then tend to agglomerate and are very difficult to fluidize.

Two preheat temperatures were investigated in connection with the duplex process for applying the bonding resin. IN-713C parts heated at a temperature of 176° C,

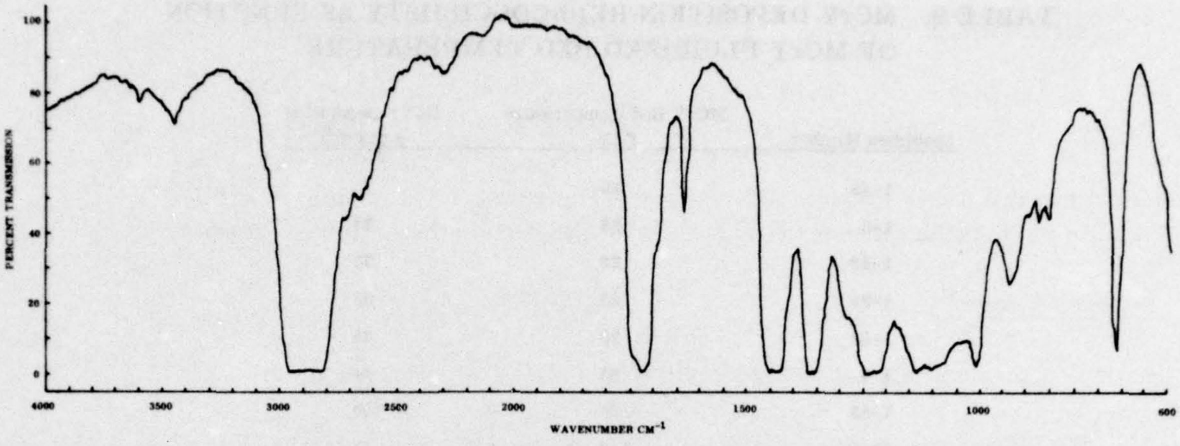


Figure 12. Infra-spectrum of surfactant washed from the U.S.I. Microthene FN-500 and FE-532 powders.

when dipped into a fluidized bed of either PMMA or polyethylene, would not pick up a coating of polymer that could be manipulated. The slightest draft of air or a bump against the side of the coating fixture would cause loss of part of the resin. Preheating to 204-230° C was investigated. These coatings could be handled and the condition was selected for use in the duplex process. The amount deposited was 11 mg/cm^2 (or a glazed thickness of 110μm) for 74μm polyethylene. PMMA (149μm) yields coatings of 24 mg/cm which were glazed to 240μm. Increasing the preheat temperature did not result in thicker coatings.

The next step in the duplex process was reheating (glazing) the resin coated part to soften the resin and thereby prepare it for binding the MCrY modifier alloy. Two glazing temperatures were investigated: 204° C and 537° C. The higher temperature required only one minute to glaze the resin coated part, while the lower temperature required ten minutes. The lower temperature was selected as there were several instances of spontaneous ignition of the resin coated parts at 537° C.

After the resin has been softened by the glazing step, the part is dipped into a fluidized bed of MCrY alloy. The viscous resin bonds the MCrY particles to the surface. Initially a 25° C MCrY bed was used; however, it was determined that the MCrY deposit was very non-reproducible as shown by the data in Table 9. Increasing the temperature of the MCrY bed to 176° C improved the reproducibility of the duplex coatings.

Immersion time in the MCrY bed was varied from 2 to 8 seconds and no variation in MCrY modifier deposition could be discerned. This independence of modifier deposition on bed immersion time is another reason for the uniform data shown at the bottom of Table 9.

TABLE 9. MCrY DEPOSITION REPRODUCIBILITY AS FUNCTION OF MCrY FLUIDIZED BED TEMPERATURE

Specimen Number	MCrY Bed Temperature (°C)	MCrY Deposition (mg/cm^2)
1-45	25	74
1-3	25	77
1-28	25	72
1-25	25	80
1-59	25	78
1-4	25	84
1-55	25	100
11-2	149	73
11-3	149	74
11-5	149	72
11-6	149	76

Notes: (1) Bonding resin: Allied Chemical 1222, high molecular weight polyethylene, 11 mg/cm^2 deposits.

(2) Part preheat temperature: 204-230° C.

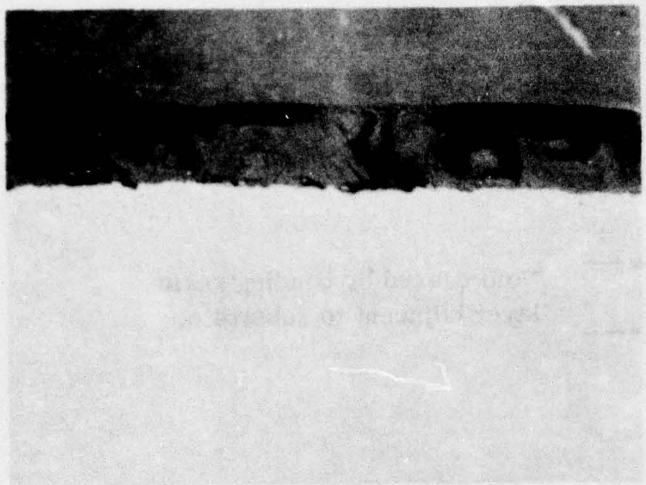
(3) Glazing conditions: 204-230° C, 10 minutes.

(4) MCrY modifier size: $< 37 \mu m$.

After removing the MCrY coated specimens from the modifier bed, they were then pack aluminized to form the MCrAlY coatings. The details of this process will be presented in a subsequent section.

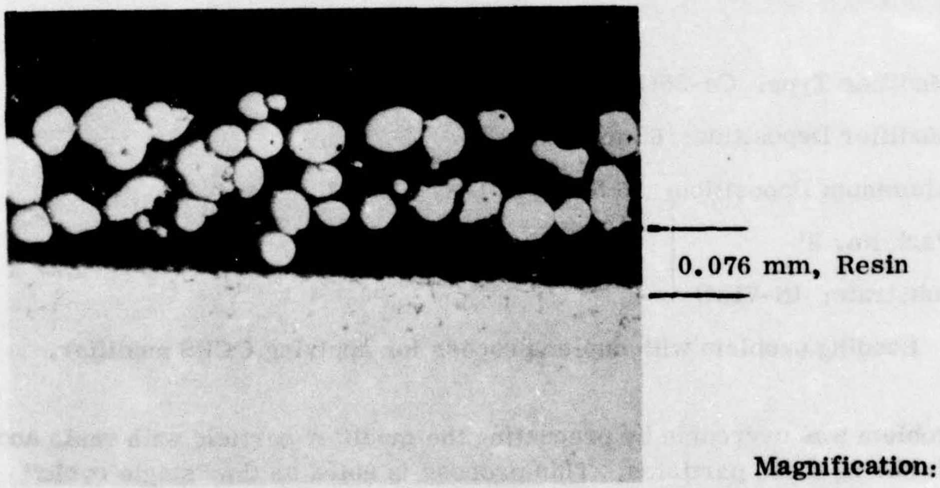
Subsequent aluminizing of the resin bonded MCrY modifier must form the β-MAl intermetallic compound which expands the volume of the modifier by approximately 100 percent, closing all surface connected and the majority of internal pores. This aluminizing step must also metallurgically bond the coating to the substrate. None of the thick PMMA bonded MCrY coatings was successfully aluminized to an adherent MCrAlY coating. The high molecular weight polyethylene (Allied Chemical) was, therefore, the selected bonding resin for the duplex process.

Fluidized bed applied polyethylene coatings, e.g., Figure 13, after glazing at 230° C were used to bond the MCrY modifier powders to the coating substrates. A typical polyethylene bonded modifier is shown in Figure 14. Because the polyethylene bonding resin particle size controlled the thickness of bonding resin, the thickness limited the amount of modifier deposited. One weight of metal modifier, 65 to 75 mg/cm^2, was investigated in the duplex process. These duplex applied modifier coatings were densely packed and easily reaction sintered to dense MCrAlY coatings; however, the bond between these coatings and the substrate was not reproducible. The 76 μm layer



Magnification: 100X

Figure 13. Polyethylene coating on IN-713C.

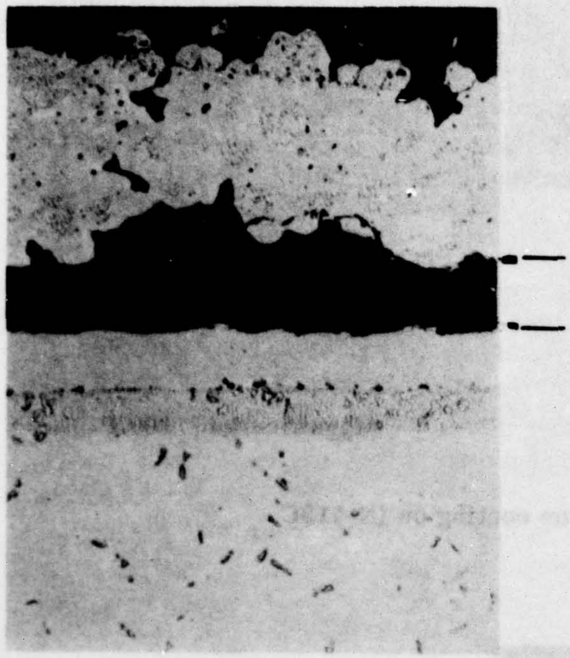


Magnification: 100X

Figure 14. Polyethylene bonded CoCrY alloy powder coating on IN-713C duplex process.

of modifier-free resin, next to the substrate (Fig. 14) apparently restricts reaction sintering and growth essential for formation of a metallurgically bonded aluminide coating. As shown in Figure 15, the modifier, upon aluminizing, develops into the dense structure desired but this is detached from the substrate.

No simple solution was found to overcome the problem of coating bond to the substrate with the fluidized bed duplex process. Decreasing resin particle size was an approach but this increased the difficulty of fluidizing the resin. As will be noted in the next



Void caused by bonding resin layer adjacent to substrate.

Unetched

Magnification: 250X

Modifier Type: Co-25Cr-0.5Y Alloy, 37-44μm

Modifier Deposition: 63 mg/cm^2

Aluminum Deposition: 16 hours at 1037° C, 4.4 mg/cm^2

Pack No. 3'

Substrate: IN-713C

Figure 15. Bonding problem with duplex process for applying CCRS modifier.

section, the problem was overcome by precoating the modifier particle with resin and subsequently fluidizing these particles. This process is noted as the "single cycle" process because only one fluidized bed operation is required.

2. Single Cycle Process

A simpler process for bonding the MCrY modifier powder to the IN-713C substrate prior to pack aluminizing was developed during Task I of this program. This process is the "single cycle" process described in the Experimental section in which the modifier particles were precoated with resin prior to application in a fluidized bed. The bonding resin selected for this process was PMMA.

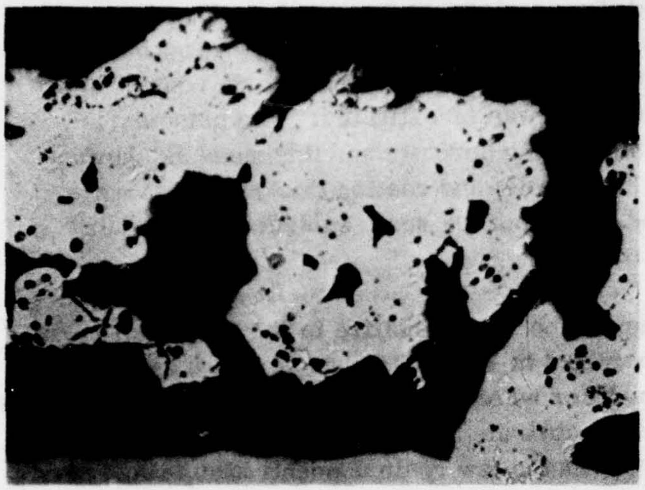
Deposition weight of the resin coated modifier powder was found to be a function of the resin content of the modifier powder and the bed immersion time. By maintaining the bed immersion time between one and two seconds, the effect of the resin content of the modifier powder on the other coating properties was investigated. The principal effects of modifier resin content was on the coating porosity and thickness as shown by the coating structure in Figure 16. The porosity and coating thickness data estimated from the structure were correlated with modifier resin content. These data are shown in Figure 17A.

The aluminized modifier porosity was found to be very sensitive to the amount of resin deposited on the modifier powders as illustrated in Figure 16. At very low resin concentrations columnar structures of the modifier were common, i.e., the coated particles bonded together vertically outward from the substrate but were not bonded laterally. This is illustrated in Figures 17B and 17C. At the low resin concentration, illustrated in Figure 17B, there is inadequate resin present to bond to all adjacent surfaces and favors collection at the most direct heat-flow-path, particle contacts. Under these conditions, resin is present in significantly lower amounts than the theoretical packing fraction of 0.37 (for uniform spheres). Low resin content coatings had a frosty appearance.

Increasing the resin content to ~4 weight percent (40 volume percent) decreases the porosity of the modifier as illustrated in Figure 17C. Thus, up to at least a volume fraction of 0.40 resin, modifier porosity decreases with resin content. Table 10 illustrates the uniform deposition rate that can be obtained with the high volume fraction coating. By automation even closer control should be possible. To enable handling of the modifier after the fluidized bed application, a ten-minute oven treatment at 204° C was found essential.

A typical fluidized bed modified coating is shown in Figure 18A. Note the uniformity of this coating with the exception of the extreme R.H.S. of the cord. This heavy build-up was a result of bed stagnation and can be minimized by orientating the specimen in the fluidized bed with the vertical surfaces nearly parallel to the direction of gas flow.

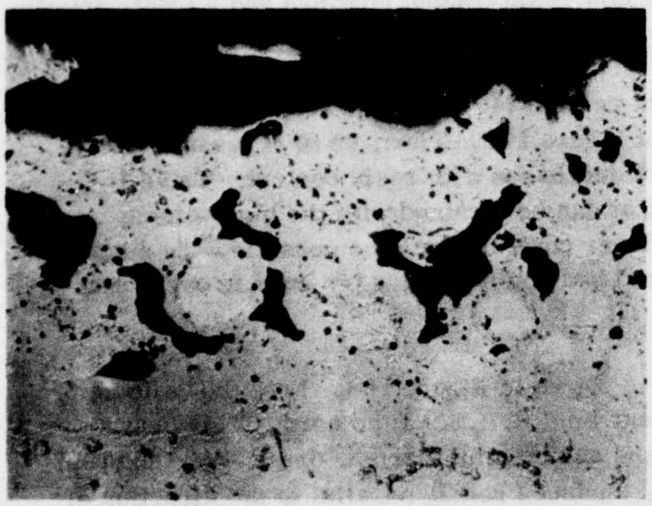
The microstructure of a CCRS CoNiCrAlY coating applied by the single cycle process with optimized resin content is shown in Figure 18B. Electron microprobe analysis of these coatings indicated that the dark grey coating matrix was a cobalt-nickel aluminide (β-MAl) which contains some chromium. The light grey areas are lower in aluminum content and are the remnants of the CoNiCrY modifier particles. The white filigree phases which appear on the substrate side of the light grey areas are high in chromium and result from the outward diffusion of cobalt and nickel and/or the inward diffusion of aluminum. The persistence of this multiphase microstructure after 16 hours of aluminum deposition illustrates the need to reduce the modifier particle diamter.



Unetched

Magnification: 250X

A. Modifier resin content, 1.7 weight percent - 10 volume percent



Unetched

Magnification: 250X

B. Modifier resin content, 2.3 weight percent - 16 volume percent

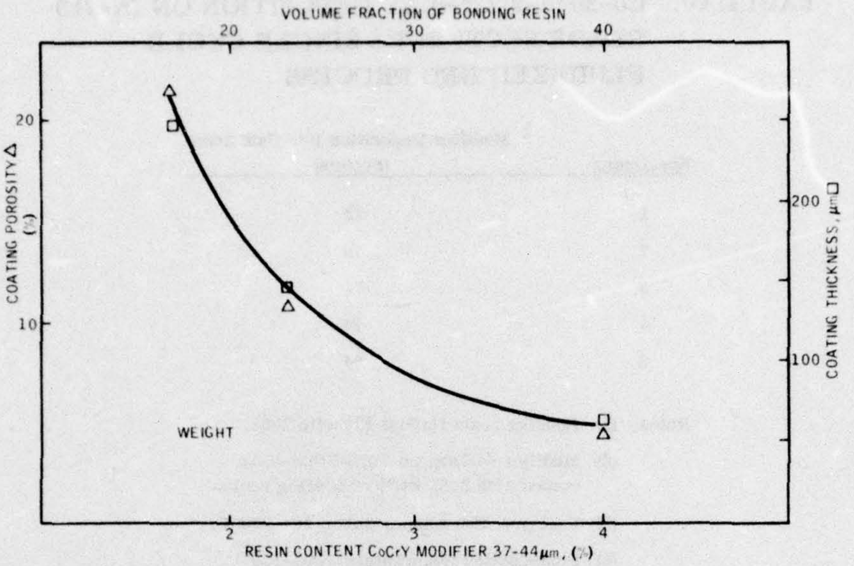
Modifier Type: Co-25Cr-0.5Y Alloy, 37-44μm

Modifier Deposition: 86 mg/cm^2

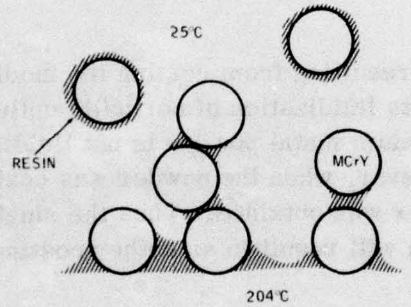
Aluminum Deposition: 16 hours at 1037° C, 12 mg/cm^2

Pack No. 3

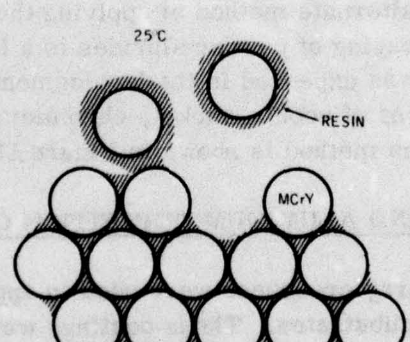
Figure 16. Effect of modifier resin content on coating porosity and thickness.



A. **Effect of modifier resin content on single cycle deposits**



B. **Low resin**



C. **Adequate resin**

Figure 17. Mechanism of porosity formation.

TABLE 10. Co-20Ni-25Cr-0.5Y DEPOSITION ON IN-713 BLADE SECTION BY SINGLE CYCLE FLUIDIZED BED PROCESS

Specimens	Modifier Deposition Per Unit Area (mg/cm)
1	72
2	70
3	74
4	74
5	64

Notes: (1) Bonding resin DuPont Elvacite 2008.

(2) Modifier < 37μm Co-20Ni-25Cr-0.5Y coated with 3.51 wt/% of bonding resin.

(3) Part pre-heat temperature: 204-230° C.

(4) Post-coating temperature: 204-230° C.

(5) Post-coating soak time: 10 minutes.

(6) Modifier bed temperature: 22-25° C.

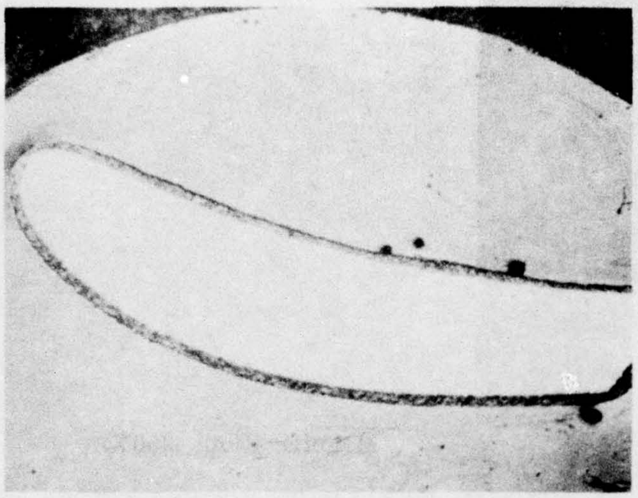
The increase in particle size resulting from coating the modifier particles with the bonding resin, PMMA, permits fluidization of normally unfluidizable metal powders. For example, 2 to 4μm chromium metal powder is not fluidizable to the boiling state under normal conditions; however, when the powder was coated with 3 to 4 percent of PMMA, a fluidizable powder was obtained. Thus the single-step process can employ finer modifier particles which will result in smoother coatings.

3. Slurry-Spray Process

This process was used as an alternate method of applying the MCrY metal powders to the coating substrates. Spraying of powder slurries is a line-of-sight limited process and thus little effort was expended in its development. It was used to deposit the elemental modifier mixtures of cobalt, nickel, chromium and yttrium. A typical modifier coating applied by this method is shown in Figure 19.

C. MODIFIER SELECTION AND ALUMINUM DEPOSITION CONDITIONS

The single-step and slurry-spray processes were used to apply modifier coatings of MCrY to the IN-713C coating substrates. These coatings were then aluminized in controlled aluminum activity packs to form MCrAlY coatings. The results of crucible sulfidation tests at 955° C clearly demonstrated the superiority of the (Co-20Ni-25Cr-0.5Y)Al coating over the (Co-25Cr-0.5Y)Al coating investigated in this program.

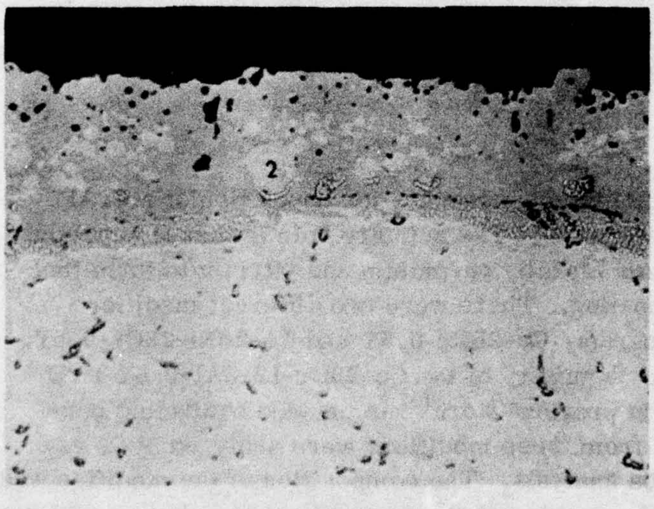


37-44μm CoCrY

77 mg/cm deposition

Magnification: 5-1/2X

A. Single cycle fluidized bed applied modifier coating on IN-713C turbine blade section



1. β-MAl
2. CoNiCrAl solid solution
3. Chromium rich areas

Unetched

Magnification: 250X

B. Coating composition by X-ray fluorescence spectrometry Co-18Ni-20Cr-17Al-0.4Y

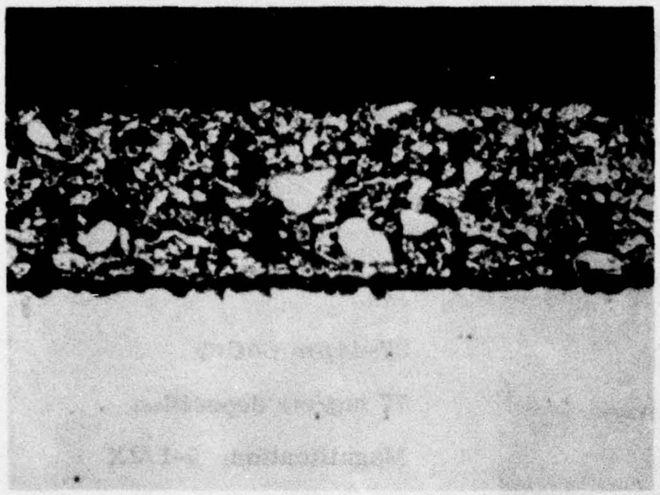
Modifier Type: Co-20Ni-25Cr-0.5Y, <37μm

Modifier Deposition: 51 mg/cm^2

Aluminum Deposition: 16 hours at 1037° C, 7.3 mg/cm^2

Pack No. 2

Figure 18. CoNiCrAlY coating deposited by single cycle CCRS process.



Magnification: 250X

Figure 19. Typical sprayed-slurry of Co-20Ni-15Cr coating (added as elemental powders) on IN-713C.

Bend ductility testing demonstrated that CCRS-MCrAlY coatings are equivalent to the PVD Co-25Cr-12.5Al-0.5Y coating in mechanical performance, when a subsequent heat treatment following aluminizing is used.

1. Modifiers

In the controlled composition reaction sintering process for deposition of MCrAlY coatings, the modifier functions in two roles. The primary role is that of supplying the correct amount of M (cobalt and/or nickel), chromium and yttrium to form the desired composition of an MCrAlY coating. There were two different modifier compositions investigated in this program, Co-25Cr-0.5Y and Co-20Ni-25Cr-0.5Y. The first was chosen to duplicate the chemistry of the Co-25Cr-12.5Al-0.5Y PVD coating while the second was shown in previous work(4) to provide equivalent performance. CCRS coatings prepared from these modifiers were analyzed by X-ray fluorescence and electron microprobe analysis. The composition of the modifier was calculated from these analyses and these calculated compositions are shown in Figure 20. The leftmost bar in each group represents the composition of the modifier mixture used to prepare these coatings. The shaded areas show the range of the element's concentration determined by X-ray fluorescent analyses and demonstrate the closer composition control with the alloyed modifier powders. The composition range found for the mixtures is due to stratification according to density in both the slurries and the fluidized beds. These results indicate that alloyed modifier powders are essential for the close composition control required in producing CCRS-MCrAlY coatings.

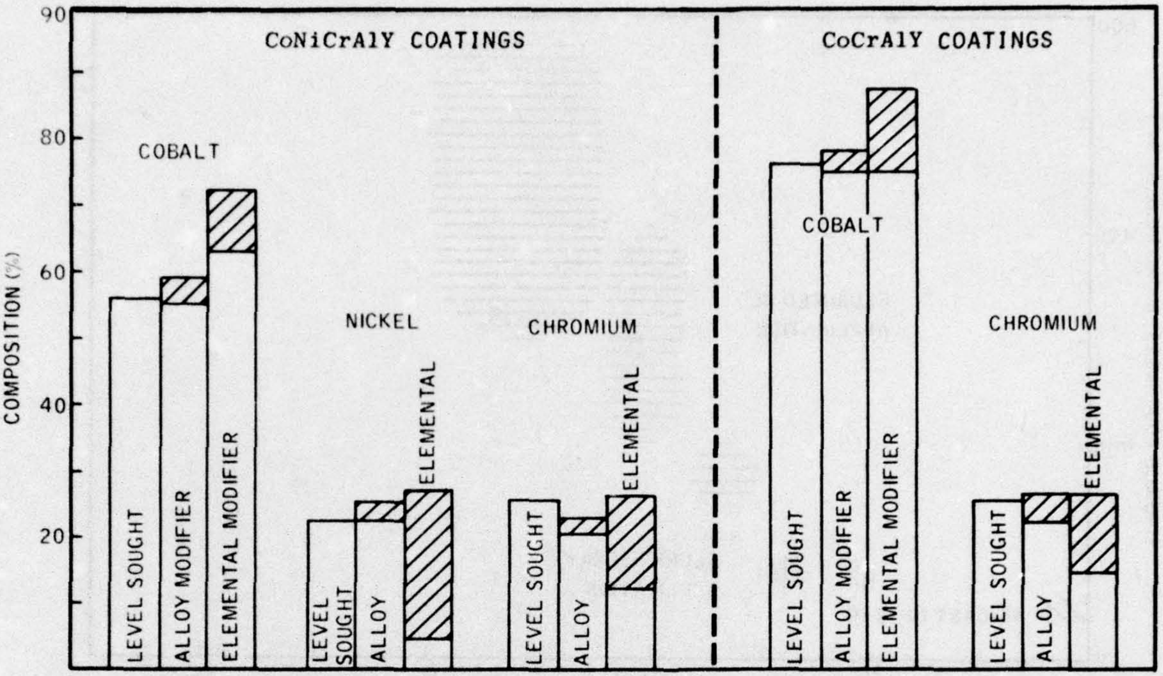


Figure 20. MCrY modifier composition calculated from CCRS MCrAlY coating analyses.

The second role of the modifier in the CCRS coating process is that of determining the surface finish on the coated part. The surface finishes of several CCRS-MCrAlY coatings versus their modifier particle sizes are plotted in Figure 21. The surface finish of these coatings (horizontal hatchings) is proportional to the particle size of the modifier powder. In the case of the slurry-sprayed (vertical hatching) coating more fine particles are entrapped in the interstices between the larger modifier particles and result in a smoother coating than that obtained by the more uniform particle sizes applied by the fluidized bed process. The surface finish of the substrate is shown in the lower lefthand corner. These data indicate that modifier particle sizes of less than 20μm would produce coatings as smooth as the cast surface of the substrate alloy.

Two additional roles of the modifier CCRS-MCrAlY coating formation and performance were discovered in the program. At a constant aluminum pack activity the nickel content of the modifier has a marked effect on the aluminum content of the resulting CCRS coating. This effect is shown in Figure 22 and Table 11. These data indicate that small changes in the nickel content of the modifier will result in significant changes in the aluminum content of a MCrAlY-CCRS coating and thus the chemistry of the modifier can be used to control the total chemistry of the coating.

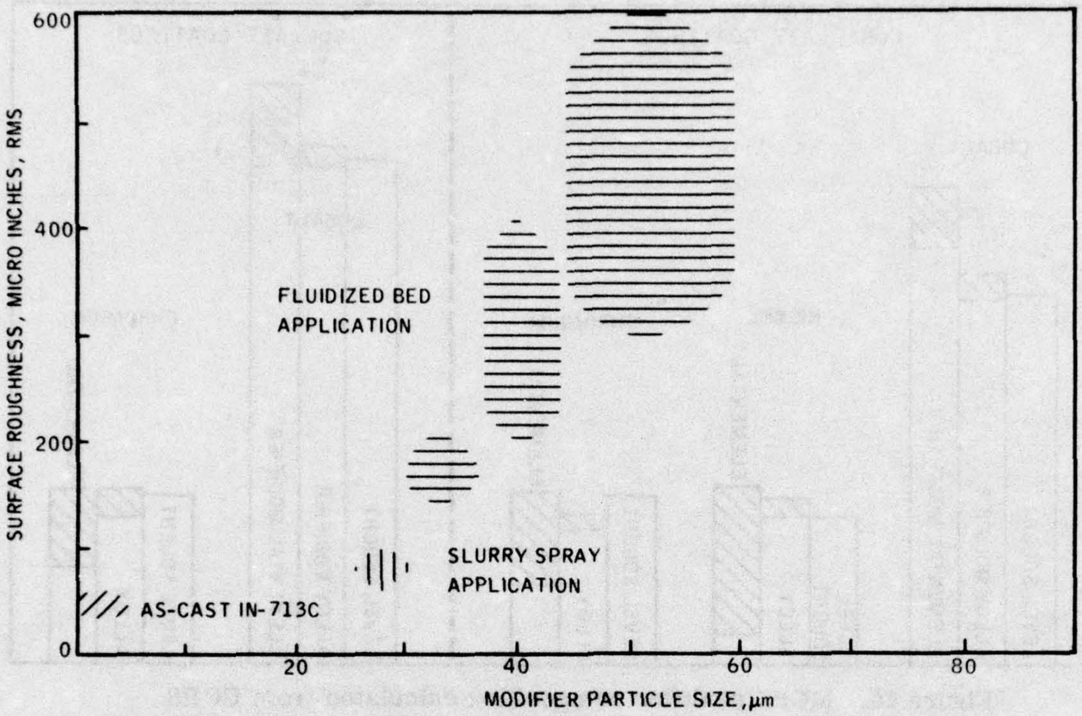


Figure 21. Surface roughness of CCRS MCrAlY coatings.

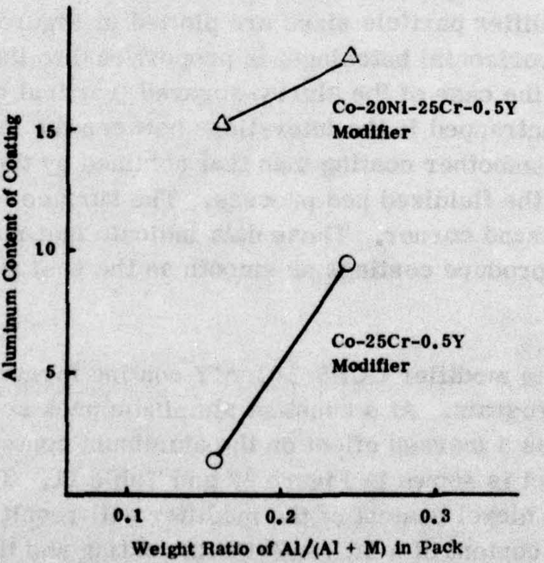


Figure 22. Aluminum content of CCRS coating as function of pack and modifier chemistry at 1038° C (M is the sum of the iron, nickel and cobalt concentrations present in the aluminizing packs).

TABLE 11. ALUMINUM CONTENT AS FUNCTION OF NICKEL CONTENT OF THE MODIFIER AND PACK ALUMINUM ACTIVITY

Modifier Type	Modifier Deposition (mg/cm^2)	Aluminum Deposition (mg/cm^2)	Pack Number	Coating Aluminum Content XRF (%)	$\frac{Al}{Al + M}$
Co-20Ni-25Cr-0.5Y <37μm, alloyed	80	18.3	1	17.4	0.24
Co-25Cr-0.5Y <37μm, alloyed	85	14.8	1	9.1	0.24
Co-20Ni-25Cr-0.5Y <37μm, alloyed	95	14.7	2	15.0	0.16
Co-25Cr-0.5Y <37μm, alloyed	85	6.9	2	2.6	0.16

Substrate: IN-713C

Aluminum Deposition Temperature: 1038° C

Aluminum Deposition Time: 64 hours

M is the sum of the concentration of Ni, Co and Fe in the pack.
These data are plotted in Figure 22.

The other effect that the nickel content of the modifier was found to have on the MCrAlY-CCRS coatings was in their crucible sulfidation resistance. These lifetimes are shown in Figure 23 and Table 12 along with that of a simple aluminide coating and a Co-25Cr-12.5Al-0.35Y-PVD coating. The excellent sulfidation resistance of the CCRS-CoNiCrAlY coatings are probably related to the enhanced aluminum content relative to the CoCrAlY coating (see Fig. 22). These results indicate that the Co-20Ni-25Cr-0.5Y alloy modifier produces a superior CCRS coating than does the Co-25Cr-0.5Y alloy on nickel-base alloys at the aluminum activity studied in the packs. The PVD coating on a IN-713 rod failed at the end which may be indicative of a thin coating rather than poor performance.

2. Aluminizing Packs

As indicated by Figures 22 and 23, the elemental aluminum content of the aluminum pack has a considerable influence on the formation and performance of the CCRS-MCrAlY coatings investigated in this program. As noted in an earlier section, six different aluminum deposition packs were investigated. The deposition temperature

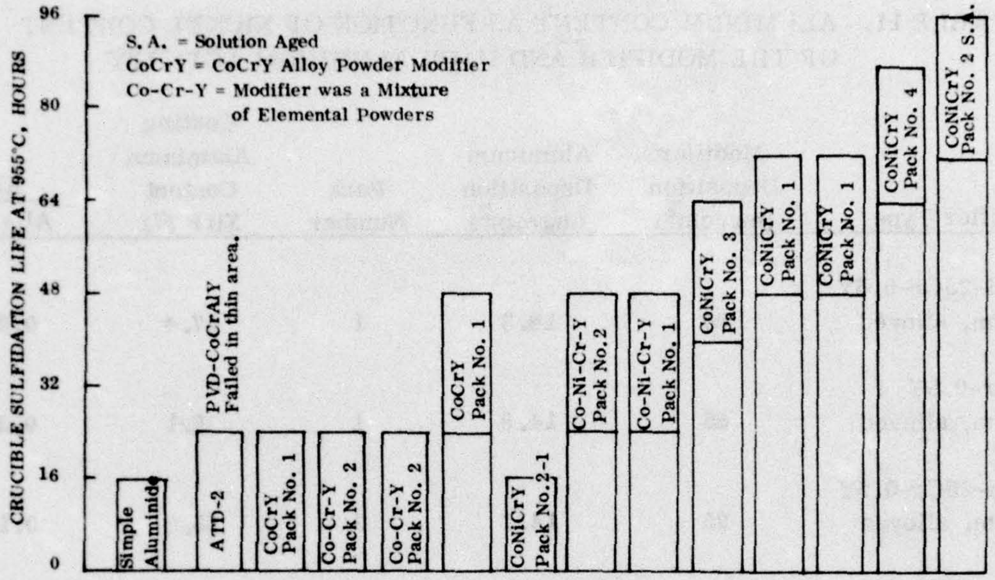


Figure 23. Failure lifetimes of CCRS coatings in crucible sulfidation test at 955° C.

was varied from 983° C to 1149° C and the deposition time was varied from 2 to 64 hours. The purpose of this variety of aluminum deposition conditions was to define the conditions required for producing the MCrAlY coatings with a performance equal to the physical vapor deposited CoCrAlY coatings.

The compositions of the six packs used in the program are shown in Table 13 and were determined by atomic absorption analysis of the aqua regia soluble portion of these packs.

The high iron content in Packs 2-1, 3 and 3' results from the extensive use of these packs in cold rolled steel liners in the Inconel 600 retorts. The chloride from the ammonium chloride transports iron chloride to the pack as well as aluminum to the modifier coated specimens. The other source of iron in these packs is the aluminum oxide diluent.

Pack Number 2-1 had the lowest aluminum activity study in the program and resulted from the continued reuse of a Number 2 pack in five consecutive 16-hour and one 64-hour depositions at temperatures of 1038 and 1149° C.

Packs 3 and 3' were also derived from a prototype Pack Number 2. Pack 3' resulted from a series of elemental aluminum additions in order to maintain the aluminum activity near that of the prototype Pack Number 2 composition. This was overestimated in the case of Pack Number 3' with the result that it was one of the higher activity packs studied. Pack Number 3 resulted from two depositions at 1038° F for

TABLE 12. CRUCIBLE SULFIDATION LIFETIME DATA FOR CCRS MCrAlY COATINGS

Modifier Type	Modifier Deposition (mg/cm^2)	Aluminum Deposition (mg/cm^2)	Deposition Time (hours)	Pack Number	Crucible Sulfidation Life at 955° C (hours)
None	None	18.7	64	3	<16
None	None	12.5	16	4	<16
PVD Deposited Co-25Cr-12.5Al-0.5Y 76-127μm Thick	--	--	--	--	<24(1)
Co-25Cr-0.5Y Elemental	68	16.3	64	1	<24
Co-25Cr-0.5Y Alloyed	80	7.2	64	2	<24
Co-25Cr-0.5Y Elemental	82	9.2	64	2	<24
Co-25Cr-0.5 Alloyed	90	18.9	64	1	24-48
Co-20Ni-25Cr-0.5Y Alloyed	49	12.4	64	2-1	<16
Co-20Ni-25Cr-0.5Y Elemental	63	10.6	64	2	24-48
Co-20Ni-25Cr-0.5Y Elemental	64	16.7	64	1	24-48
Co-20Ni-25Cr-0.5Y Alloyed	60	26	64	3	40-64
Co-20Ni-25Cr-0.5Y Alloyed	96	18	64	1	48-72
Co-20Ni-25Cr-0.5Y Alloyed	49	10	4	1	48-72
Co-20Ni-25Cr-0.5Y Alloyed	49	11	4	1	48-72
Co-20Ni-25Cr-0.5Y Alloyed	91	38	16	4	64-88
Co-20Ni-25Cr-0.5Y Alloyed	106	13.4	64	2	72-96(2)
Co-20Ni-25Cr-0.5Y Alloyed	50	7.5	16	2	72-96(2)
Co-20Ni-25Cr-0.5Y Alloyed	55	25	2	4	72-96(2)

Notes: (1) This specimen failed at the end of the bar where the coating was probably thin.

(2) All of these coatings were solution aged at 815° C for at least 24 hours before test.

(3) These data are shown in Figure 23.

TABLE 13. CONDITIONED ALUMINIZING PACK COMPOSITIONS

Pack Number	Co	Ni	Fe	Cr	Al	Al_2O_3
1	13.2	0.05	0.41	3.77	4.38	Balance
2	15.05	0.06	0.69	4.52	3.0	Balance
2-1	15.75	0.08	3.69	4.58	0.91	Balance
3	14.0	0.06	3.48	2.12	3.36	Balance
3'	15.04	0.06	2.50	2.06	8.79	Balance
4	0.22	0.05	0.68	17.46	2.37	Balance

16 hours each and two 64-hour depositions at 1149 and 983° C. These data indicate that these alloy packs will need to be analyzed and conditioned to maintain the control of their aluminum activity.

Deposition of aluminum from halide activated packs to form aluminide coatings on superalloys has been shown to be a diffusion controlled process. The data in Figure 24 and Table 14 demonstrate that the formation of the CCRS coatings is also diffusion controlled. However, there are two distinct regions of aluminum deposition. Aluminum deposition at short time (0-4 hours) is a rapid process which forms the (Co-20Ni-25Cr-0.5Y)Al coating. Continued aluminum deposition for times to 64 hours proceeds at a slow rate similar to that observed for the formation of aluminide coatings on the nickel-base alloy, IN-100, by Levine and Caves(10). They found that these aluminum deposition rates for a 1 percent aluminum pack were 4 $mg/cm^2/hr^{1/2}$ at 1149° C and 1.5 $mg/cm^2/hr^{1/2}$ at 1038° C, which are to be compared with the values of 3.2 $mg/cm^2/hr^{1/2}$ at 1149° C (not shown) and 1.4 $mg/cm^2/hr^{1/2}$ on IN-713 found in this work.

The slopes of the measured portions of the plots (solid lines) in Figure 24 decreased as the aluminum deposition pack was changed from 4 to 2 as would be expected for a diffusion controlled process. When these slopes, both the measured values at long times (4-64 hours) and the estimated values at short time (0-4 hours), are plotted versus the aluminum activity of the deposition pack, two straight lines are obtained as shown in Figure 25. The measure of an aluminum deposition pack activity is the ratio, Al/Al + (Co+Ni + Fe = M), and since the modifier and the substrate are identical in all these experiments, it is proportional to the aluminum concentration gradient. Chromium is not included in this activity measure because almost pure Cr can exist in contact with nickel, cobalt and iron β-MAl aluminides.

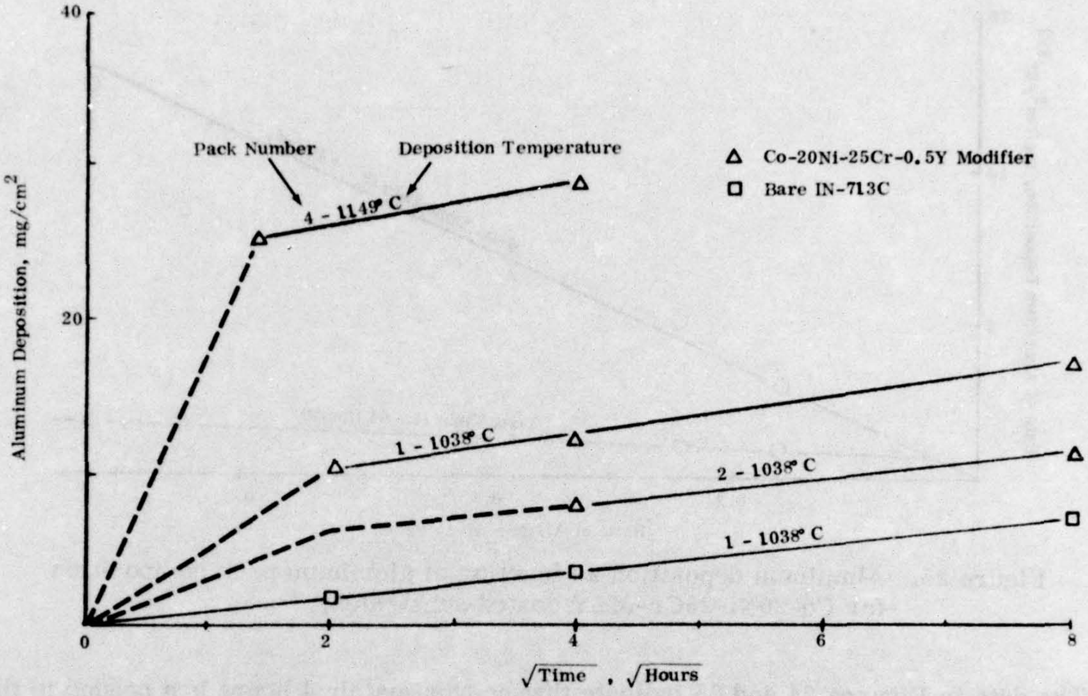


Figure 24. Aluminum deposition as function of time for Co-20Ni-25Cr-0.5Y coated substrates.

TABLE 14. ALUMINUM DEPOSITION ON Co-20Ni-25Cr-0.5Y COATED IN-713C SPECIMENS AS A FUNCTION OF TIME AND PACK ACTIVITY

Modifier Deposition (mg/cm^2)	Pack Number	Deposition Temperature (° C)	Deposition Time (hours)	Aluminum Deposition (mg/cm^2)
58	4	1149	2	25
59	4	1149	16	29
49	1	1038	4	10.3
60	1	1038	16	11.8
63	1	1038	64	18.0
50	2	1038	16	7.5
80	2	1038	64	11
None	1	1038	4	2.1
None	1	1038	16	3.8
None	1	1038	64	9.2

Note: These data are presented in Figure 24.

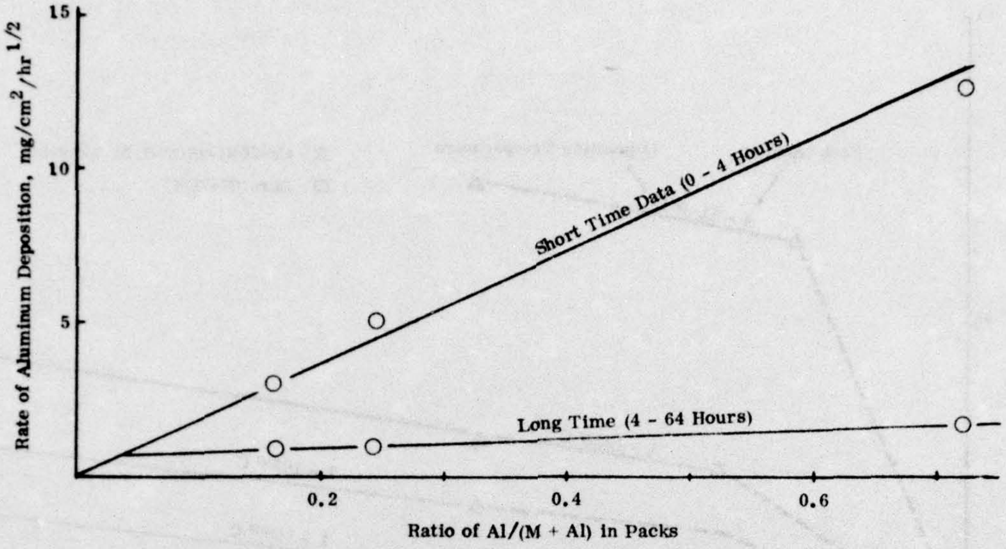


Figure 25. Aluminum deposition as function of aluminum pack composition for Co-20Ni-25Cr-0.5Y coated substrates.

The data in Figures 24 and 25 indicate that approximately 4 hours are needed in the CCRS process to seal the surface of the modifier coated specimen. Since the modifier coated specimens have a large surface area relative to the modifier-free specimen, the deposition rate is larger also. After 4 hours, however, the composite structure has been reduced in effective surface area to a value similar to that of an uncoated specimen and the rate of deposition of aluminum is also similar.

The correlation of the data in Figure 25 with aluminum activity indicates that the temperature dependence of the aluminum deposition in forming (Co-20Ni-25Cr-0.5Y)Al coatings is minor in contrast to the formation of β-NiAl from dense nickel base superalloys(10). It was determined that (Co-20Ni-25Cr-0.5Y)Al and (Co-25Cr-0.5Y)Al coatings formed at 982° C were poorly bonded to the underlying substrate alloy; whereas, MCrAlY coatings formed at 1038° C and higher temperatures were adequately bonded to the IN-713C substrate. This minimal temperature dependence of the formation of the (Co-20Ni-25Cr-0.5Y)Al coating above 1038° C will permit the concurrent deposition of this coating and heat treatment of the superalloys.

When the conditions of coating formation are restricted further to a single aluminum deposition temperature (1038° C) and deposition time (64 hours), the aluminum activity of the pack in concert with the nickel content of the modifier determines the aluminum content of the coating. This effect was shown in Figure 22. These data also demonstrate the effect of a small addition of nickel on the aluminum content of the CCRS-MCrAlY coatings. This enhanced aluminum content of the nickel bearing coatings is responsible for the increased crucible sulfidation life of these coatings as shown in Figure 23. In this figure all the CoCrAlY with the exception of the PVD ATD-1 coating have aluminum contents less than 10 percent while the CoNiCrAlY coatings have aluminum contents in excess of 15 percent. Referring to the phase diagram (Fig. 26), it will be seen that aluminum contents above 5 percent lead to increasing amounts of β-MAl. The Al content in concert with the Cr content provides the sulfidation resistance of the MCrAlY coating.

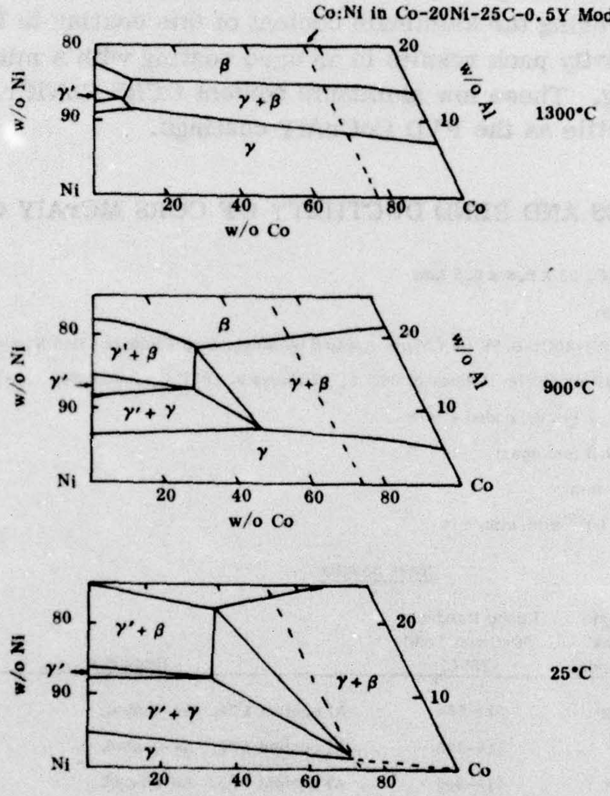


Figure 26. Al-Co-Ni phase diagram (11).

The CCRS-MCrAlY coatings were tested for furnace oxidation and furnace sulfidation resistance as well as bend ductility in order to demonstrate that their performances are equivalent to the PVD CoCrAlY coating. Furnace oxidation of these MCrAlY coatings was discontinued as a viable test since it was not easy to distinguish between the durability of the substrate and a simple aluminide coating. The results of these tests have been summarized along with the furance sulfidation results in the Appendix.

The final test applied to compare the CCRS (Co-20Ni-25Cr-0.5Y)Al coating with the PVD Co-25Cr-12.5Al-0.5Y was bend ductility and microhardness of the coatings. The results of these tests are presented in Table 15. As expected, the as-coated 17 percent aluminum content CCRS CoNiCrAlY coating lacks ductility at 537° C and has a microhardness of 514-565 KHN. However, when this coating is aged for 36 hours at 955° C to precipitate some γCo-Ni-Cr in the β-MAl matrix, the 537° C ductility increases and the microhardness drops to 488 KHN. (The formation of the γCo-NiAl phase in the solution aged Co-17Ni-21Cr-15Al-0.4Y coating could not be resolved optically.) Lowering the aluminum content of this coating to 15 percent by forming it in a lower activity pack results in an aged coating with a microhardness less than the PVD coating. These low aluminum content CCRS CoNiCrAlY coatings are expected to be as ductile as the PVD CoCrAlY coatings.

TABLE 15. HARDNESS AND BEND DUCTILITY OF CCRS MCrAlY COATINGS

Substrates: IN-713C, 25 x 9.6 x 0.5 mm

Coating Parameters:

Modifier: Co-20Ni-25Cr-0.5Y or <37μm Applied by Single Step Fluidized Bed Process

Aluminum Deposition Cycle: 1 Hour at 342° C, 64 Hours at 1037° C, Packs No. 1 and 2.

Bend Test Fixture: 3 Point Loaded Beam

Beam Supports: 19.5 mm apart

Punch Radius: 1.5 mm

Strain Rate: 6.8 x 10^{-3} mm/mm/min

Test Results

Temperature	Bend Angle To Crack Appearance	Knoop Hardness 50-Gram Load (25° C)	Remarks
537° C	0.69°	514-565	Al content 17%. As-coated.
537° C	2.1°	514-565	Al content 17%. As-coated.
510° C	1.2°	514-565	Al content 17%. As-coated.
537° C	6.0°	488	Al content 17%. Solution treated at 1037° C 15 minutes and aged 36 hours at 955° C.
537° C	>10°	447-458	Al content 12.5%. Co-25Cr-12.5Al-0.35Y PVD coating.
510° C	>10°	447-458	Al content 12.5%. Co-25Cr-12.5Al-0.35Y PVD coating.
482° C	>10°	447-458	Al content 12.5%. Co-25Cr-12.5Al-0.35Y PVD coating.
454° C	3°*	447-458	Al content 12.5%. Co-25Cr-12.5Al-0.35Y PVD coating.
25° C	**	426-436	Al content 15%. Solution aged 24 hours at 916° C.
537° C	74°	371-379	Al content 6%. IN-713C substrate.

* The progressive bend test of this coating resulted in a total bend angle to coating cracking of 33°.

** Not tested.

SECTION IV

CONCLUSION

The single-cycle fluidized bed application of the MCrY modifier and controlled composition reaction sintering in an aluminizing pack have shown themselves to be feasible processes for depositing the MCrAlY coating on simple blade shapes. The chemistry and thus the performance of these coatings can be controlled by the chemistries of the modifier, control of aluminum pack activity and the use of post-coating heat treatments. The CoNiCrAlY has superior sulfidation resistance to CoCrAlY coating deposited by CCRS process because of the higher aluminum content of the former.

These CoNiCrAlY coatings with 15 percent aluminum in the solution treated and aged condition afford measurable ductility at temperatures as low as 537° C. The ductility is less than for the PVD CoCrAlY coating at 12.5 percent aluminum but far greater than conventional aluminized coating or the CCRS coatings in the "as applied" condition.

The goals of Task I of this program have been met and the next phase of this program coating development should be pursued.

SECTION V
RECOMMENDATIONS

The successful attainment of the objectives of Task I is strong justification for continuation of development of the fluidized bed CCRS process for applying the MCrAlY coatings. The continuation and completion will be divided into three tasks:

Task II - Coating/Process Development

In this task the fluidized bed-CCRS process will be developed to produce Co-17Ni-21Cr-15Al-0.4Y coating on the nickel-base alloy, IN-100. The composition of this coating will be systematically changed by varying the aluminum content of the modifier to improve the oxidation and hot corrosion resistance or the thermal expansion and other mechanical properties of the CoNiCrAlY coating. Diagnostic evaluation of these composition changes on the properties and microstructure of the CoNiCrAlY coating will be conducted and documented. The utility of the fluidized bed-CCRS process will be verified by coating multiple vane segments which cannot be coated satisfactorily by physical vapor deposition methods.

Task III - Coating Process Evaluation

In this task, the effectiveness of the fluidized bed-CCRS process for producing the CoNiCrAlY coatings will be evaluated by a rigorous test program. Specimens of MA-754 (an oxide dispersion strengthened nickel-base alloy) and PVD-CoCrAlY coated IN-100 will be performance tested in the burner rig for hot corrosion and oxidation-erosion resistance. They will also be tested for stress rupture, low cycle fatigue and impact resistance. This testing program will adequately demonstrate the effectiveness of the fluidized bed-CCRS produced CoNiCrAlY coatings in protecting nickel-base superalloys.

Task IV - Scale-up and Cost Analysis

A production plan for applying the fluidized bed-CCRS deposited CoNiCrAlY to gas turbine components will be prepared. This plan will also include a survey of the capital equipment, labor, energy and material required for the production level coating of both new and used turbine blades and vanes. A survey of coating jobbers and manufacturers will be made to determine the cost and availability of suitable facilities for producing these CoNiCrAlY coatings. An estimate of typical blade-vane processing costs will be made.

SECTION VI

REFERENCES

1. Goward, G.W., Proceedings 1974 Gas Turbine Materials Conference, Ed. John W. Fairbanks and Irving Machlin, Metals and Ceramics Information Center, Battelle, Columbus, Ohio, pp. 277-296 (1975).

2. Fairbanks, John W., Ibid, pp. 429-456.

3. Stetson, A.R. and Moore, V.S., Ibid, pp. 457-480.

4. Moore, V.S. and Stetson, A.R., "Hot Corrosion Resistant Aluminide Coatings of Controlled Composition for Nickel-Base Superalloys", Contract N00156-71-C-1020, Naval Air Propulsion Test Center (July 1973).

5. Miller, G.W., "Thermal Characterization of Polymers", Applied Polymer Symposia, No. 10, pp. 35-72 (1969).

6. Landrock, A.H., "Fluidized Bed Coating", Encyclopedia of Polymer Science and Technology, Ed., H. F. Mark, N. Gaylord and N. M. Bikales, Vol. 3, Interscience, New York, pp. 808-830 (1965).

7. Hansen, M., Constitution of Binary Alloys, McGraw-Hill, New York, p. 80 (1958).

8. Hollenberg, G.W., Terwilliger, G.R. and Gordon, R.S., J. Am. Ceramic Soc., 54, pp. 196-199 (1971).

9. Blocher, Jr., J.M., "The Development of Chromium-Base Heat Resistant Alloys", WADC Technical Report 53-470, Contract AF33(616)-48 (January 1954).

10. Levine, S.R. and Caves, R.M., J. Electrochem. Soc., 121, pp. 1051-1064 (1974).

11. Schramm, J., Metallkunde, 33, pp. 412-463 (1941).

APPENDIX

RESULTS OF FURNACE OXIDATION AND SULFIDATION TESTING OF THE CCRS-CoCrAlY AND CoNiCrAlY COATING

APPENDIX

RESULTS OF FURNACE OXIDATION AND SULFIDATION TESTING OF THE CCRS-CoCrAlY AND CoNiCrAlY COATINGS

The furnace oxidation and sulfidation testing of a portion of the CCRS CoNiCrAlY and CoCrAlY coatings produced during the program resulted in the data shown in Figures 27 and 28. These data indicate that the coating degradation mechanisms are following parabolic kinetics. These tests were discontinued because of the difficulty in intrepreting the changes in slope and relating them to a possible failure sequence in the coating. For example, Figures 29 and 30 show presumably failed specimens tested as in Figures 27 and 28. Both micrographs, however, show the coatings to be intact in the region examined and no failure seems eminent.

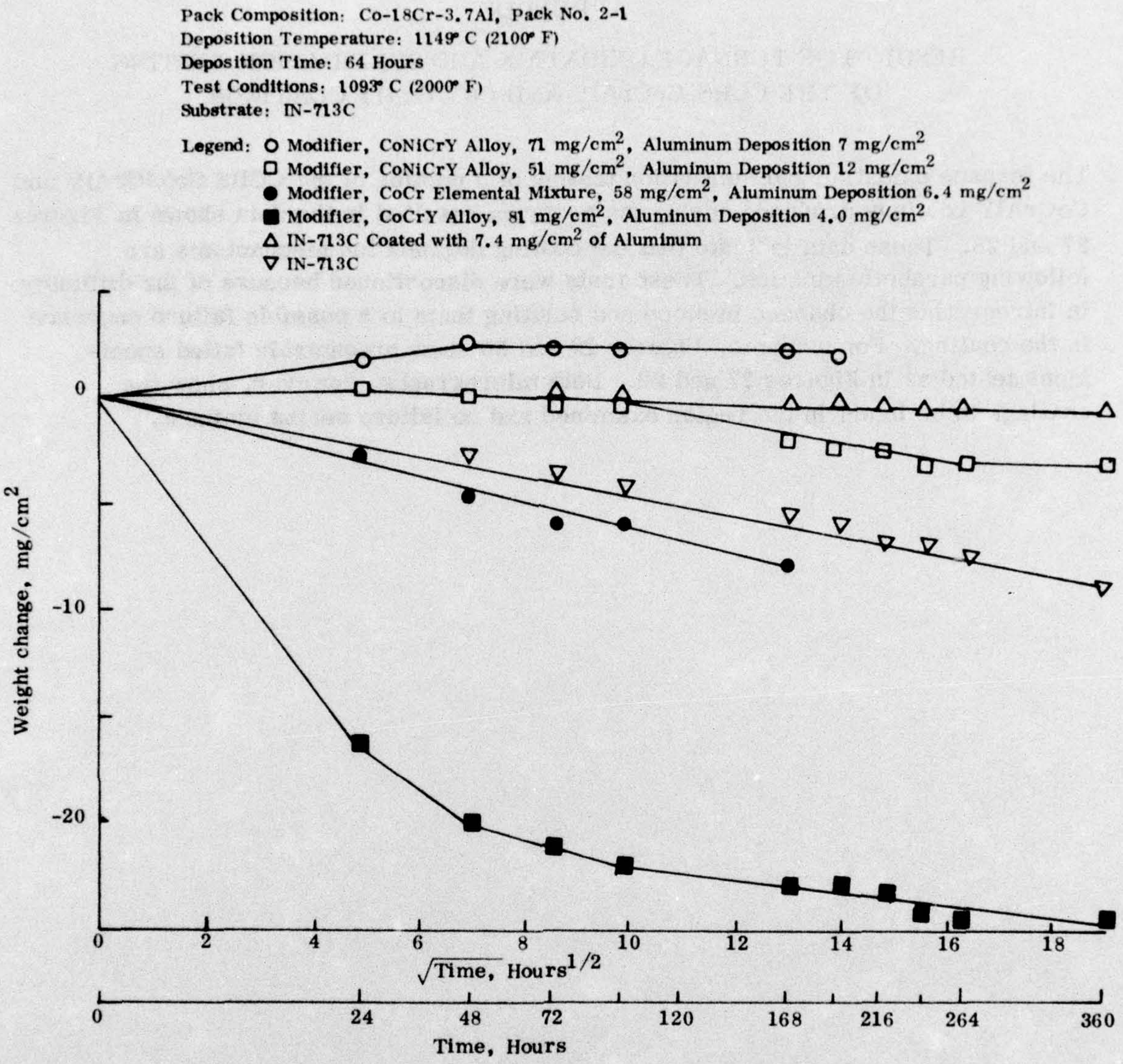


Figure 27. Furnace oxidation behavior of CCRS coatings.

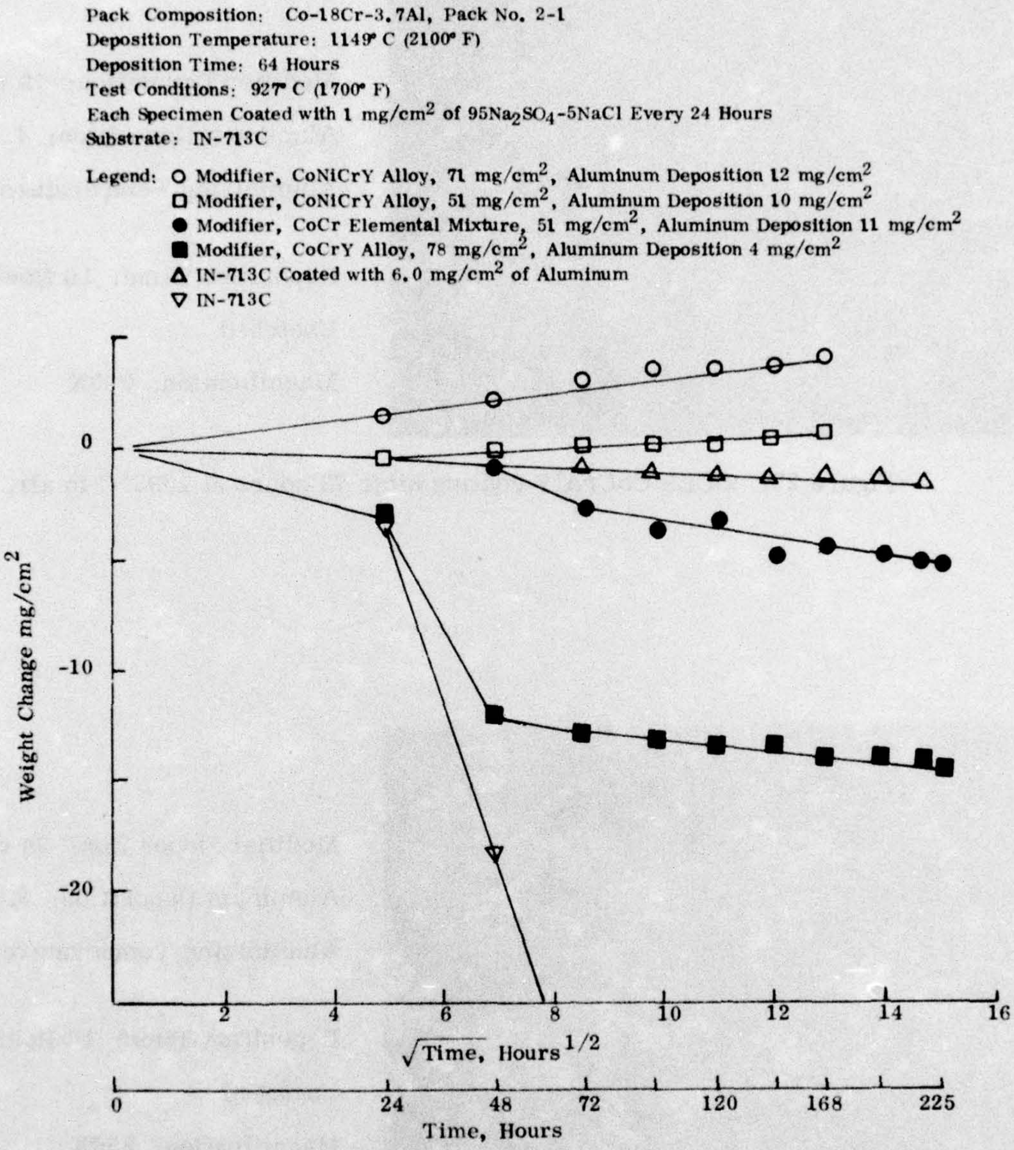
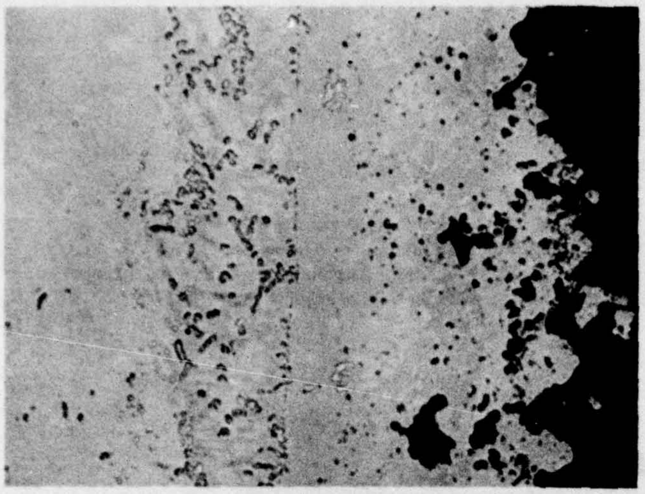


Figure 28. Furnace sulfidation behavior of CCRS coatings.



Modifier Deposition: 73 mg/cm^2

Aluminum Deposition: 4.5 mg/cm^2

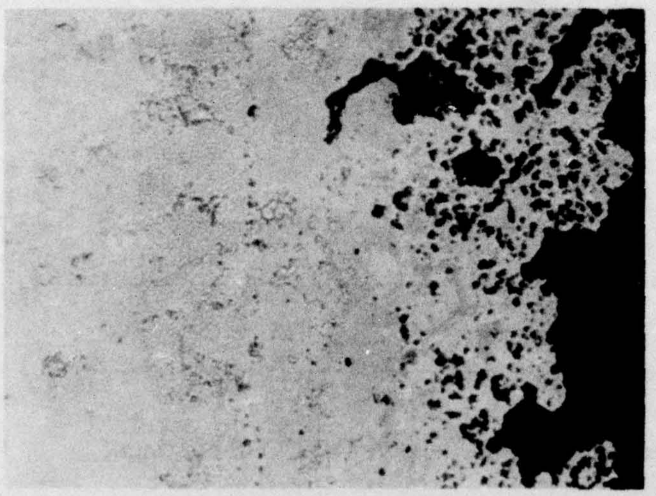
Aluminizing Temperature: 1037° C, Pack 3'

Deposition Time: 16 Hours

Unetched

Magnification: 250X

Figure 29. CCRS CoCrAlY coating after 72 hours at 1093° C in air.



Modifier Deposition: 70 mg/cm^2

Aluminum Deposition: 8.5 mg/cm^2

Aluminizing Temperature: 1037° C, Pack 3'

Deposition Time: 16 Hours

Unetched

Magnification: 250X

Figure 30. CCRS CoCrAlY coating after 72 hours furnace sulfidation at 937° C.

☆ U. S. GOVERNMENT PRINTING OFFICE: 1976 — 757-001/46