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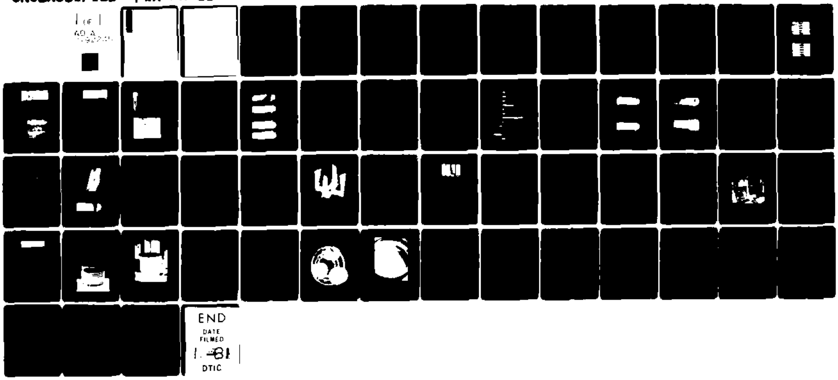

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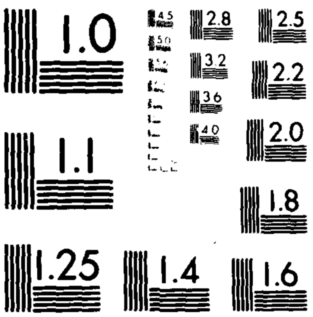

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The objectives of this program were to design, construct, and qualify a new, large reactor suitable for coating titanium alloy compressor components with titanium carbonitride (Ti-Cote C®) on a production basis. Materials Technology Corporation (MTC), the sole source of Ti-Cote C, was responsible for the reactor scale-up and subsequent development effort. Microprobe and metallographic studies, erosion testing, the establishment of an S/N curve with coated airfoils, and a determination of the thermal shock resistance of coated airfoils were performed at Pratt & Whitney Aircraft/Government Products Division (P&WA/GPD) on parts coated in the new reactor.

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20. At the conclusion of the program, the scaled up reactor was still unable to deliver the consistent coating quality required for production. Coating coverage, adhesion and thermal shock resistance were acceptable, but the erosion resistance varied greatly between reactor runs of identical parameters. The problem with the erosion resistance appeared to be related to the somewhat porous and granular microstructure of Ti-Cote C deposited in the new, hot wall reactor. No compositional variations were detected in the coating to explain the grainy structure and inconsistent erosion resistance. MTC performed a parametric study to improve coating reproducibility but it was not entirely successful.

FOREWORD

The report was prepared by the Government Products Division of the Pratt & Whitney Aircraft Group of United Technologies Corporation for the U.S. Army Materials and Mechanics Research Center under Contract DAAG-46-77-C-0057 and covers work accomplished during the period ending June 1979.

Mr. Charles C. McComas was the Program Manager for the contract at the Pratt & Whitney Aircraft Group and Mr. Larry S. Sokol was the responsible Engineer.

Technical monitor of the program for the U. S. Army Materials and Mechanics Research Center was Mr. Milton Levy of the Metals Research Division.

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SECTION I

INTRODUCTION

The use of Ti-Cote C® (titanium carbonitride) as an erosion-resistant coating for protection of titanium alloy compressor airfoils in small gas turbine engines has previously been investigated in AMMRC contracts: DAAG46-71-C-0173, DAAG46-73-C-0249, DAAG46-76-C-0079 and DAAG46-76-C-0080. During these programs it was demonstrated that Ti-Cote C provided a significant increase in erosion resistance compared to uncoated Ti-6Al-4V components. However, several major problems surfaced with the Ti-Cote C coated airfoils. First, fatigue strength reductions as great as 60% resulted from the application of the Ti-Cote C system. Secondly, the adhesion of the Ti-Cote C was erratic and the coating was prone to spalling along the airfoil edges. Finally, in the current state of development, the process to apply Ti-Cote C was not suited to coating gas turbine engine hardware on a production basis.

Materials Technology Corporation (MTC), the sole source for application of Ti-Cote C, believed that all of the problems could be eliminated by a change in reactor design from a cold-wall reactor to a hot-wall reactor. The primary purpose of this contract, therefore, was to build and qualify a new, large hot-wall reactor suitable for coating small compressor airfoils on a production basis.

The design and construction of the scaled-up, hot-wall, production-type reactor was performed by MTC under subcontract to Pratt & Whitney Aircraft Government Products Division (P&WA/GPD). MTC was also responsible for the establishment of the necessary operating parameters and for the application of titanium carbonitride to titanium alloy test specimens and compressor airfoils. P&WA/GPD was responsible for conducting the detailed laboratory investigations necessary to determine the physical characteristics of titanium carbonitride coatings deposited in the new reactor. The laboratory investigations at P&WA/GPD consisted of microprobe and metallographic studies, erosion testing, the establishment of an S/N curve with coated airfoil samples, and a determination of the thermal shock resistance of coated airfoils. Preliminary nondestructive inspection (NDI) requirements for coated airfoils were also investigated.

In addition, 12 Krouse fatigue specimens were coated with the Ti-Cote C system and delivered to AMMRC. These specimens incorporated a copper strike layer of increased thickness (greater than 0.00025 in.) under the PWA 36 electroless nickel.

The electroless nickel with copper strike serves as an undercoat for the titanium carbonitride. These samples were prepared because microprobe analysis performed under Contract DAAG46-76-C-0079 suggested that an increased thickness of the copper strike may be beneficial in preventing large losses in fatigue strength of Ti-Cote C coated titanium alloy parts.

DESIGN, CONSTRUCTION AND OPERATION PARAMETER DEVELOPMENT FOR THE SCALED-UP, HOT-WALL REACTOR

The reactor design and construction, and the optimization of operating parameters for deposition of Ti-Cote C titanium carbonitride were all performed by MTC under subcontract to the P&WA/GPD. The MTC has prepared a complete report detailing their activities which is presented in Section III with several notes added by P&WA/GPD based on laboratory evaluation of the Ti-Cote C coated airfoils and sample coupons.

SECTION II

TECHNICAL DISCUSSION

INTRODUCTION

Laboratory verification of the physical characteristics of the Ti-Cote C (titanium carbonitride) consisted of the following efforts:

1. Metallographic Evaluation
2. Verification of Erosion Resistance of Production Samples
3. Establishment of an S/N Curve
4. Determination of the Thermal Shock Resistance of Coated Airfoils.

METALLOGRAPHIC EVALUATION

Early in the program it became apparent that Materials Technology Corporation (MTC) was having considerable difficulty obtaining adequate adhesion between the Ti-Cote C and the new PWA 36 electroless plated nickel underlayer.

This problem was clearly evident during the application of Ti-Cote C to the electroless nickel-plated Krouse rotating beam specimens. Figure 1 illustrates the difficulty encountered in obtaining adequate adhesion of the Ti-Cote C. Spalling of the Ti-Cote C has occurred on three of the twelve Krouse beam samples. Several attempts were made by MTC to improve the adhesion, and Figure 1 represents the best results that were obtained.

MTC did report success, however, in applying Ti-Cote C directly onto titanium-alloy coupons, which were then sent to GPD for metallographic analysis. Examination of the bond line between the titanium carbonitride coating and titanium alloy substrate under the scanning electron microscope disclosed a uniform bond line free of voids and other defects. Furthermore, there was no indication of any corrosive damage to the titanium 6Al-4V. This had been a matter of concern due to the corrosive nature of the reactive gases and reaction products in the Ti-Cote C coating process. The electroless-plated nickel undercoat was previously thought to be necessary as a barrier layer to prevent corrosion to the titanium 6Al-4V substrate and to promote adhesion of the Ti-Cote C. No damage was visible, however, to the titanium 6Al-4V substrate. One major concern still remained, and that was the possibility of hydrogen embrittlement to the titanium substrate resulting in fatigue strength reductions even greater than those seen in the previous AMMRC contracts. The establishment of an S/N curve ultimately answered the question. Fatigue strength reductions were comparable to those obtained with a sulfamate nickel underlayer and were slightly greater than those obtained with the electroless-plated nickel phosphorous underlayer. Hydrogen embrittlement, therefore, although a possible cause of the loss of fatigue strength, created no more of a problem under the testing conditions than was experienced with nickel-plated titanium alloys.

One immediately obvious microstructural characteristic of the Ti-Cote C deposited in the hot-wall reactor was the decrease in coating integrity. Figure 2, is an optical microscope photomicrograph of the Ti-Cote C deposited on one of the small compressor airfoils. Figure 3 is a scanning electron microscope (SEM) picture taken of the same coated airfoil section. The porosity in the Ti-Cote C is plainly visible in the SEM photomicrograph. Under the optical microscope at lower magnification (Figure 2) this porosity gives the Ti-Cote C a very grainy appearance. By contrast, Figure 4 is a photomicrograph of Ti-Cote C deposited during one of the prior AMMRC contracts using the cold-wall reactor design. Notice the solid and void-free microsctructure of the cold-wall reactor titanium carbonitride compared to material applied during this current contract.

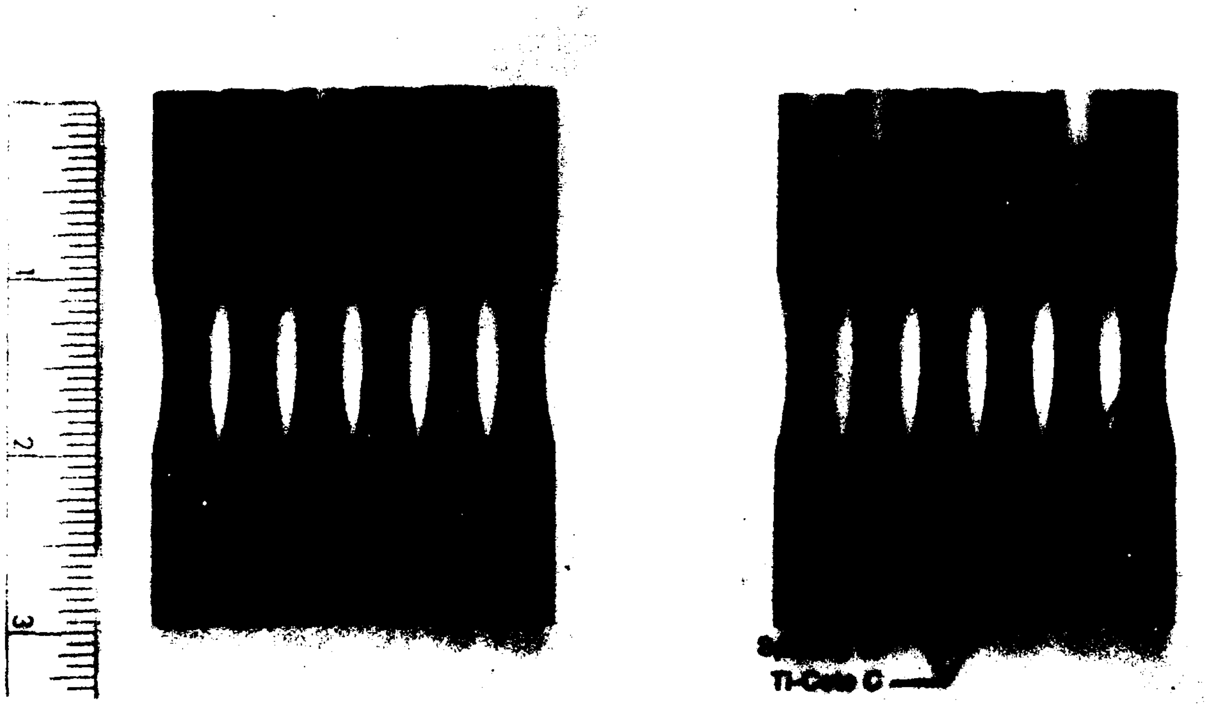


Figure 1. Krouse Rotating Beam Specimens Incorporating a Copper Strike Greater than 0.00025 in. Thick Within the PWA 36, Ti-Cote C System.

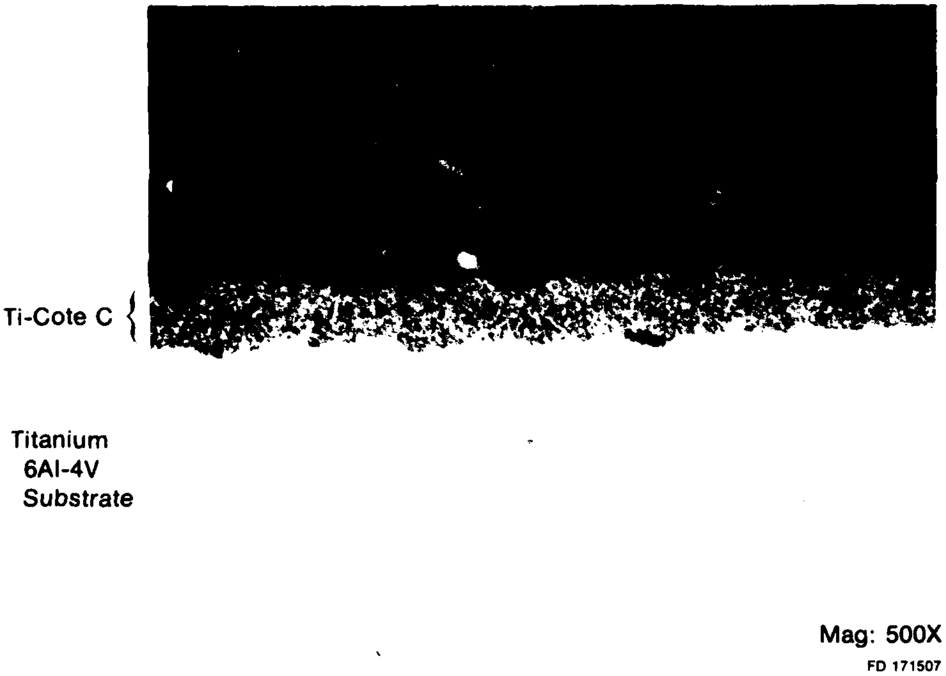


Figure 2. *Ti-Cote C on JT12 Compressor 7th-Stage Airfoil — Optical Photomicrograph*

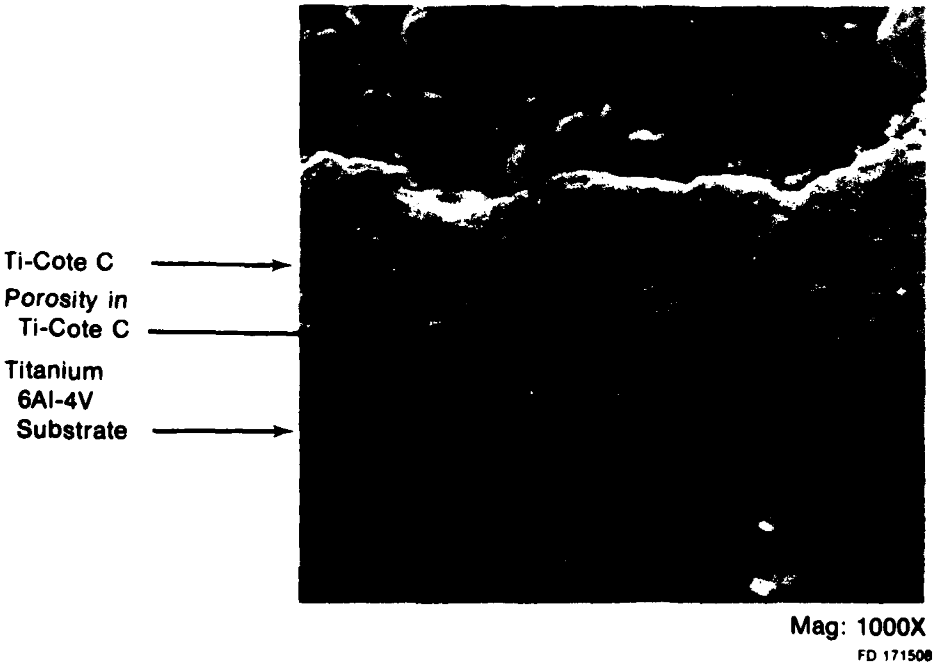


Figure 3. *Ti-Cote C on JT12 Compressor 7th-Stage Airfoil — Scanning Electron Microscope (SEM) Photograph*

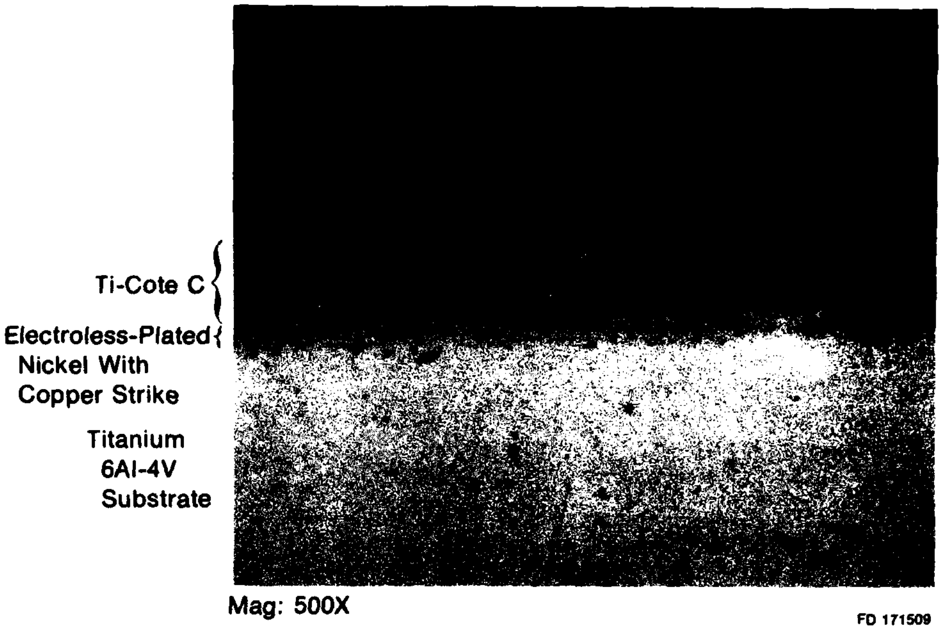


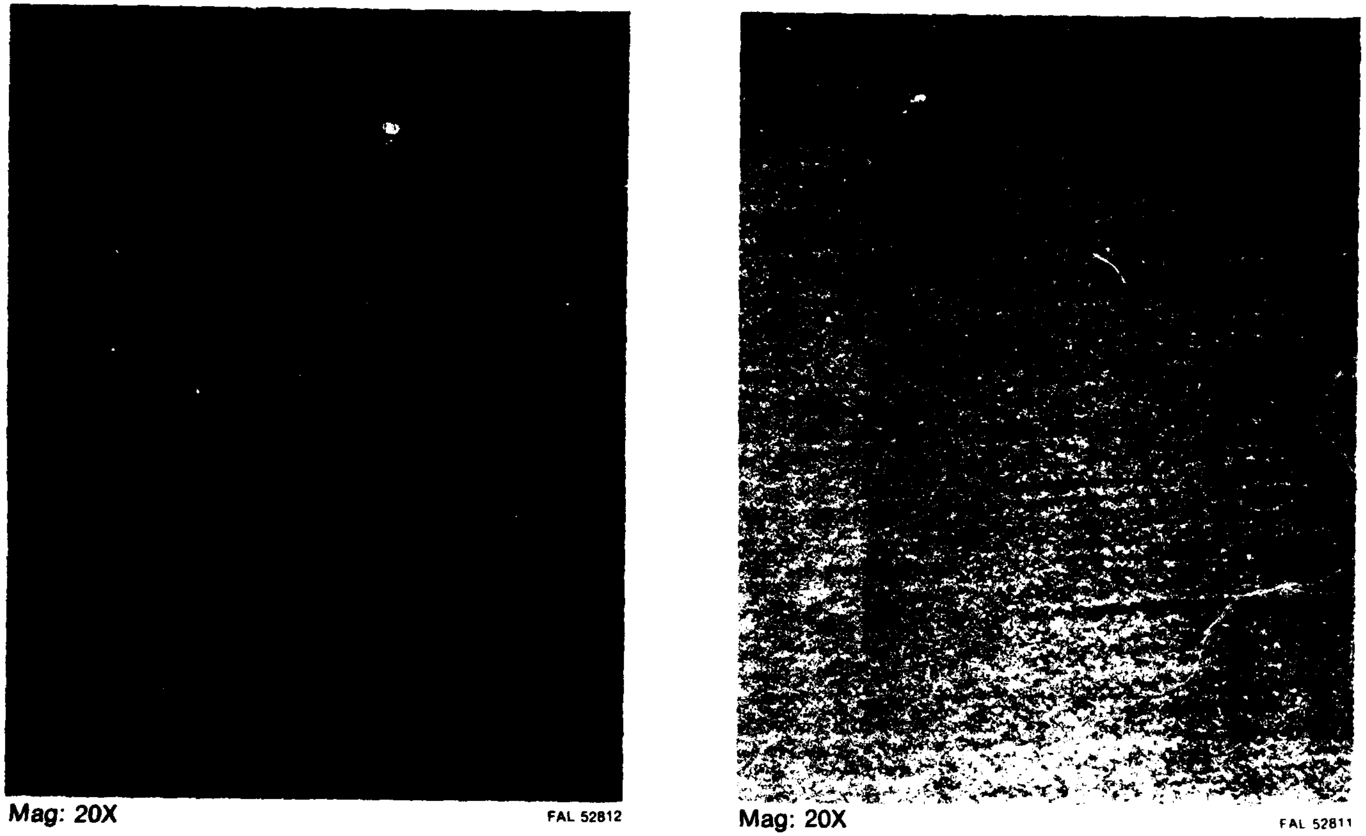
Figure 4. Ti-Cote C Deposited in a Cold-Wall Reactor

In an effort to determine if a change in chemical composition was producing the porosity and grainy texture in the titanium carbonitride microstructure, the Ti-Cote C was scanned with the microprobe on the SEM. Because the microprobe is unable to accurately detect levels of light elements such as carbon or nitrogen, the probe was primarily useful in measuring the total quantity and distribution of titanium and chlorine. Chlorine is an impurity and probably results from incomplete reaction of the titanium tetrachloride.

The results of the scan show that the chlorine level was evenly distributed throughout the Ti-Cote C at a concentration of about one weight percent. This was consistent with previous scans of cold-wall reactor deposited Ti-Cote C. No detectable amount of chlorine had diffused into the titanium 6Al-4V substrate.

The concentration of titanium in the Ti-Cote C was measured at 70 weight percent. Once again, this is comparable to the results obtained on cold-wall reactor coatings. Distribution of the titanium was uniform. In summary, no compositional variations were found with the SEM that would account for the porosity and grainy texture of the titanium carbonitride. These coating defects, therefore, are most probably a result of premature reaction of the titanium tetrachloride and trimethylamine. As discussed in the MTC report, prereaction is a potential drawback of the hot-wall reactor system.

The grainy appearance of the hot-wall reactor titanium carbonitride is reflected in the surface finish of the coating. Figure 5 is a 20X magnified photograph of the convex and concave Ti-Cote C coated surfaces of one of the JT12 compressor 7th-stage titanium alloy airfoils. This part is typical of all the airfoils and test coupons. In almost all cases, one surface was smoother than the other. On airfoils, however, it was not always the convex surface that displayed the most roughness. There was an equal probability that the concave surface would have the roughest finish.



Convex

Concave

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Figure 5. *Surface Appearance at 20X Magnification of Ti-Cote C on a JT12 Compressor 7th-Stage Airfoil.*

A study was also made of the completeness of coating coverage and uniformity of coating deposition on an airfoil. Figure 6 shows two of the JT12 compressor 7th-stage blades after Ti-Cote C application. These parts were in the last batch coated, and therefore should be considered representative of the typical production quality attainable in the present state of development of the hot-wall reactor.

As illustrated in Figure 6, coating coverage was very good. Only a small area at the base of the airfoil on the platform showed any indication of poor coating adhesion. On the airfoil surface itself, coating adhesion appeared to be excellent.

Two cross sections were made through the coated airfoil to determine the uniformity of coating coverage around the part. One cut was made just below the blade tip and the second section was taken immediately above the platform. Figure 7 maps the coating thickness at various locations around the airfoil. All coating thicknesses were measured optically at 1000X magnification. Thickness control appears to be quite acceptable. The rough surface finish of the Ti-Cote C is partially responsible for the deviations that do exist in coating thickness.

VERIFICATION OF EROSION RESISTANCE OF PRODUCTION SAMPLES

Erosion resistance testing at best is only useful in determining relative rates of erosion between different materials. The primary purpose of this test, therefore, was to ascertain if any change in erosion resistance could be noticed between Ti-Cote C applied in the scaled-up hot-wall reactor and Ti-Cote C deposited under either Contracts DAAG46-76-C-0079 or DAAG46-73-C-0249 using a cold-wall reactor.

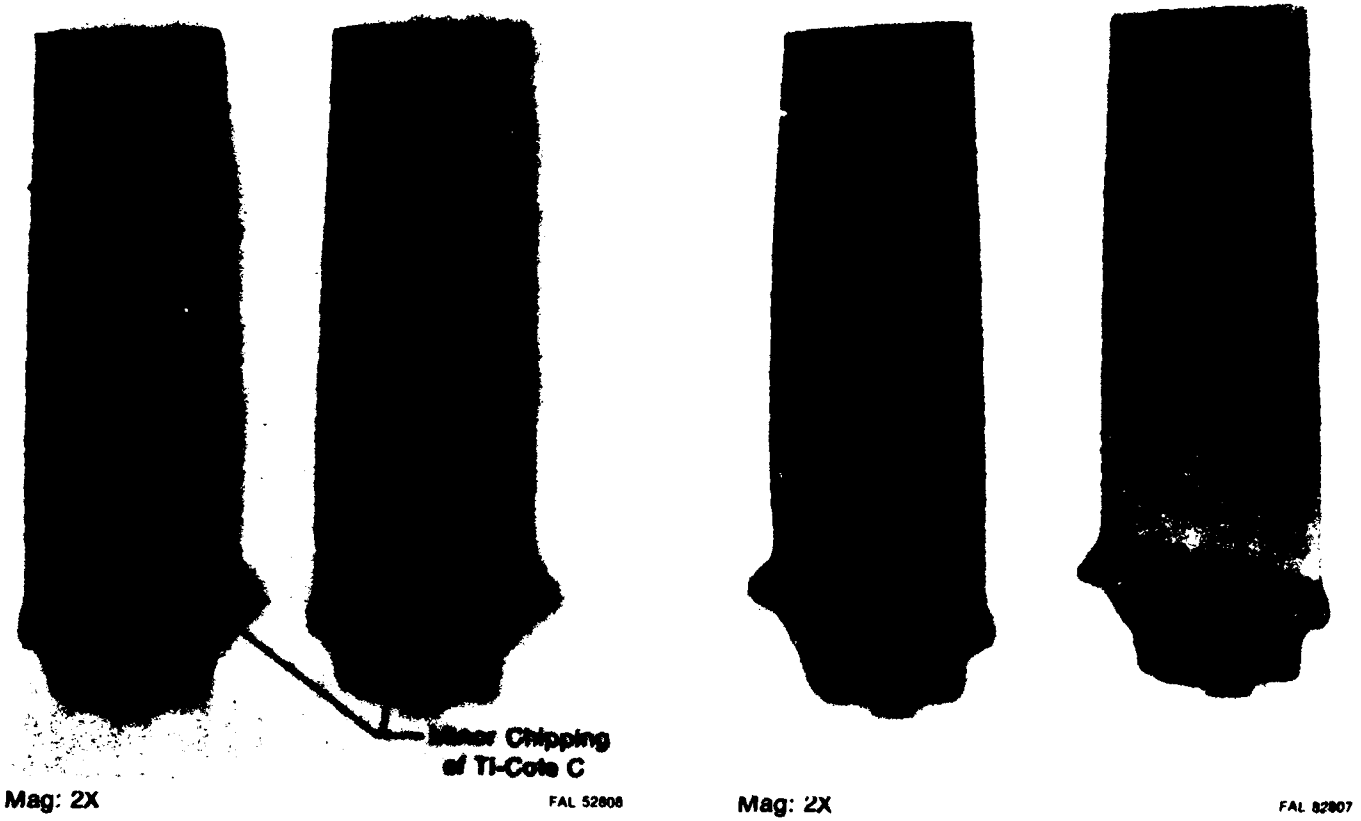
All erosion testing was initially performed at 75°F utilizing an SS White Airbrasive unit. The abrasive media was SS White Powder Number 1 which is a nominal 27μ aluminum oxide. Impingement velocity was calculated at approximately 500 feet per second. In all cases, test coupons coated with Ti-Cote C under Contracts DAAG46-73-C-0249 and DAAG46-76-C-0079 were run as a reference along with uncoated titanium 6Al-4V (AMS 4911).

The erosion resistance of the Ti-Cote C deposited in the scaled-up hot-wall reactor was initially very poor. Table 1 lists the results of the first erosion testing performed under this contract. At this stage, Ti-Cote C applied in the hot-wall reactor provided little protection as compared to titanium carbonitride applied in the cold-wall reactor. In addition, the pattern of material removal was significantly different between the current and previous Ti-Cote C coatings. The hot-wall reactor-deposited material would fail by the sudden loss of small granular particles. Ti-Cote C applied in the cold-wall reactor eroded in a uniform manner with no indication of granular particle breakouts.

The erosion pattern of the hot-wall reactor coating was not unexpected. The surface of the Ti-Cote C from the hot-wall reactor is rough and grainy, and the microstructure is grainy and porous as discussed in the section on metallographic examination. No correlation was evident between microhardness and erosion resistance; however, all samples tested for erosion resistance were of similar hardness, 2200-2400 Knoop.

Elevated temperature erosion testing at 600°F was not performed at this time because of the extremely poor room temperature test results.

MTC was immediately notified of the lack of erosion resistance and they began work at once to correct the problem. During the time period when MTC was working to improve the erosion resistance, all erosion testing was performed at MTC and the results are reported in Section III of this report on Reactor Development. Whenever MTC believed a significant improvement had been attained, samples were sent to GPD for verification of results.



Convex Surface

Concave Surface

Figure 6. JT12 Compressor 7th-Stage Airfoils After Being Coated With Ti-Cote C

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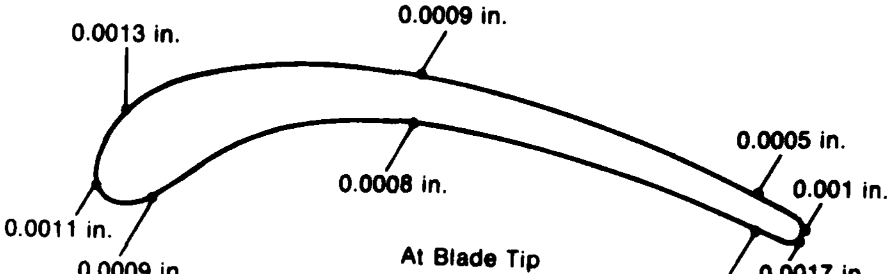
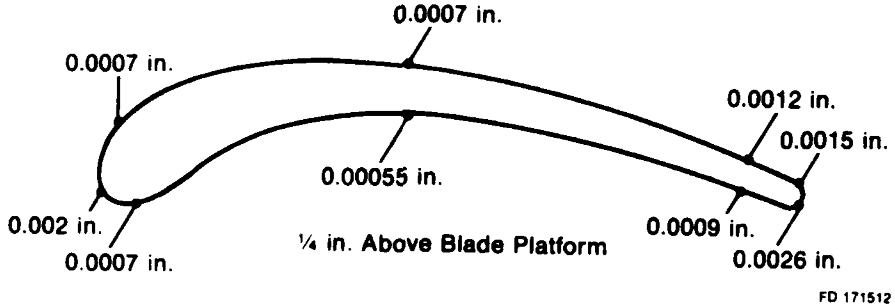


At Blade Tip



¼ in. Above Blade Platform

Figure 7. Thickness Distribution of Ti-Cote C on a JT12 Compressor 7th-Stage Airfoil

TABLE 1. INITIAL EROSION TESTING OF TI-COTE C

	Time to Penetrate	*0.001 in. of Ti-Cote C*
	90-deg Impingement	*20-deg Impingement*
Ti-Cote C (Hot-Wall Reactor)	25 to 40 sec	112 to 150 sec
Ti-Cote C (Cold-Wall Reactor, Contract DAAG46-73-C-0249)	890 to 900 sec	3860 sec

Tables 2 and 3 present the 75 and 600°F relative erosion rates of the last test coupons submitted to GPD for evaluation. As previously mentioned, the 75°F testing was performed using an SS White Abrasive unit and 27μ aluminum oxide. The 600°F testing was accomplished utilizing a specially designed elevated temperature erosion rig previously developed by GPD. The GPD erosion rig impacts the test coupon with 27μ aluminum oxide traveling at a velocity of 1000 feet per second in a hot (600°F+) gas stream. The surface temperature of the part being tested is continually monitored by a thermocouple thereby guaranteeing reproducible and accurate data. The heated gas stream carrying the abrasive assures that the surface temperature of the test coupon is maintained at the test temperature. This represents a considerable improvement over most other elevated temperature erosion rigs that heat the back side of test samples in a furnace while cooling the surface being eroded with a cold blast of abrasive and propellant gas.

TABLE 2. ROOM TEMPERATURE EROSION RATES AT A 90-DEG IMPINGEMENT ANGLE MEASURED WITH FLAT TEST COUPONS

	Erosion Rate	*Time to Penetrate 0.001 in. of coating*
AMS 4911 (Uncoated)	31 × 10^{6} g/sec (7.0 × 10^{6} cc/sec)	—
Ti-Cote C (Cold-Wall Reactor, Contract DAAG46-73-C-0249)	—	887 sec
Ti-Cote C (Small Hot-Wall Reactor, Contract DAAG46-76-C-0079)	11 × 10^{6} g/sec (2.2 × 10^{6} cc/sec)	360 sec
Ti-Cote C (Hot Wall Reactor, Run D-48)	9.1 × 10^{6} g/sec (1.8 × 10^{6} cc/sec)	370 sec

TABLE 3. 600°F EROSION RATES AT VARIOUS IMPINGEMENT ANGLES MEASURED WITH FLAT TEST COUPONS

	Erosion Rate		
	90-deg Impingement	*60-deg Impingement*	*30-deg Impingement*
AMS 4911 (Uncoated)	25 × 10^{6} g/sec (5.7 × 10^{6} cc/sec)	39 × 10^{6} g/sec (8.8 × 10^{6} cc/sec)	7.6 × 10^{6} g/sec (1.7 × 10^{6} cc/sec)
Ti-Cote C (Cold-Wall Reactor Contract DAAG46-73-C-0249)	9.6 × 10^{6} g/sec (1.86 × 10^{6} cc/sec)	4.1 × 10^{6} g/sec (0.8 × 10^{6} cc/sec)	3.6 × 10^{6} g/sec (0.7 × 10^{6} cc/sec)
Ti-Cote C (Hot-Wall Reactor Run D-48)	8.2 × 10^{6} g/sec (1.6 × 10^{6} cc/sec)	2.3 × 10^{6} g/sec (0.45 × 10^{6} cc/sec)	4.6 × 10^{6} g/sec (0.88 × 10^{6} cc/sec)

The test data detailed in Tables 2 and 3 indicated that MTC had been able to successfully increase the erosion resistance of the Ti-Cote C to the same level as that achieved under prior AMMRC contracts. To assure the accuracy of the erosion rates in Tables 2 and 3, the samples from run D-48 were tested concurrently with uncoated AMS 4911 titanium and Ti-Cote C specimens prepared under Contracts DAAG46-73-C-0249 and DAAG46-76-C-0079. The surface finish was still rough on the D-48 samples but large grains of Ti-Cote C were not being removed during testing. Consequently, MTC was advised to coat the small airfoils with duplicate parameters and submit the Ti-Cote C-coated airfoils to GPD for evaluation.

The results of 75 and 600°F erosion testing performed on coated airfoils are given in Tables 4 and 5, respectively. As is readily apparent from the calculated erosion rates, the erosion resistance of the airfoil coatings is not consistent with the test coupons. In fact, the Ti-Cote C on the airfoils offers little if any erosion resistance at 600°F except at a 30-deg impingement angle.

Figure 8 summarizes the data presented in Tables 2 through 5 in a graphical format. All erosion rates in Figure 8 are expressed in terms of rate of volume loss of Ti-Cote C relative to that of titanium 6Al-4V under identical conditions. Bars above the 1.0 line indicate better erosion resistance than Ti-6Al-4V, while bars below the 1.0 line represent less erosion resistance than Ti-6Al-4V. The lowest erosion resistance was measured on the Ti-Cote C-coated JT12 blades at 600°F. At a 90-deg impingement angle, the Ti-Cote C had only 34% of the erosion resistance of uncoated Ti-6Al-4V. This contrasts sharply with the results obtained on flat test coupons. Under identical conditions, Ti-Cote C deposited on the flat coupons was 2.5 times as resistant to erosion as Ti-6Al-4V.

Materials Technology Corporation was unable to find any deviation between the parameters used to coat the test coupons and the airfoils. The only conclusion that can be drawn, therefore, is that despite an intensive effort by MTC, the Ti-Cote C application process in a production-type reactor is very inconsistent. The reasons for the inconsistent erosion results are presently not understood by MTC, and the process at this time cannot be relied upon for production coating of titanium compressor airfoils.

TABLE 4. ROOM TEMPERATURE (75°F) EROSION RATES

	Erosion Rate	
	90-deg Impingement	*30-deg Impingement*
AMS 4911 (Uncoated)	38 × 10^{-6} g/sec (8.6 × 10^{-6} cc/sec)	120 × 10^{-6} g/sec (27 × 10^{-6} cc/sec)
Ti-Cote C on JT12 7th Stage Airfoil (Hot-Wall Reactor Run D-49)	63 × 10^{-6} g/sec[1] (12 × 10^{-6} cc/sec)	76 × 10^{-6} g/sec[2] (15 × 10^{-6} cc/sec)

[1] Ti-Cote C began to fail at 19 sec. Test discontinued at 30 sec

[2] Ti-Cote C began to fail at 25 sec. Test discontinued at 60 sec

TABLE 5. 600°F EROSION RATES AT VARIOUS IMPINGEMENT ANGLES

	Erosion Rate	
	90-deg Impingement	*30-deg Impingement*
AMS 4911 (Uncoated)	13.6 × 10^{-6} g/sec (3.1 × 10^{-6} cc/sec)	40.7 × 10^{-6} g/sec (9.2 × 10^{-6} cc/sec)
Ti-Cote C on JT12 7th-Stage Airfoil (Hot-Wall Reactor Run D-49)	47 × 10^{-6} g/sec (9.1 × 10^{-6} cc/sec)	11.6 × 10^{-6} g/sec (2.3 × 10^{-6} cc/sec)

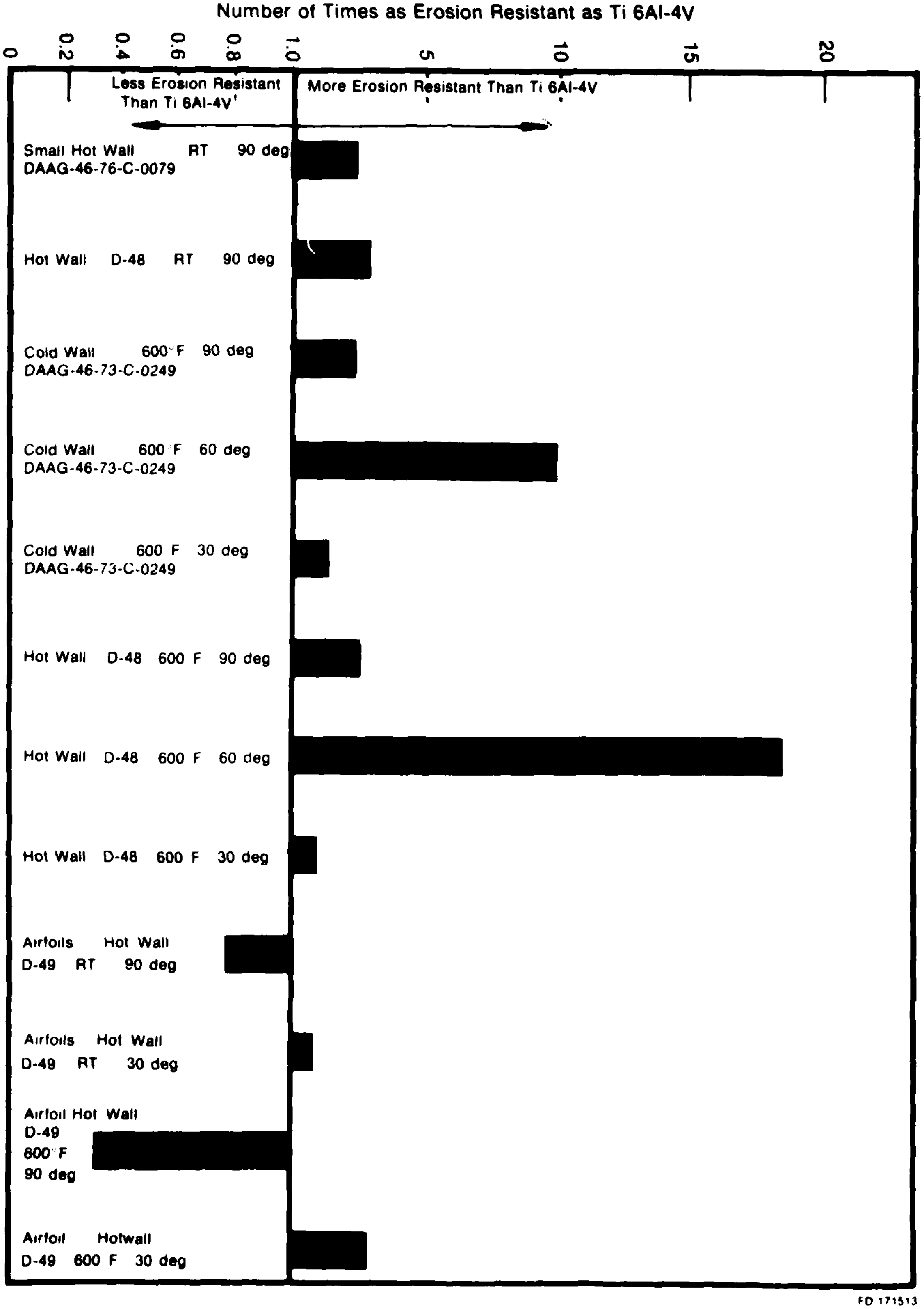


Figure 8 Ti-Cote C Erosion Protection for Ti-6Al-4V

ESTABLISHMENT OF AN S/N CURVE

P&WA/GPD conducted 600°F fatigue testing using JT12 7th-stage compressor blades (P/N 536207A/AMS 4928) as the test vehicle. Coated and uncoated blades were tested to establish baseline results and hot-wall reactor coated results for comparison with previous HCF cold-wall reactor coated results (Contract DAAG 46-73-C-0249) established using Krouse rotating beam specimens.

Test Procedure

Blade-coating configurations tested were:

1. Uncoated blades (baseline).
2. Blades coated with Ti-Cote C in a hot-wall reactor by chemical vapor deposition.
3. Ti-Cote C blades stripped and recoated with Ti-Cote C at increased reactor temperatures.

All testing was conducted with blade roots restrained in a JT12 7th-stage broached fixture and jackbolt-loaded from the rear. Maximum stress (calibration) locations were determined from stresscoat patterns obtained in the first bending mode of vibration at room temperature (Figure 9). Calibration strain gages were located as shown in Figure 10, and stress vs blade tip double amplitude relationships established, Figure 11, from which fatigue stress levels could be determined.

Each blade was fatigue tested to failure (or 10^7 cycles) at 600°F in the first bending mode of vibration. Test results are listed in Table 6 and S-N curves are shown in Figures 12 and 13. A typical concave leading edge fatigue failure is illustrated in Figure 14.

Elevated temperatures were accomplished using electric resistance heating to produce a uniform 600°F test environment allowing elevated temperature test amplitudes to be determined from the AMS 4928 modulus change at 600°F.

The stripped and recoated blades received were badly damaged on the trailing edge near the platform as a result of the acid etch process used to strip away the original coating. The trailing edge damage was blended out prior to testing to prevent premature failures in the damaged area. Stresscoat patterns, calibration strain gage locations (Figure 15), and calibration curves (Figure 16) were established for the modified blades.

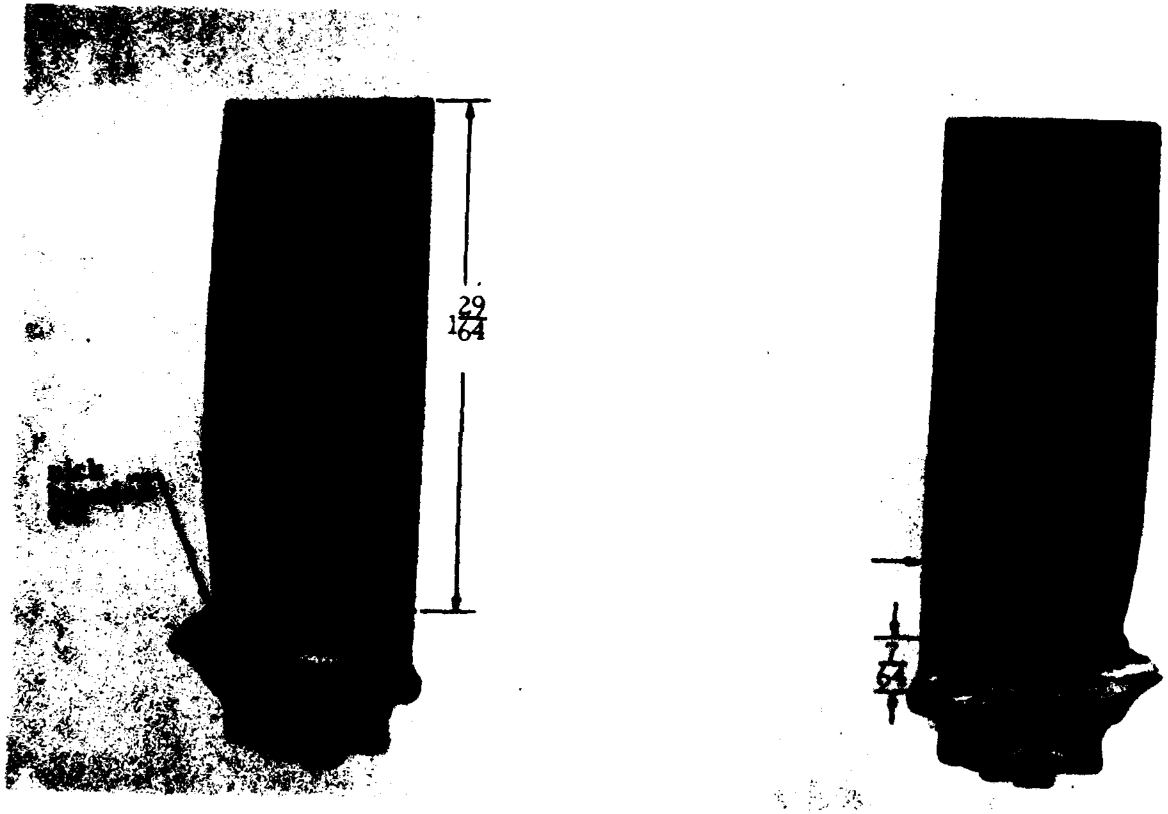


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Figure 9. JT12 7th-Stage Compressor Blade, P/N 536207-A Showing Stresscoat Pattern and Strain Gage Locations Resulting from the First Bending Mode of Vibration With Trailing Edge Nicks Blended Out

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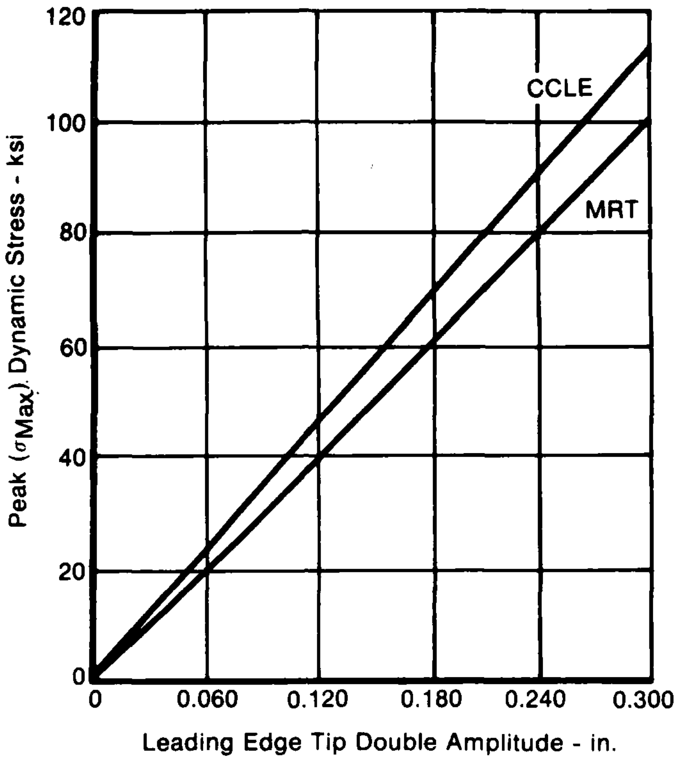
Figure 10. JT12 7th-Stage Compressor Blade, P/N 536207-A Showing Stresscoat Pattern and Strain Gage Locations Resulting from the First Bending Mode of Vibration



*Stress Based on E = 16.5 x 10^6 psi and Measured at Locations Shown in Figure 10.

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Figure 11. JT12 7th-Stage Compressor Blade, P/N 536207A Vibrated in First Bending Mode of Vibration

TABLE 6. FATIGUE TEST DATA FOR JT12 AMS 4928 7TH-STAGE COMPRESSOR BLADES, P/N 536207A, VIBRATED IN THE FIRST BENDING MODE OF VIBRATION AT 600°F

Serial Number	*Heat Code*	*Type of Coating*	*Test Frequency (Hz)*	*Dynamic Stress (ksi)*	*Cycles to Failure*	*Remarks*
1	AS6	Uncoated	815	80	0.12 × 10^6	Failed on LE.
3	AS6	Uncoated	819	70	2.83 × 10^6	Failed on LE.
4	AS6	Uncoated	842	70	10.0 × 10^6	Did not fail.
5	AS6	Uncoated	783	75	0.175 × 10^6	Failed on LE.
6	AS6	Uncoated	830	75	2.19 × 10^6	Failed on LE.
8	AS6	Uncoated	807	65	10.0 × 10^6	Did not fail.
2	AS6	Ti-Cote C	961	50	0.002 × 10^6	Failed on LE.
3	AS6	Ti-Cote C	944	30	0.067 × 10^6	Failed on LE.
5	AS6	Ti-Cote C	927	25	10.0 × 10^6	Did not fail.
6	AS6	Ti-Cote C	900	30	0.216 × 10^6	Failed on LE.
3	AS6	Ti-Cote C*	819	30	0.029 × 10^6	Failed on LE, MRT, TE.
4	AS6	Ti-Cote C*	864	25	10.0 × 10^6	No failure.
5	AS6	Ti-Cote C*	839	30	0.022 × 10^6	Failed on LE, MRT, TE.
6	AS6	Ti-Cote C*	325	25	10.0 × 10^6	No failure.

*Applied at a higher reactor temperature.

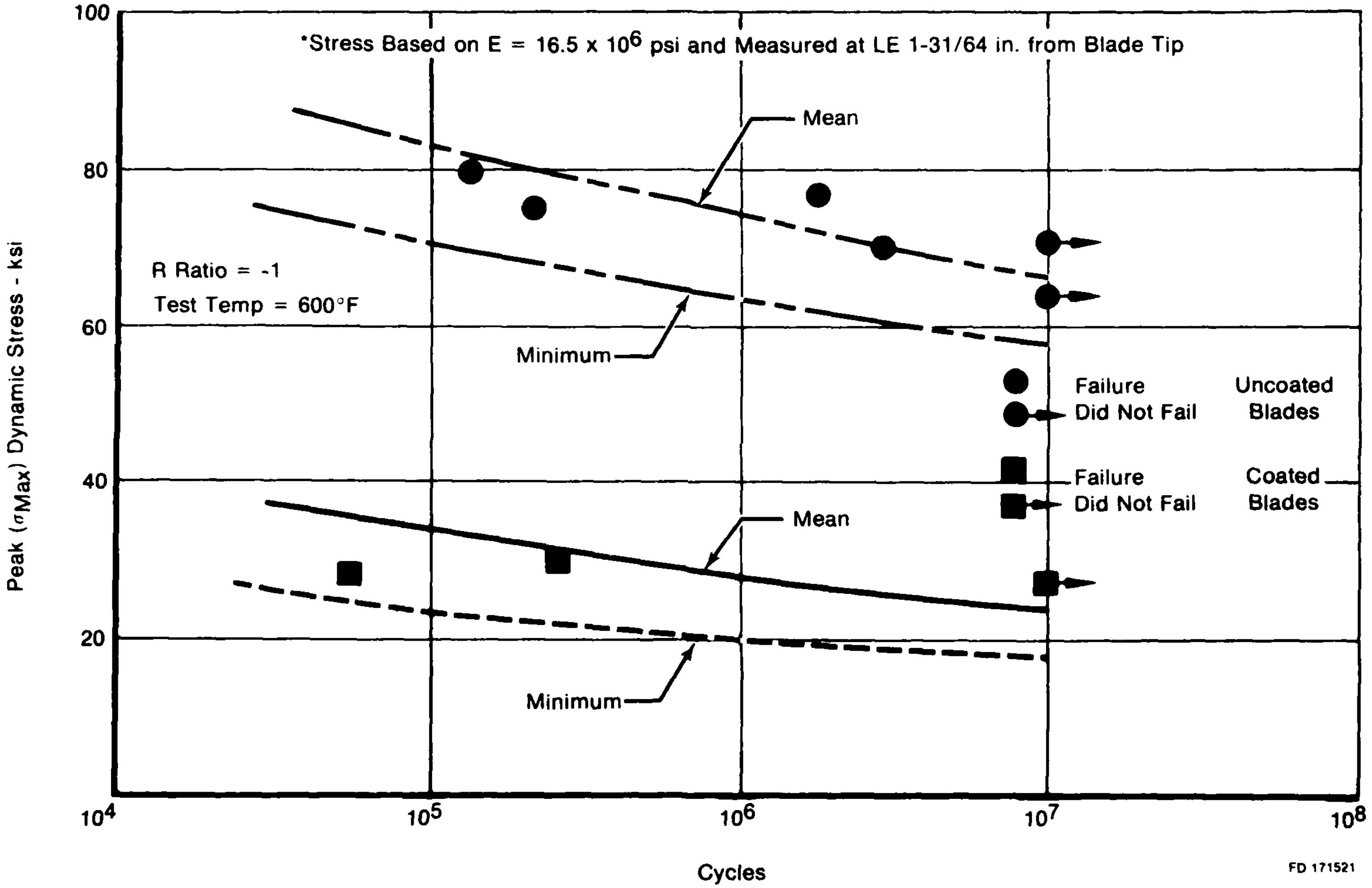

Figure 12. JT12 7th-Stage Compressor Blade, P/N 536207A Coated and Uncoated Ti-Cote C in a Hot-Wall Reactor and Vibrated in First Bending Mode of Vibration

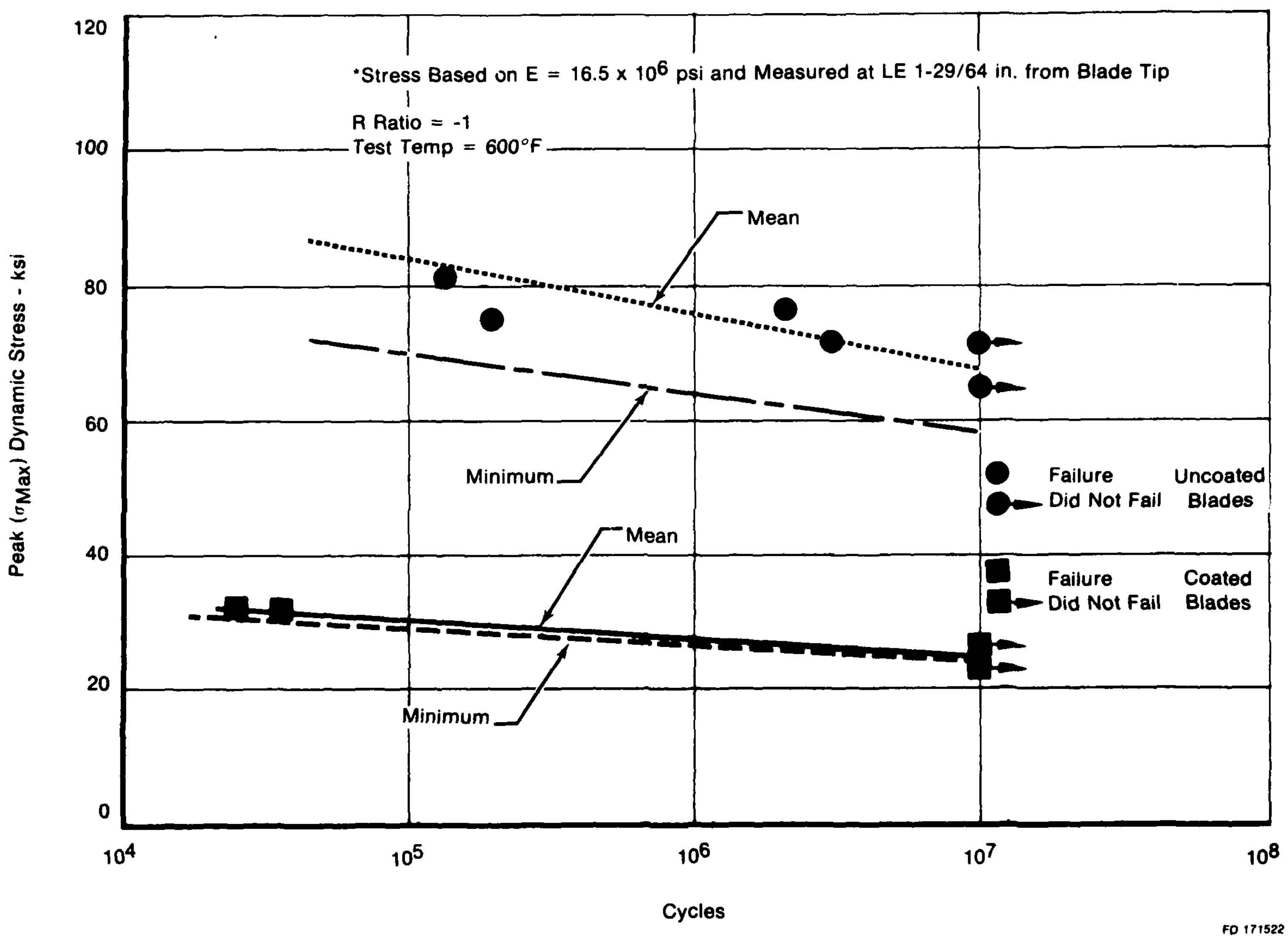

Figure 13. JT12 7th-Stage Compressor Blades, Uncoated and Coated With Ti-Cote C, at Increased Reactor Temperature and Vibrated in First Bending Mode of Vibration

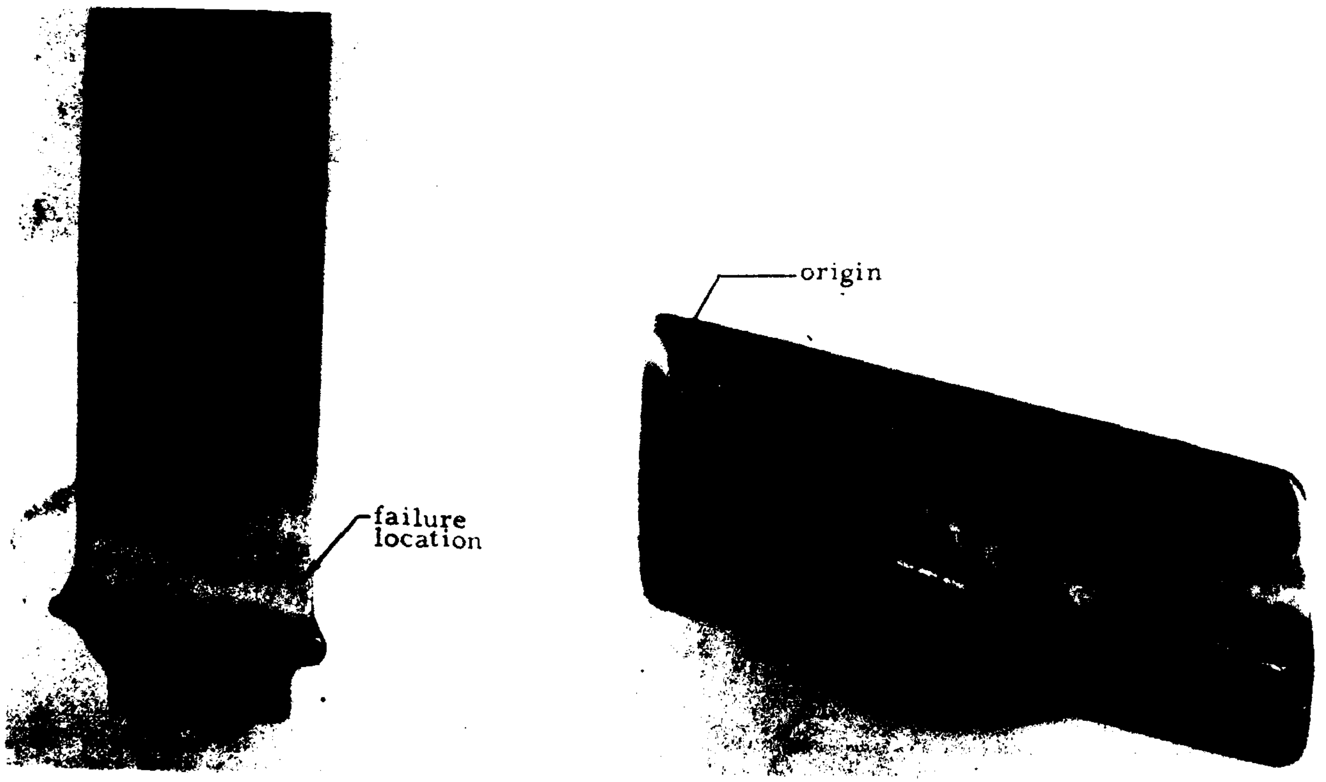

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Figure 14. Compressor Blade Showing Typical Failure Resulting from Fatigue Tests in the First Bending Mode of Vibration at 600°F

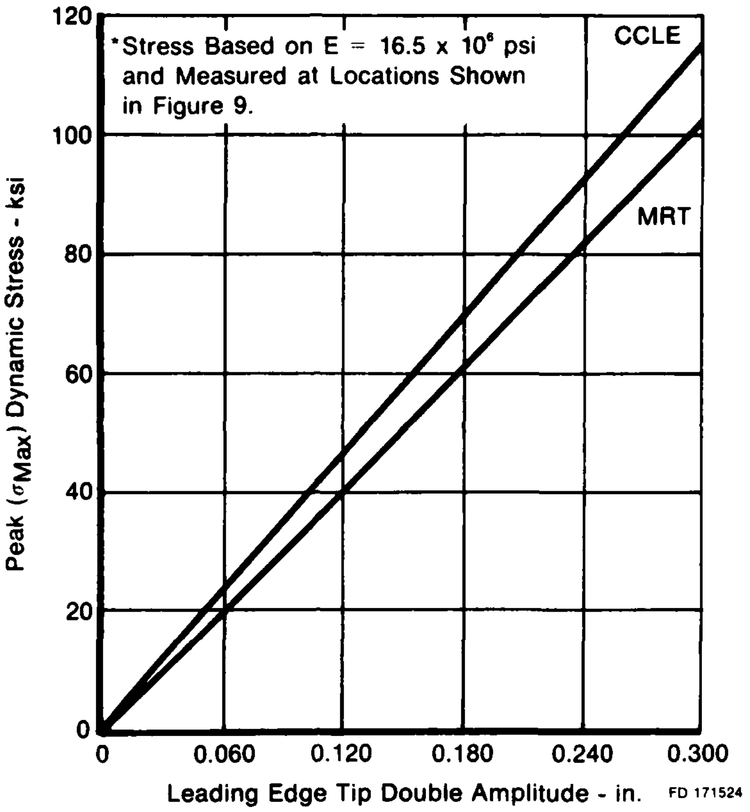
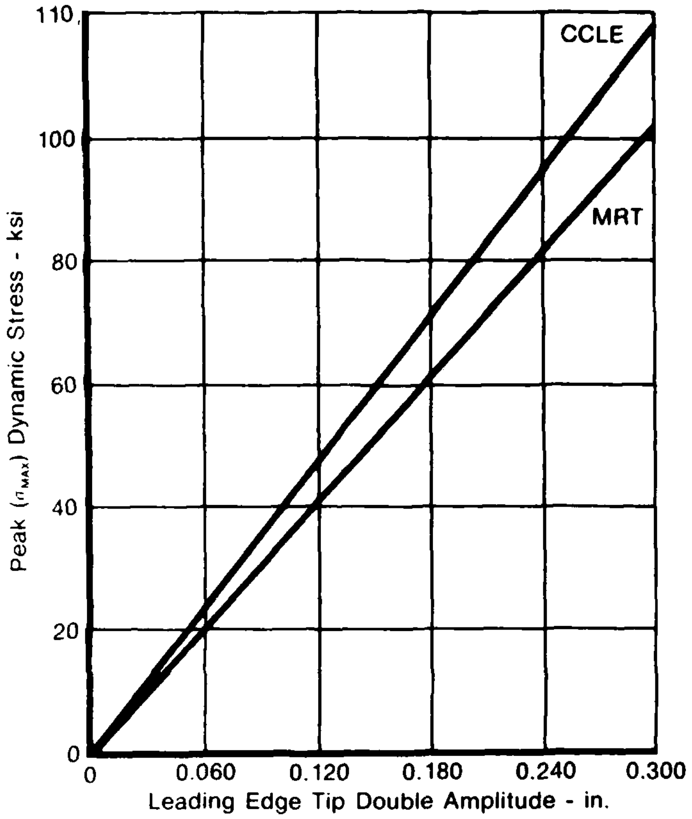


Figure 15. JT12 7th-Stage Compressor Blades Vibrated in First Bending Mode of Vibration With TE Blended Out

JT-12 AMS 4928 7th Stage Compressor Blades, P/N 536207A, Vibrated in First Bending Mode of Vibration with T.E. Nicks Blended Out.



*Stress Based on E = 16.5 x 10^6 psi and Measured at Locations Shown in Figure 9.

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Figure 16. Dynamic Stress vs Tip Double Amplitude*

Conclusions and Results of Fatigue Testing

1. Significant reductions in the 10^7-cycle fatigue strength occur in AMS 4928 airfoils coated with Ti-Cote C using either a cold- or hot-wall reactor for coating application.

2. 10^7-cycle fatigue strength reductions of 64 and 62% were established for the two sets of blade specimens tested as compared to uncoated blade fatigue strength. This compares to a 50% reduction established for 600°F test of rotating beam specimens coated in a cold-wall reactor (Contract DAAG 46-73-C-0249).

3. Mean and minimum fatigue strengths established for all test specimen configurations are:

	600°F — 10^7 Cycle Fatigue Strength (ksi)	
Coating Configuration	*Mean*	*Minimum*
Uncoated	67	59
Coated with Ti-Cote C	24	18
Coated with Ti-Cote C applied at increased reactor temperature	25	24.7

4. The loss of fatigue strength measured on Ti-Cote C coated titanium airfoils is a serious problem. A case-by-case design review of any airfoils considered to be potential candidates for coating will be necessary to determine if such a debit in fatigue strength can be tolerated.

DETERMINATION OF THERMAL SHOCK RESISTANCE OF COATED AIRFOILS

Four "Ti-Cote C"-coated, 7th-stage compressor blades (P/N 536207) were submitted to the P&WA/GPD Cyclic Structures group for thermal shock testing in a fluidized bed. Zirconium silicate marketed by DuPont under the name "Florida Zircon Sand" was used as the medium for the fluidized bed. The fluidized bed provides for rapid thermal transients typical in aircraft engine operation. The four specimens were mounted vertically on a single fixture (Figure 17) and simultaneously cycled in an attempt to provide equivalent test conditions. Calibration runs were made with an uncoated blade, thermocoupled near the airfoil midchord end and operating at the same location as specimen B occupied within the fixture.

The blade airfoils experienced a 100 to 900°F thermal cycle controlled by a cyclic timer which controlled specimen transfer from cold to hot baths. Hot bath temperature was maintained at 970°F ±5°F, and cold bath temperature at 100°F ±5°F for all test cycles.

Figure 18 indicates a typical cycle run of 51 sec with the 900°F temperature reached in 6 sec, and room temperature reached in 29 sec upon entry into hot and cold baths, respectively. Transfers between baths were accomplished in 8 sec. Figure 18 represents six typical thermal cycles superimposed over a single calibration cycle for the airfoil midchord end.

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Figure 17. Fluidized Bed Fixturing for Ti-Cote C Coated F100 7th-Stage Compressor Blades (P/N 536207)

Based on a cursory visual inspection, it can be concluded that the Ti-Cote C coating for airfoil application is acceptable for 1000 cycles within the tested thermal shock environment.

The results of the thermal shock testing are as follows:

1. Each blade experienced spalling of the coating along the root; however, several chips in the root coating were noted before testing and/or weld attachments may have caused this situation.

2. Each specimen exhibited surface oxidation of the airfoil section as evidenced by the coating discoloration (Figure 19).

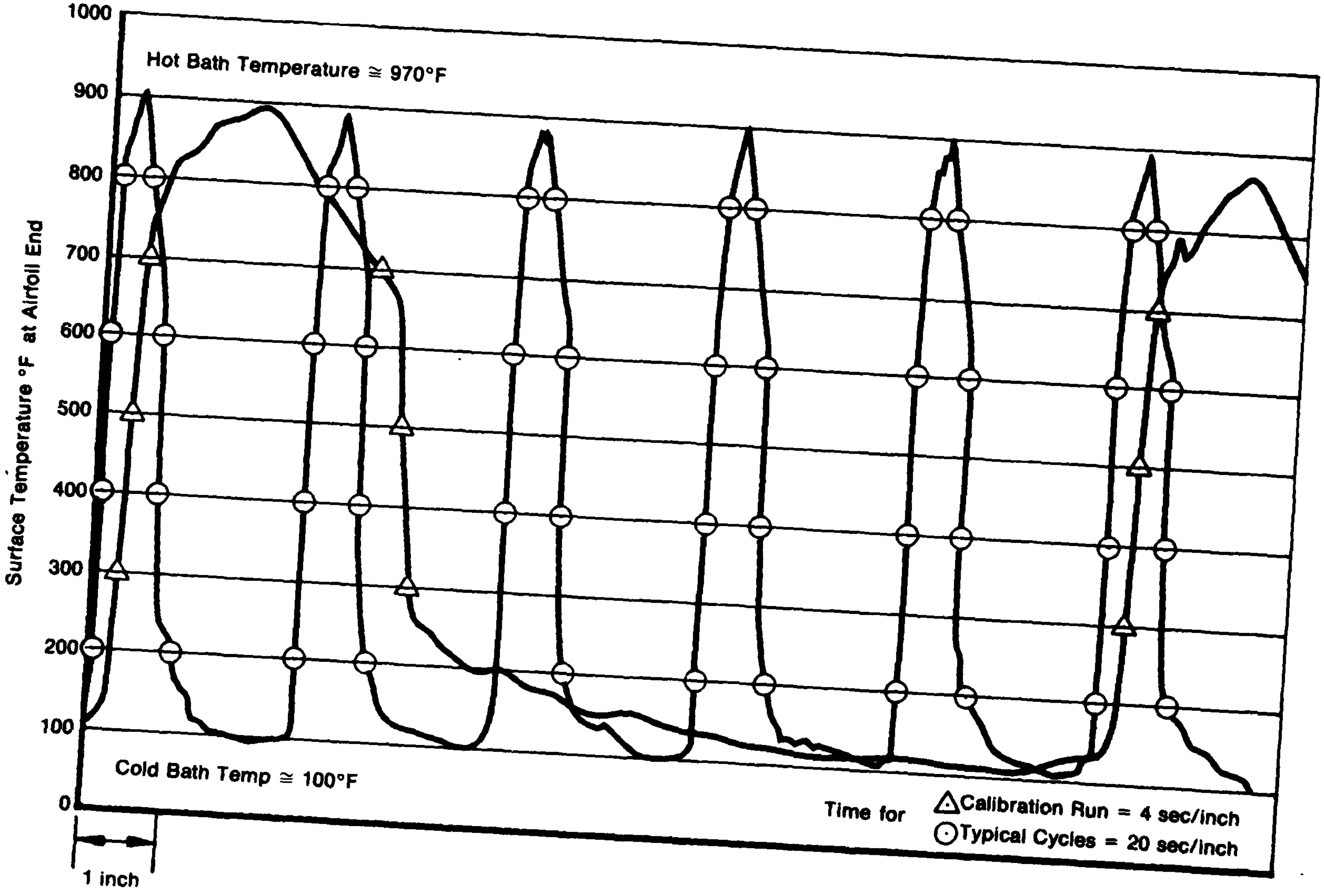

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Figure 18. *Calibration and Typical Thermal Shock Cycles for Fluidized Bed Testing of Ti-Cote C Coated F100 7th-Stage Compressor Blades (P/N 536207).*

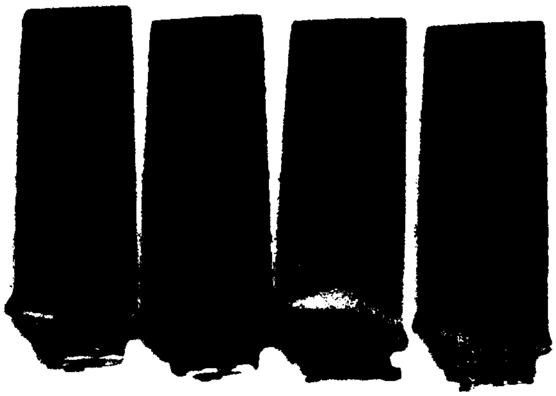

Figure 19. Concave Side of Ti-Cote C Coated F100 7th-Stage Compressor Blades (P/N 536207) After 1000 Fluidized Bed Cycles

PRELIMINARY NONDESTRUCTIVE INSPECTION REQUIREMENTS

An effective Nondestructive Inspection (NDI) technique should address those items that can significantly affect the performance of the Ti-Cote C. Past and present experience with Ti-Cote C-coated parts dictates that the items requiring inspection to prevent premature coating failure are:

- Completeness of Coating Coverage
- Distribution of Coating Thickness
- Coating Adhesion
- Coating Erosion Resistance.

Several of these areas require only very simple inspection techniques. Completeness of coating coverage, for instance, can readily be ascertained by visual inspection usually without the aid of magnification. Verification of a uniform distribution of coating at the required coating thickness is largely dependent upon the geometry of the coated parts. Simple shapes can be measured directly with micrometer-type instruments. More complex configurations represent a greater challenge. Sonic or eddy-current instruments may be effective, but testing will be necessary for each particular part number to determine if the required accuracy can be achieved.

Nondestructive inspection to verify Ti-Cote C adhesion and erosion resistance is another source of concern. Adhesion and erosion testing are by their very nature destructive tests. An indication of Ti-Cote C adhesion can probably be obtained, however, by subjecting coated airfoils to a thermal shock. These tests are similar to that described in the previous section of this report. Test conditions can be established so coatings with inadequate adhesion will show indications of chipping or spalling. Well-adhered coatings will not be damaged during testing thus providing a workable go or no-go scheme for evaluating the Ti-Cote C bonding.

Because of the difficulties encountered during this contract in obtaining consistent erosion resistance, NDI testing in this area will be extremely valuable. The surface finish of the

Ti-Cote C does appear to be indicative of the erosion resistance to some extent. Generally, the rougher or more grainy the surface texture of the Ti-Cote C, the lower the resistance to erosion.

Ti-Cote C deposited early in the program had a surface finish of 170 to 220 microinches AA and very poor erosion resistance. As the surface finish of the Ti-Cote C improved, usually the erosion resistance also improved.

Table 7 lists the surface finish of Ti-Cote C as a function of contract and reactor run. Ti-Cote C deposited in both the cold-wall reactor (DAAG-46-73-C-0249) and small hot-wall reactor (DAAG-46-76-C-0079) had consistently good erosion resistance and a much smoother surface than Ti-Cote C deposited in the scaled-up hot-wall reactor.

TABLE 7. SURFACE FINISH OF TI-COTE C

	Microinches AA
Cold-Wall Reactor (DAAG46-73-C-0249)	22-31
Small Hot-Wall Reactor DAAG46-76-C-0079	45-55
Scaled-up Hot-Wall Reactor Run D-48	81-87
Scaled-up Hot-Wall Reactor Run D-49	80-90

Extensive work is necessary, however, to determine if surface finish measurements alone can be relied upon as an effective NDI technique. Ti-Cote C from reactor runs D-48 and D-49 had essentially the same surface finish but differed markedly in erosion resistance (Figure 8). This may suggest that surface finish measurements have only a limited usefulness as an NDI technique.

SECTION III

DESIGN CONSTRUCTION AND OPERATION PARAMETER DEVELOPMENT FOR THE SCALE-UP HOT-WALL REACTOR

INTRODUCTION

This section of the report was prepared by Materials Technology Corporation (MTC) for United Technologies Corporation, Pratt & Whitney Aircraft Group, Government Products Division under U. S. Army Materials and Mechanics Research Center Contract DAAG46-77-C-0057. Mr. Robert Post was the Program Manager, and Mr. Frank Fonzi was Project Engineer for the contract at Materials Technology Corporation. Mr. Fonzi was the author of this report which covers work accomplished during the period ending April 1979. The program consisted of three phases and yielded a prototype hot-walled reactor capable of producing 100 small compressor blades per run.

In Phase I, experiments in the existing laboratory reactor were directed to determining optimum materials of construction for the large reactor design, optimum gas inlet distribution, and a feasible rotation mechanism. Process gas velocity and temperature control were also examined in Phase I.

In Phase II, major efforts were the design, procurement, and construction of a production "prototype" reactor using the results of Phase I. This reactor was designed to coat 100 or more small compressor blades in one batch.

Phase III consisted of a series of optimization runs on the new reactor to find the best flows, temperatures, and positioning of the compressor blades. Once the process was optimized, test samples using these conditions were examined for coating integrity, bond, hardness, erosion, and fatigue resistance.

BACKGROUND

Titanium Carbonitride coatings, or Ti-Cote C, were developed under Government contracts at Texas Instruments, Inc. Initial work was aimed at coating steel alloy compression section components of turbine engines. Later, through funding by the Army Materials and Mechanics Research Center with Pratt & Whitney Aircraft, Government Products Division (P&WA/GPD) as the prime contractor, it was demonstrated that Ti-Cote C could be successfully applied to titanium, utilizing an electroless nickel interlayer. However, fatigue strength of the finished parts was less than uncoated parts. This work was accomplished under Contracts DAAG46-71-C-0173 and DAAG46-73-C-0249.

Ti-Cote C has demonstrated superior erosion resistance as a compressor section erosion coating for the Air Force. The relatively low temperature at which it is deposited permits restoration of fatigue strength in many alloys with post-coating treatments.

In work on steel alloys, an electrolytic sulfamate nickel plate was used as an interlayer to produce coating adherence. In the case of titanium substrate materials, an electroless nickel plate developed by P&WA/GPD was used. With the electroless nickel plate it was necessary to control initial coating temperature more closely than with the steel-sulfamate nickel system in order to achieve good coating adhesion.

In 1974 MTC bought from Texas Instruments, Inc., equipment and rights to produce Ti-Cote C coatings.

Along with the equipment from Texas Instruments used to apply Ti-Cote C coatings on steel compressor blades, an existing laboratory reactor was adapted to produce Ti-Cote C coatings in a hot-wall system. It was also demonstrated that a system like this can successfully be used to coat titanium alloys with Ti-Cote C, with or without a nickel interlayer.

TECHNICAL DISCUSSION

The processing equipment utilized in the Texas Instruments process has a power supply — a 450 KHz RF generator. The compressor blades to be coated by this process must be supported in nonconducting apparatus (fused quartz) and *must* be rotated inside the RF coil to achieve any reasonable temperature uniformity. Thus, the rotating parts are the only really hot items in the reactor and temperature measurement by thermocouple is virtually impossible — even ignoring the possibility of inducing currents in very thin wires, with 450 KHz radiation. This leaves the radiation temperature sensing devices. The optical pyrometer is only effective at temperatures higher than the 650 to 700°C deposition temperatures used for Ti-Cote C. Infrared pyrometry seems to be the best candidate. These readings, however, are affected by the varying emissivities of different substrates and different emissivities of uncoated and coated materials. Incompleted knowledge of the rate at which emissivity changes as coating builds up further complicates the problem. Also, mixing of the $TiCL_4$ and amine reactant in the chamber produces smokey solid compounds of unknown IR absorptivities, which tend to deposit on the clear reactor walls and eventually entirely obscure the parts before the end of the coating run.

Nevertheless, if enough skill and care are used, remarkably good results can be achieved. However, the sensitivity of the temperature problem added to the fragile nature of fused quartz fabrications makes this an unlikely candidate for a production process of any reasonable magnitude, as all of the quartz must be disassembled and cleaned at the end of every run — then reassembled before the next one.

A "hot wall" reactor system, where the parts are heated primarily by thermal radiation from the wall of the container or some internal heater or both, alleviates many of these problems. First, low-frequency energy (down to 60Hz) can be used, which has very little effect upon the readings of thermocouples in the vicinity. Temperature gradients are much smaller and quite constant in a steady-state system. Thus, if it is desirable to rotate the work parts, the thermocouple can be applied to a static nearby part. The correct thermocouple reading can then be "titrated" experimentally and remains valid over the range of normal operating process variations.

Second, the solid complexes formed in the gas phase are vaporized at the wall temperature and do not remain in the reactor at the end of the run.

Third, radio frequency transparency is no longer a requirement for reactor hardware and many cheaper and more durable materials can be used.

There is obviously a price to be paid for all of the above benefits from the hot-wall system as compared to the cold-wall system.

In a hot-wall system, virtually all reactor internals are at or near coating temperatures and therefore coat during the run. Thus, a much larger area is being coated and deposition rates on a given area are less, as is product yield per unit of raw material. Also, unless the reactor internals are fabricated of a material to which the coating does not adhere, they will eventually be coated thick enough to require replacement. (In fairness, the attrition due to breakage of quartz in the cold-wall system is probably a worse problem economically.)

The main problem in a hot-wall system is prereaction due to overheating during the gas phase. CVD processes rely on the surface of the substrate providing the activation energy for the desired chemical reaction. This increases enormously the odds that the desired reacted molecule (a solid) will remain at and be captured by the surface of the substrate one molecule at a time. In this manner a crystal lattice will be formed and the desired hard and dense coating will be produced. If the reaction takes place in the gas phase, the molecules collected tend to form into small agglomerates with poor affinity for the substrate surface, and a dusty, poorly adhered and cohered coating results.

With the proper design of systems for gas feed, mixing injection into the reactor, and flow patterns inside the reactor, it is possible to achieve the benefits of the hot-wall system without any effect of gas phase reaction on the coated parts. Parts produced in this system rate at least as well as parts from the cold-wall system in all of MTC's quality tests.*

DESCRIPTION OF THE EXISTING LABORATORY REACTOR

All of the basic internal components used in this reactor were made from graphite. Lampblack was used as the insulating material between the graphite susceptors and the coil, with a high temperature fiberfrax tube put between the coil and lampblack. A graphite tube was machined with threaded ends, and a top and bottom plate were then screwed in providing the inlet and outlet of the coating chamber. Graphite rings with slots were machined to fit inside this coating chamber to hold the small compressor blades. Utilizing a large, medium, and small ring on one plane, 35 small blades could be coated at one time. (The dimensions of this graphite can were 6 in. ID by 7 in. long.)

Power Supply

A 100 KW, 3KHz inductotherm motor generator set was used to heat up the laboratory reactor. This same power supply was used in the scaled-up system.

With a 3KHz unit, various coil configurations as to diameter and length of a reactor can be accomplished and still keep the system "tuned" providing maximum power and efficiency.

Temperature Control

An optical pyrometer would normally be used with a hot-walled coating system, but with the low temperatures** used in the Ti-Cote C process, it was felt that T/C's would give much better control over temperature. A thermocouple was positioned through the center of the reactor between the coil turns, through the susceptor and then touched the graphite can on the outer skin. To prevent any stray voltages from the coils giving us an erroneous reading, grounded thermocouples were used. T/C's were also put through the graphite can onto the parts to be coated to see if there was a variation in temperature between the skin of the can and the parts.

The results of a series of test runs showed that the variation in temperature between the outer surface of the graphite can and the actual part inside differed no more than 10°C.

Process Control Panel — Rotation System

A semiautomatic gas control panel was fabricated and piped into the small reactor as shown in Figure 20.

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*Metallographic studies at P&WA/GPD showed that the titanium carbonitride coatings applied in a hot-wall reactor were more porous than titanium carbonitride applied in a cold-wall reactor. In addition, the erosion resistance of the hot-wall reactor coatings was erratic.

**Ti-Cote C is deposited at about 700°C. This is 200 to 300°C lower than the temperature at which many other CVD coatings are applied.

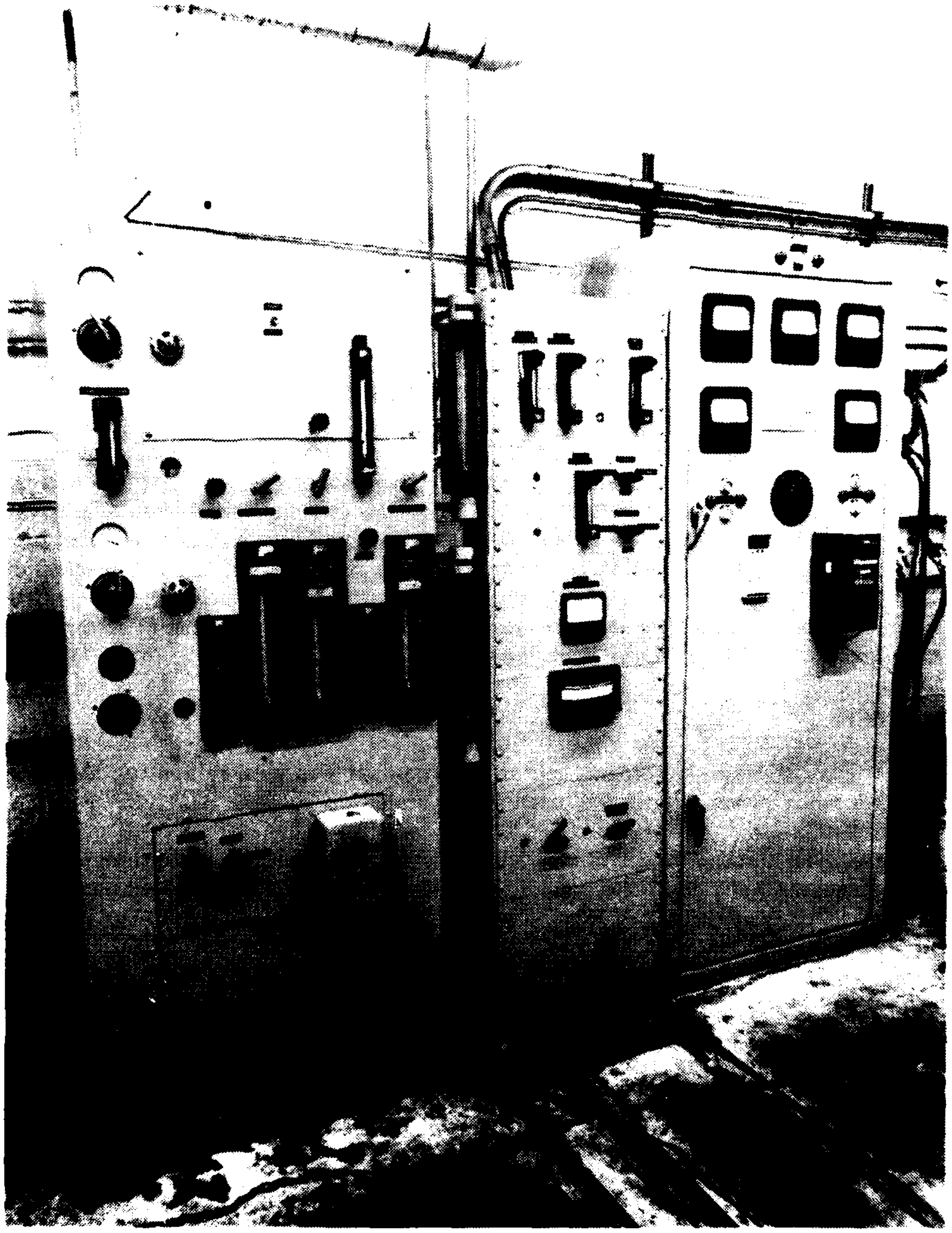

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Figure 20. Gas Flow Panel and Power Supply

Past experience has shown that the titanium tetrachloride and trimethylamine used in the process have to be introduced simultaneously into the reactor chamber to achieve a good bond on the surface of the parts.

The semiautomatic control panel was designed to achieve this effect as well as indicate and control the various flows involved.

A rotation system was put into the small reactor by inserting a sealed water-cooled spin shaft through the bottom of the reactor and connecting this shaft to pulleys and variable speed motor.

The purpose of the rotation system was to try and minimize surface roughness and variations in coating thickness.

Optimization of Coating in Small Reactor

Utilizing the control panel, T/C monitoring, rotation etc., a series of runs was made in the small reactor to optimize conditions that could be used in the scaled-up system. Titanium 6Al-4V plates were used as substrates in this system. A series of 20 coating runs were made in this system varying temperature, flows, and rotation. The following results were obtained:

1. Temperature — Runs were made at temperatures as low as 650°C and as high as 750°C. The optimum temperature is in the range of 710°C ±10°C. At the lower temperatures the coating became porous, and at the higher temperatures "sooting" occured on the parts.

2. Process Gases — Starting with a total flow and titanium tetrachloride to trimethylamine ratio used in previous runs, it was found that varying these flows produced a nonadherent and porous coating in all cases. It was then decided that these original flow conditions were the optimum required to give a hard, dense coating of titanium carbonitride.

3. Rotation — Rotating the parts in this system had no great affect on either surface quality of the coating or eveness of coating.

4. Cleaning of Parts Prior to Coating — Using various methods of cleaning the Ti-6Al-4V plates prior to coating did not produce any significant results as far as adhesion or bond of the TiCN coating on Ti-6Al-4V. Using ultrasonic, a caustic solution, a diluted nitric acid solution, and methanol, all produced the same results. The TiCN coating bonds well to Ti-6Al-4V no matter what prior treatment is given to the parts. In fact, adhesion of the coating on parts that were given no treatment looked as good as parts that had pretreatment.

5. Optimum Conditions — Using a deposition temperature of 710°C ±10°C, total gas flow of 111 SCFH and a ratio of 1 to 1.6 between the titanium tetrachloride and trimethylamine produced a hard, dense coating of TiCN on bare Ti-6Al-4V in this hot-walled system as shown in Figure 21. The hardness of the coating ran between 2300 to 2500 KHN using a 25gm load. The parts were cleaned with methanol prior to coating and no rotation was used.

   Total deposition time to coat 35 small compressor blades with 1.2 to 1.5 mils of TiCN was 4.5 hr.

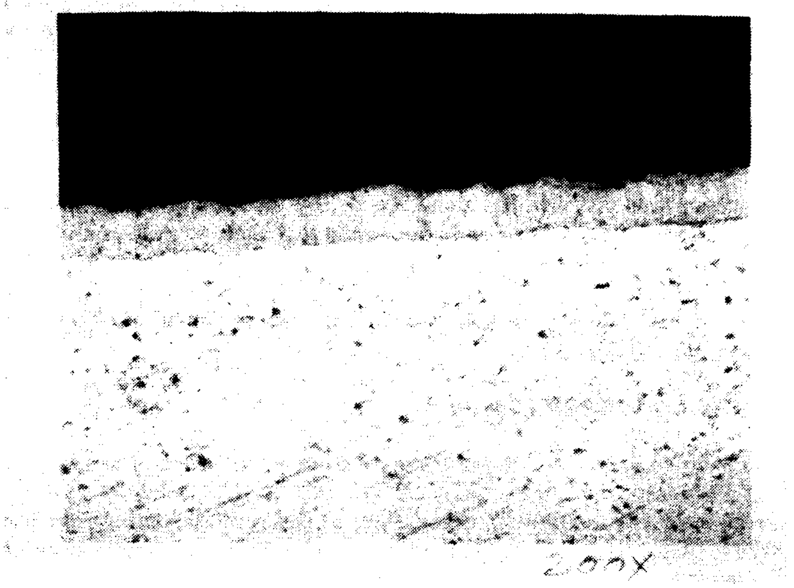

Figure 21. TiCN Coating on Titanium 6Al-4V

DESIGN AND CONSTRUCTION OF PRODUCTION REACTOR

The reactor was made using water-cooled copper coils and a water-cooled steel plate as shown in Figure 22. Fiberfrax insulation was used between the coil and the reactor chamber to hold the insulating lampblack. The bottom plate had two 1¼-in. dia holes for exhaust ports and a 2-in. dia hole in the center for a rotation shaft. The reactor itself was 18 in. in dia by 16 in. high to the top of the fiberfrax insulation.

Furnace Chamber

The furnace chamber and lid were made from ⅛-in. walled 316SS 15-in. dia as shown in Figure 23. Two pipes were welded to the bottom of the chamber for exhaust and a hole was made in the center for a rotation shaft. A flat lip welded to the top of the can allowed a seal between the lid and can. A ⅝-in., 316SS tube was welded to the center of the lid for the process gases to enter. A 1⅝-in. dia baffle plate was positioned on the underside of the lid 1 in. below where the gases would enter the chamber, allowing even distribution of the gases into the chamber. Two T/C's were put through the lid into the chamber. The outer T/C, shown in Figure 23, touched the inner wall of the chamber at the level of the blades to be coated. The inner T/C was positioned close to the parts during rotation and on a scrap part during stationary deposition. This can would slip into the reactor. Lampblack was packed between it and the fiberfrax liner.

The reasons for using a metal can vs a graphite can as used in the laboratory reactor were two-fold:

1. The cost of fabricating a graphite can this size, with related hardware, would be prohibitive.

2. It was found that in the laboratory reactor the TiCN coating on the graphite chamber would build up to such thickness that the graphite can would crack and have to be discarded. The bond of the TiCN coating on the hotwall of the graphite was so strong that a method of stripping it after each run could not be devised.

Since the TiCN does not bond well to stainless steel, cleaning the chamber out after each run can be accomplished with minimal effort.

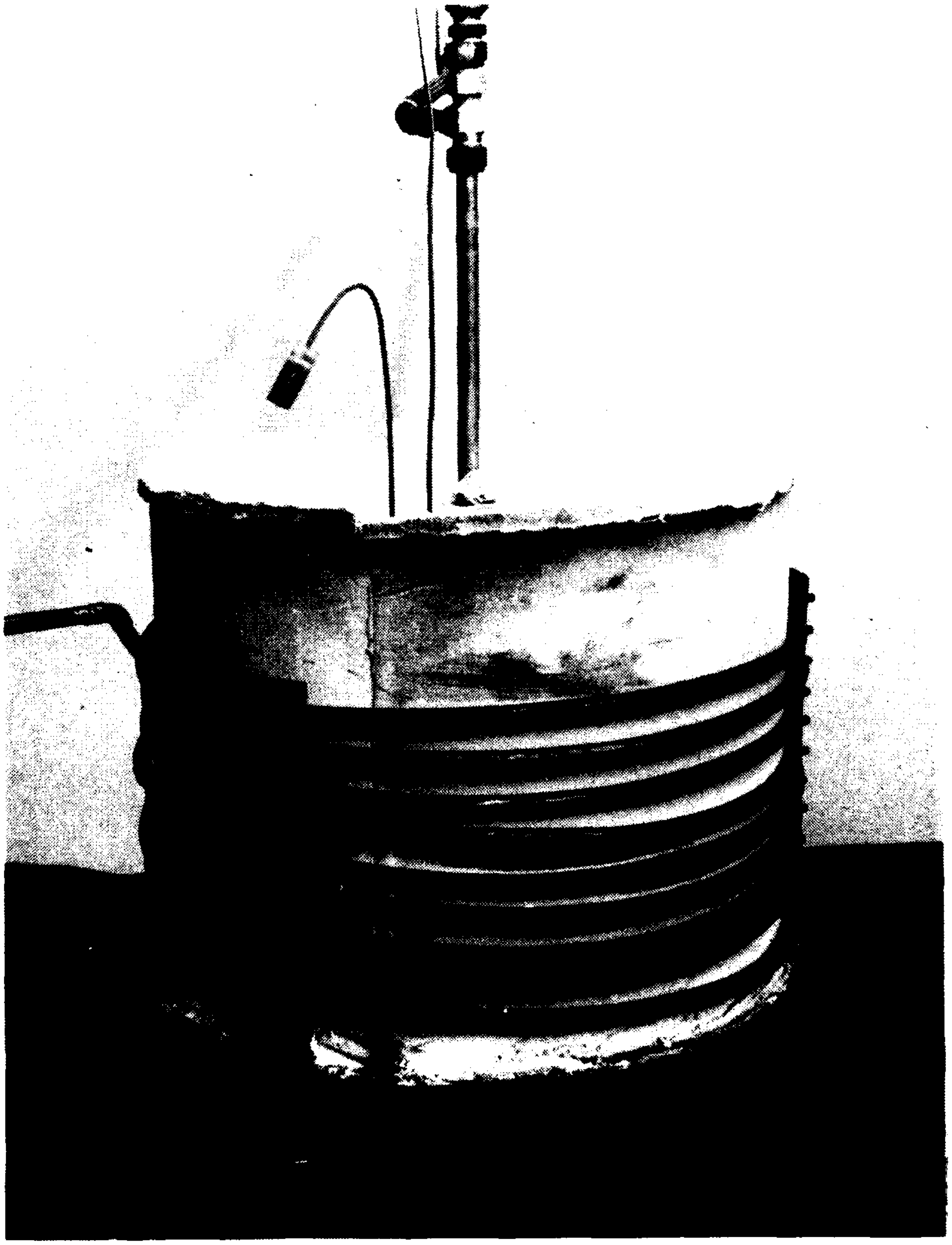

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Figure 22. Hot-Walled Production Reactor

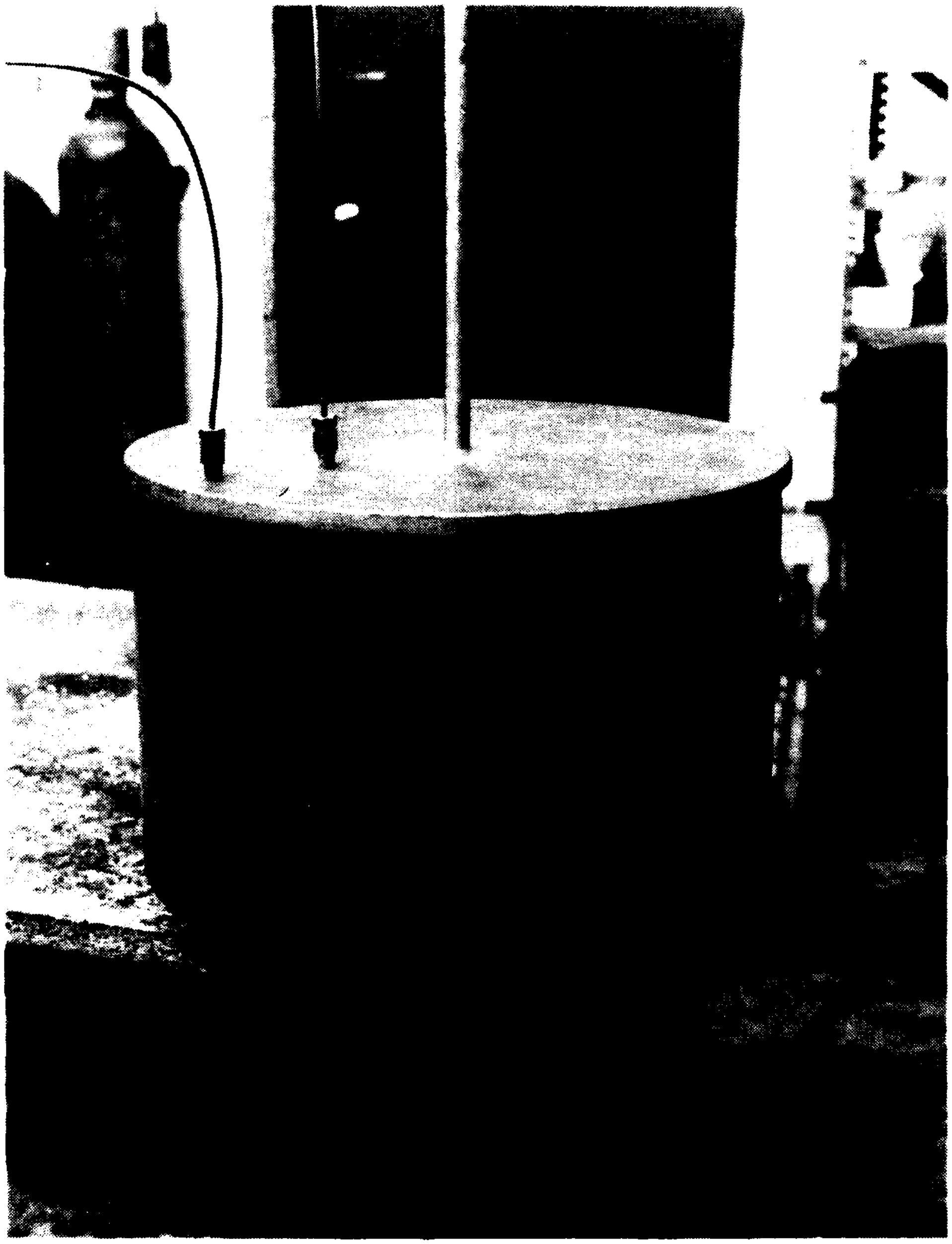

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Figure 23. Metal Can Used as Furnace Chamber

TEMPERATURE CONTROLLER

An electronic temperature controller was mounted and connected to the existing 100KW control panel as shown previously in Figure 20. The controller not only gave an accurate readout on the temperature, but also provided an automatic control over power input to the reactor. The controller was checked in use against an optical pyrometer and potentiometer and agreement was within ± 10°C.

Fixturing (Blade Holders)

Rings were machined from graphite with notches in them to hold the foot of the compressor blades as shown in Figure 24. These three rings can hold 110 blades and there is enough room in the chamber to hold two larger rings and increase the capacity to approximately 250 to 300 blades. The rings were positioned in the chamber, as shown in Figure 25, in the stationary position. If rotation was used, the shaft that would come into the center hole would have a spider assembly attached to it and the rings would sit on this for rotation.

Flow Panel

The automatic flow panel used with the laboratory reactor was also used in the scaled-up system. Piping was run from the flow panel to the scaled-up reactor. The flow panel and lines to the reactor were pressurized, leak-checked, and purged prior to use.

OPTIMIZATION OF SCALED-UP REACTOR SYSTEM

During the term of this contract, 49 furnace runs were made in this system using a variety of deposition conditions (Table 8). Calculating the volume of the new chamber vs the volume of the laboratory reactor determined that an increase of 2.5 times the total flow was necessary. The ratio of the gases was kept the same, except in some of the latter runs the amine flow was increased. Titanium coupons of 6Al-4V, 0.060 by 1 by 3 in., were used as test samples in this program. Two major problems encountered in this scaled-up system were bonding of the coating to the substrate and porosity. We had neither of the problems in the laboratory reactor. It was found by trial and error that more than one variable was causing these problems. The following were observed during this scale-up and each step has led to the conclusion and goal of the contract:

1. Rotation of the parts has no effect on uniformity of coating, smoothness of coating, porosity or bond. Rotation is needed in a cold-wall system for temperature uniformity etc., but with the correct total flow and distribution of gases in a hot-walled system, it is not necessary to rotate the parts.

2. In some of the runs the amount of hydrogen used in the process was eliminated as it was thought that hydrogen embrittlement of the titanium was occuring which could be detrimental to fatigue strength. The coating became very sooty when this was done. In this type of CVD process the hydrogen is a "getter" for the chlorine, thus a minimal amount of hydrogen must be used.

3. Since temperature is an important factor in this process, temperature studies were conducted to determine any variations inside the reactor. Thermocouples were placed at various points inside the reactor and on the parts to be coated. A thermocouple was also placed on the outside of the metal can or "susceptor" to see what difference there was in temperature between the outside of the can and the parts inside.

   At 800°C on the outside of the can, the temperature of the parts inside was 790°C. This 10°C difference was the same down to 700°C. The 10°C variation inside the reactor was the same from the center of the can to the outside wall. A thermocouple was positioned near the baffle plate inside the metal can directly below the gas inlet tube. The temperature of the gas as it enters the can was 670°C when the wall of the can was at 800°C. As the coating gases are introduced into the reactor there is an initial drop in temperature of 10°C. At 800°C taken on the outside of the can, the actual part temperature when deposition is started is 780°C. The temperature varied ±10°C throughout the coating cycle. Controlling the temperature posed no problem in this system.

4. Distribution of gas flows and gas inlet temperatures was found to be a key variable in this process. Insulation at the top of the furnace was changed to increase or decrease the gas temperature as it entered the furnace chamber. Different types of baffle plates were tried to distribute the gas evenly, and the parts to be coated were positioned at different levels in the chamber. The conditions that gave the best results were an inlet temperature of 650°C, an inlet baffle plate 2 in. in diameter 1½ in. below the inlet to the chamber and the parts positioned 4 to 5 in. below the baffle plate.

5. In all cases of the electroless nickel-plated parts supplied by P&WA/GPD, the TiCN coating spalled off the parts and in some cases the nickel came off the parts with the TiCN. The coating looked good when the parts were taken out of the reactor but spalling occurred when the specimens cooled to room temperature. This was particularly true of the nickel-plated Krouse fatigue bars.* Some of these nickel-plated parts were baked in H_2 at various temperatures up to 800°C prior to depositing TiCN, but results were unfavorable. The spalling seemed to be due to a stress buildup when electroless nickel was used as an intermediate layer. This condition did not exist when steel parts were plated with sulfamate nickel and then coated with TiCN.

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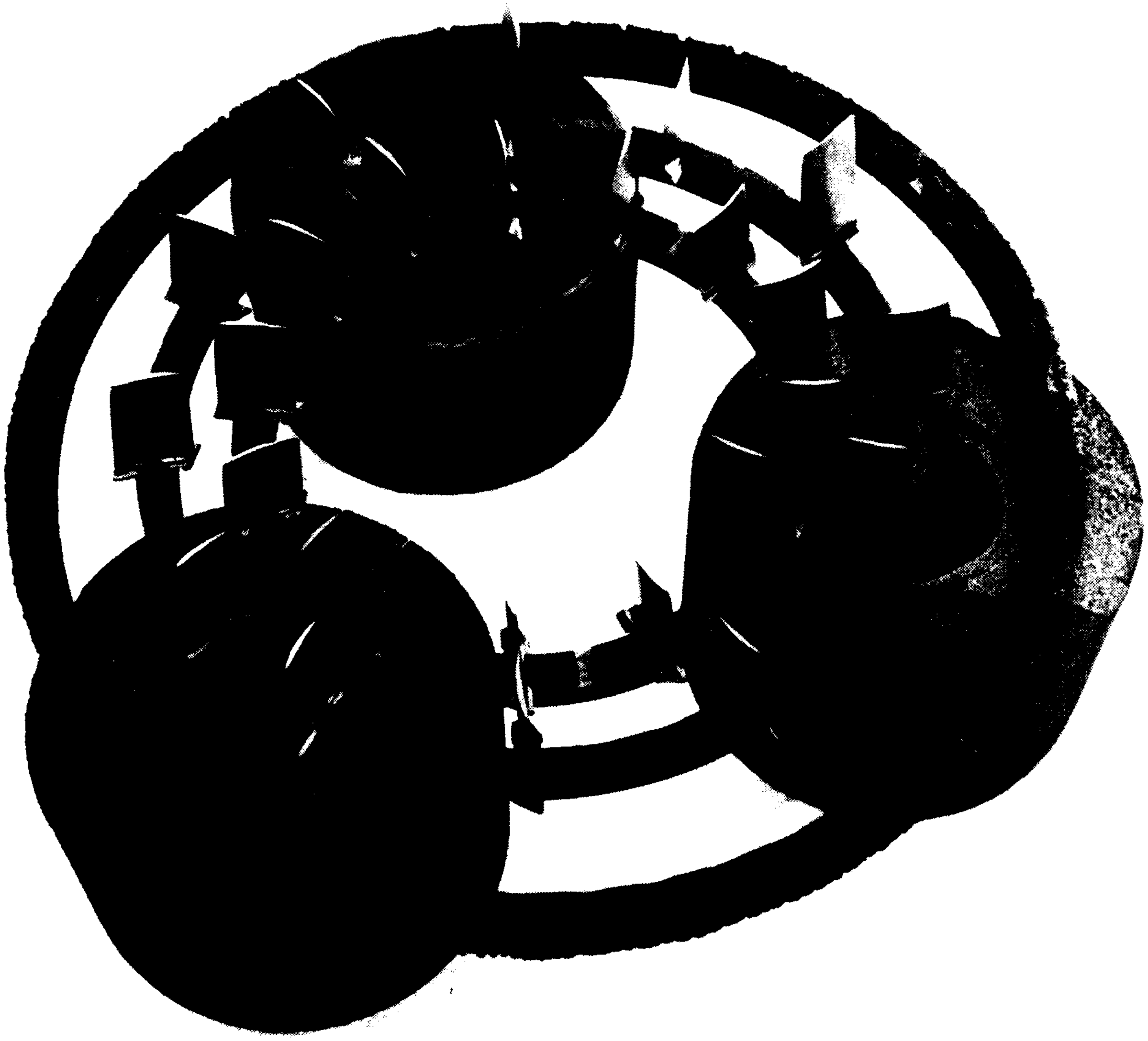
*After several attempts, 9 of the 12 electroless nickel-plated Krouse fatigue bars were coated without spalling of the Ti-Cote C.



FD 171519

Figure 24. Graphite Rings Used as Blade Holders

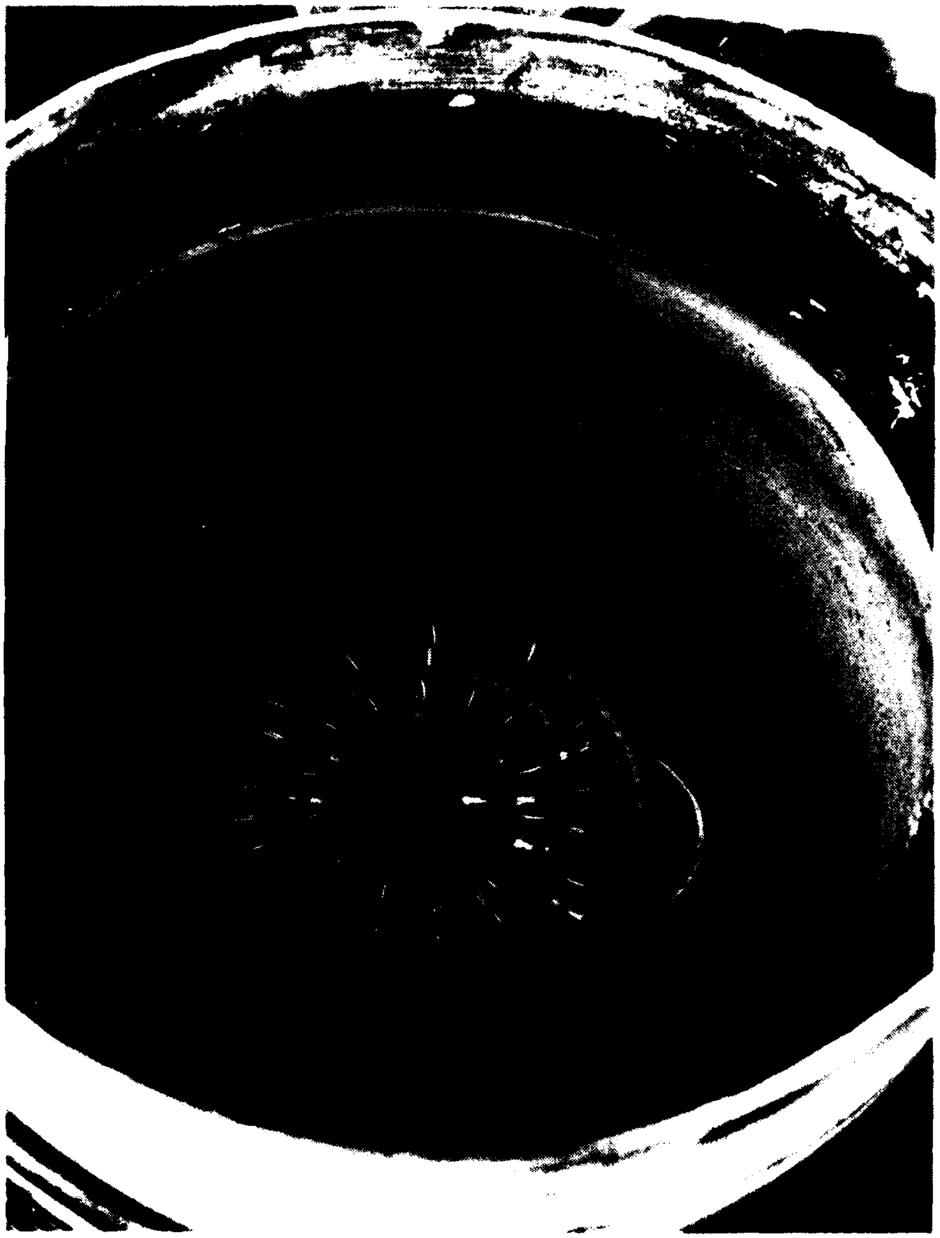


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Figure 25 — Blades Positioned in Furnace Chamber

TABLE 8. FURNACE RUNS MADE IN PRODUCTION REACTOR SYSTEM

Run No.	*Date*	*Deposition Temperature*	*Dep. Time*	*Material Source*	*Vaporizer Temperature*	*N_2 Total Flow to Vaporizer*	*H_2 + N_2 Total Flow*	*Total Amine Flow*	*Substrate Material*	*Results*	*Special Conditions*
D-1	02/01/78	700°C	5 hr	$(CH_3)_3N$ $TiCL_4$	Room Temperature	95.0	N_2 Only 25.4	2.09	18 Titanium Coupons 6Al-4V	Negative — Coating Spalled.	a. New flow panel. b. Temperature monitored by TC in well touching outside of can.
D-2	02/02/78	750°C	5 hr	$(CH_3)_3N$ $TiCL_4$	Room Temperature	95.0	N_2 Only 25.4	2.09	19 Titanium Coupons	Negative — Coating Sooty.	Same as above.
D-3	02/03/78	700°C	4 hr	$(CH_3)_3N$ $TiCL_4$	Room Temperature	90.0	N_2 Only 179.0	2.33	19 Titanium Coupons	Negative — Coating Spalled.	a. New flow panel. b. Changed total flow. c. Rotation
D-4	02/08/73	650°C	4 hr	$(CH_3)_3N$ $TiCL_4$	Room Temperature	90.0	N_2 Only 179.0	2.33	18 Titanium Coupons	Coloring and texture of samples looked better. Coating came off with sandblaster.	Same as above.
D-5	02/09/78	700°C	4 hr	$(CH_3)_3N$ $TiCL_4$	Room Temperature	90.0	179.0	2.33	18 Titanium Coupons	Thickness 0.2 mils. No spalling. Coating came off when lightly sandblasted at 50 psi.	a. Rotation.
D-6	02/10/78	725°C	8 hr	$(CH_3)_3N$ $TiCL_4$	Room Temperature	90.0	179.0	2.33	18 Titanium Coupons 4 Carbide Inserts	Coating spalled on coupons but adhered well on WC inserts.	a. No rotation b. Bottom 2 ft of $TiCL_4$ vaporizer insulated
D-7	02/13/78	800°C	1-1/6 hr	$(CH_3)_3N$ $TiCL_4$	Room Temperature	90.0	179.0	2.33	18 Titanium Coupons	Aborted run due to closed water system failure.	Same as above.
D-8	02/14/78	730°C	8 hr	$(CH_3)_3N$ $TiCL_4$	Room Temperature	90.0	179.0	2.33	18 Titanium Coupons	Coating bonded well. Thickness 0.545 to 0.84 mils.	a. Rotation b. Lampblack as insulation.
D-9	02/21/78	750°C	8 hr	$(CH_3)_3N$ $TiCL_4$	Room Temperature	90.0	179.0	2.33	18 Titanium Coupons	Negative — Coating Spalled.	Problem with H_2 flow.
D-10	02/22/78	750°C	8 hr	$(CH_3)_3N$ $TiCL_4$	Room Temperature	90.0	179.0	2.33	18 Titanium Coupons	Coating bonded well, would not sandblast off.	Coating Porous Thickness 0.7 mils
D-11	02/27/78	750°C	8 hr	$(CH_3)_3N$ $TiCL_4$	Room Temperature	90.0	179.0	2.33	18 Titanium Coupons	Coating appeared to adhere well. Thickness 0.5 mils	a. New flow panel b. Changed $TiCL_4$ line from flow panel to furnace from ½ in. to ¼ in c. Placed amine bottle near reactor
D-12	03/01/78	750°C	16 hr	$(CH_3)_3N$ $TiCL_4$	Room Temperature	90.0	179.0	2.33	18 Titanium Coupons	Vaporizer had plug in inlet line. Plugged several times during run. Coating did not adhere.	Same as above.
D-13	03/03/78	800°C	12 hr	$(CH_3)_3N$ $TiCL_4$	Room Temperature	90.0	179.0	2.23	18 Titanium Coupons	Coating Spalled. Titanium was attacked under the masked area of coupon.	Same as above.
D-15	03/08/78	700°C	16 hr	$(CH_3)_3N$ $TiCL_4$	Room Temperature	90.0	179.0	2.23	18 Titanium Coupons	Coating came off when hit with 50 psi. on sandblaster.	Small reactor flow panel
D-16	03/21/78	710°C	8 hr	$(CH_3)_3N$ $TiCL_4$	Room Temperature	90.0	179.0	2.23	17 Titanium Coupons	Coating looked good 0.5 mils thickness	a. Small reactor flow panel. b. Eliminated furnace liner and put lamphlack up to wall of cannister.
D-17	03/22/78	710°C	12 hr	$(CH_3)_3N$ $TiCL_4$	Room Temperature	90.0	179.0	2.23	10 Titanium Coupons	Unetched coupons looked good. Etched coupons did not adhere.	a. Small reactor flow panel. b. Half of coupons put in HNO_3 for 5 minutes prior to cleaning.
D-18	03/29/78	710°C	12 hr	$(CH_3)_3N$ $TiCL_4$	Room Temperature	90.0	179.0	2.23	10 Titanium Coupons	Adherence good except lower ½ in. of coupon which coating sandblasted off	a. New flow panel. b. New $TiCL_4$ bottle

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*All Flows in (SCFH) Standard Cubic Feet Per Hour.

TABLE 8. FURNACE RUNS MADE IN PRODUCTION REACTOR SYSTEM (Continued)

Run No	*Date*	*Deposition Temperature*	*Dep Time*	*Material Source*	*Vaporizer Temperature*	*N_2 Total Flow to Vaporizer*	*$H_2 + N_2$ Total Flow*	*Total Amine Flow*	*Substrate Material*	*Results*	*Special Conditions*
D-19	03/31/78	710°C	12 hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	90.0	179.0	2.23	10 Titanium Coupons	Negative — Coating Spalled.	a. New flow panel. b. Heated up with argon, then switched to N_2 5 minutes before coating
D-20	04/04/78	710°C	10¼ hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	90.0	179.0	2.23	10 Titanium Coupons	Negative — Coating Spalled. Exhaust plugged shut run down 1¾ hr early.	Same as above Heated up with argon
D-21	04/20/78	710°C	16 hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	90.0	179.0	2.23	16 Titanium Coupons 3 Ni plated blades	Negative — Ran out of amine after 4¾ hr coating time.	a. New flow panel
D-22	05/04/78	710°C	16 hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	90.0	179.0	2.33	15 Titanium Coupons 3 Ni plated blades	Negative — Coating Spalled.	a. New flow panel b. Heated up with argon
D-23	05/09/78	710°C	12 hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	90.0	179.0	2.33	8 Titanium Coupons 3 Ni plated blades	Negative — Coating Spalled. Partial plug in saturator line.	a. New flow panel b. Heated up with argon
D-24	05/11/78	710°C	12 hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	90.0	179.0	2.33	8 Titanium Coupons 3 Ni plated blades	Exhaust plugged several times during run. Coating adhered to flats of blades but edges spalled. Ti coupons coating spalled 0.75 and 0.65 mil.	Same as above
D-25	05/15/78	710°C	12 hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	90.0	179.0	2.33	4 Titanium Coupons 4 Ni plated blades 3 Ni plated blades	Exhaust plugged several times during run. Coating spall on all parts, coating and nickel came off Ni plated titanium coupons.	a. Small reactor flow panel.
D-26	05/31/78	710°C	12 hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	90.0	179.0	2.33	4 Titanium Coupons 3 Stripped Ni plated Titanium Coupons	Coating looked good, but came off with 50 psi from sandblaster.	a. Small reactor flow panel. b. Spin shaft was removed leaving large exhaust in center of furnace to prevent plugging.
D-27	06/02/78	720°C	12 hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	90.0	179.0	2.33	6 Titanium Coupons	Negative — Coating Spalled.	a. Small reactor flow panel b. Controlling furnace temperature by by monitoring temperature of coupon inside furnace with a T/C
D-28	06/05/78	720°C	8 hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	90.0	179.0	2.33	6 Titanium Coupons	Negative — Coating Spalled.	a. Small reactor flow panel b. Using magnesium oxide on top of furnace as insulation
D-29	06/06/78	690°C	8 hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	90.0	179.0	2.33	6 Titanium Coupons	Metering temperature on side of cannister. Negative — Coating Spalled.	a. Small reactor flow panel b. Samples set 4 in. higher in furnace c. Exhaust hose lowered 6 in. from exit d. Lampblack as insulation
D-30	07/13/78	720°C	9 hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	90.0	179.0	2.33	Large Al 4V titanium valve part 13 in. diameter × 7 in. high.	Coating adhered except in a few small areas of part after 2 days. Coating started flaking off of visor. Exhaust plugged after 9 hr.	a. Small reactor flow panel b. Measuring temperature off part c. Installed spin shaft for rotation
D-31	07/17/78	720°C	16 hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	90.0	179.0	2.33	7 Stage 6 Titanium Blades 9 Stage 7 Titanium Blades	Aborted run after 7¼ hr due to exhaust plugging. Coating spalled.	a. Small reactor flow panel b. Exhaust tubes shortened to 1 ft c. No rotation d. Temperature controlled by touching blade in furnace with T/C

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*All Flows in (SCFH) Standard Cubic Feet Per Hour

TABLE 8. FURNACE RUNS MADE IN PRODUCTION REACTOR SYSTEM (Continued)

Run No	Date	Deposition Temperature	Dep Time	Material Source	Vaporizer Temperature	N_2 Total Flow to Vaporizer	$H_2 + N_2$ Total Flow	Total Amine Flow*	Substrate Material	Results	Special Conditions
D-32	07/19/78	720°C	16 hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	90.0	179.0	2.33	14 Stage 6 Titanium Blades 17 Stage 7 Titanium Blades	Coating looked good. Appeared to adhere good and did not sandblast off. Shipped all 33 blades to Pratt & Whitney.	a. Small reactor flow panel b. Removed spin shaft to allow for larger exhaust c. Reading temperature off of blade d. Ni stripped from all blades before coating
D-33	07/25/78	720°C	16 hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	90.0	179.0	2.33	12 Nickel plated Krouse fatigue bars.	Coating spalled off. Nickel spalled off bars also.	Same as above
D-34	08/27/78	738°C	16 hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	90.0	179.0	2.33	4 Stage 6 Blades 6 Stage 7 Blades	Coating looked good but erosion results 22-39 sec on jet abrador.	Same conditions as D-32
D-35	10/02/78	800°C	12 hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	90.0	179.0	2.33	3 Stage 6 Blades 3 Stage 7 Blades	Coating Spalled.	Raised coil on reactor
D-36	10/04/78	754°C	12 hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	90.0	179.0	3.02	5 Stage 6 Blades 6 Stage 7 Blades	Coating thickness 1.0 mils porosity better.	Increased amine flow by 30%
D-37	11/01/78	768°C	8 hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	90.0	179.0	3.02	4 Titanium Plates	Coating thickness 0.7 to 0.9 mils. Erosion results 4-21 sec.	Raised coil on reactor for better heat distribution. Increased amine.
D-38	11/07/78	768°C	8 hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	135.0	272.0	3.995	4 Titanium Plates	Coating thickness 0.7 mils. Erosion results 264-428 sec. Still have porosity.	Increased total flow
D-39	11/16/78	770°C	12 hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	135.0	272.0	3.995	4 Titanium Plates	Coating thickness 1.28. Still porous. Hardness 1110 KHN/110 gm load. Erosion results 243-279 sec.	Duplication of D-38 except for time.
D-40	11/21/78	800°C	10 hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	135.0	272.0	3.995	4 Titanium Plates	Coating bonded well. Thickness 0.9 mils. Erosion 122-238 sec still porous.	Duplication of D-39 except for temperature
D-41	12/01/78	810°C	12 hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	135.0	272.0	3.995	4 Stage 8 Blades (steel) 2 Titanium	Coating still porous. Thickness 1 mil. Hardness 1500 KHN/100 gm load.	Used 8 in. diameter graphite cylinder in center of reactor for heat distribution.
D-42	12/07/78	800°C	8 hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	90.0	179.0	3.02	4 Stage 8 Blades (steel) 2 Titanium Coupons	Coating adherence good, but still porous.	Raised parts in reactor closer to gas inlet.
D-43	12/13/78	800°C	12 hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	90.0	179.0	3.02	4 Stage 8 Blades (steel) 2 Titanium Coupons	Coating looks good. Thickness 0.84 mils. Hardness 2175 KHN/50 gm load. Erosion 457-663 sec.	Repositioned parts in reactor. Purged reactor overnight with N_2.

*All Flows in (SCFH) Standard Cubic Feet Per Hour

TABLE 8. FURNACE RUNS MADE IN PRODUCTION REACTOR SYSTEM (Continued)

Substrate Material	*Results*	*Special Conditions*	*Run No*	*Date*	*Deposition Temperature*	*Dep. Time*	*Material Source*	*Vaporizer Temperature*	*N_2 Total Flow to Vaporizer*	*H_2 + N_2 Total Flow*	*Total Amine Flow*
4 Steel Blades 1 Titanium Coupon	Porosity much better. Run aborted. Plug in $TiCl_4$ line	Sent parts to Pratt & Whitney for evaluation. Reduced total flows and temperature	D-44	02/12/79	700°C	5 hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	67.5	135.0	2.89
4 Steel Blades 1 Titanium Coupon	Run aborted. Leak in furnace chamber. Coating that was there spalled	Duplication of D-44.	D-45	02/13/79	700°C	5 hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	67.5	135.0	2.89
6 Titanium Coupons	Coating thickness 1.2 mils. Hardness 2350 KHN/50 gm load. Erosion results 15-24 sec. Coatings porous	Duplication of D-42	D-46	03/07/79	800°C	16 hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	90.0	179.0	3.02
6 Titanium Coupons	Coating spalled. In places where coating did adhere it looked very dense	Put new baffle plate in reactor. Opened up extra exhaust port	D-47	03/22/79	800°C	16 hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	90.0	179.0	3.02
6 Titanium Coupons	Parts looked good. Thickness 1.1 mils. Coating would not sandblast off at 50 psi. Erosion results 584 sec. Hardness 2250 KHN/50 gm load. Coating dense — parts sent to Pratt & Whitney	Exhaust port duplication of D-47, except parts were positioned 4 in below baffle	D-48	03/27/79	800°C	16 hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	90.0	179.0	3.02
6 Titanium Coupons	Approximately same results as D-48. Surface finish of blades a little rough.	Duplication of D-48	D-49	04/09/79	800°C	16 hr	$(CH_3)_3N$ $TiCl_4$	Room Temperature	90.0	179.0	3.02

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*All Flows in (SCFH) Standard Cubic Feet Per Hour

CONCLUSIONS

Using the conditions as stated in run No. D-49 enabled the production of a hard, dense coating of TiCN* on a number of small titanium compressor blades. A total deposition time of 16 hr is needed to deposit 1.2 to 1.5 mils of TiCN on these parts. The deposition time is long, but since 250 to 300 blades can be coated at one time, and the yield rate is reasonable, this should not have a drastic effect on cost in production.

The results of the program show that more must be learned about the Ti-Cote deposition process in the scaled-up, hot-wall reactor. The reason for the erratic erosion resistance has not been found. Until the causes of the problem are thoroughly understood, it will not be possible to have a successful production system.

RECOMMENDATIONS

Even though a large reactor system has been used to produce a TiCN coating on bare titanium blades, it is felt that the following will have to be looked at in any new programs prior to production:

1. Reproducibility from one batch of blades to the next. This includes uniformity of the coating.
2. Improvement of the surface finish of the TiCN coating. (Roughness, etc.)
3. Examination of an interlayer other than electroless nickel between the titanium part and the coating. This may help in reducing fatigue loss in the blades.
4. Determination of just what is an acceptable coating on titanium blades using a simple NDT procedure.

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*MTC was premature in their evaluation of the TiCN on the compressor blades. Testing performed at P&WA/GPD revealed that the Ti-Cote C deposited on the compressor blades using the D-49 parameters had very poor erosion resistance.

SECTION IV

REVIEW OF THE MATERIALS TECHNOLOGY CORPORATION REPORT

Several discrepancies exist between statements in the report prepared by Materials Technology Corporation (MTC) and test data generated at P&WA/GPD. This can be attributed to the fact that MTC does not have testing facilities equivalent to P&WA/GPD and consequently MTC was simply premature in their evaluation of the Ti-Cote C quality. MTC was, in fact, very surprised to learn that reactor run D-49 had poor erosion resistance. Reactor runs D-48 and D-49 used duplicate parameters and no satisfactory explanation for the performance difference was available.

The fact that no cause was discovered for the variation in erosion resistance of TiCN deposited in run D-48 vs run D-49 is typical of problems encountered with reproducibility throughout the program. A review of the runs made in the MTC reactor shows that runs D-42, D-43 and D-46 through D-49 all used essentially identical parameters. The results, however, varied considerably with respect to Ti-Cote C adhesion, porosity, surface finish, hardness and erosion resistance. It is obvious, therefore, that one or more unidentified variables exist in the scaled-up, hot-wall reactor system. These undefined variables were apparently of little significance in the small, hot-wall reactor but they have had a significant effect as the reactor size increased.

Based on the testing and evaluations performed at P&WA/GPD, the scaled-up reactor cannot now successfully be used as a model for a production system. We strongly agree with the recommendations offered by MTC. It is essential to address these areas prior to instituting any production program for Ti-Cote C application.

SECTION V

CONCLUSIONS

1. The scaled-up, hot-wall reactor is not suitable for production in its current state of development. The major problem is that consistent erosion resistance has not been obtained between reactor runs and MTC has not been able to solve the problem.

2. Erosion resistance of Ti-Cote C was very poor on JT12 compressor 7th-stage airfoils coated in the production reactor. Flat test coupons, however, coated immediately prior to the airfoils under duplicate conditions, had acceptable erosion resistance. The erosion resistance of Ti-Cote C on the JT12 compressor blades varied from four times greater than bare titanium (600°F, 30-deg impingement) to three times worse than uncoated titanium 6Al-4V (600°F, 90-deg impingement). The erosion resistance of Ti-Cote C on the flat test coupons ranged from 19.5 times greater than uncoated Ti-6Al-4V (600°F, 60-deg impingement) to twice as good as bare Ti-6Al-4V (600°F, 30-deg impingement).

3. MTC was unable to achieve consistant adhesion between Ti-Cote C deposited in the scaled-up, hot-wall reactor and electroless nickel-plated titanium alloy substrates.

4. MTC was able to deposit Ti-Cote C directly onto a titanium 6Al-4V substrate in the scaled-up, hot-wall reactor. All airfoils and erosion coupons were coated in this manner.

5. Coating coverage and coating adhesion were good on JT12 7th-stage compressor blades. This represents a marked improvement over results obtained with either a cold-wall or small hot-wall reactor.

6. Ti-Cote C applied to JT12 7th-stage compressor blades appears to have acceptable thermal shock resistance to 900°F.

7. Fatigue strength reductions of 62-64% were measured at 600°F on Ti-Cote C-coated JT12 7th-stage compressor blades.

SECTION VI

RECOMMENDATIONS

To obtain consistent erosion resistance of the Ti-Cote C, it will first be necessary to better define the reaction kinetics of titanium carbonitride formation. A research program directed toward this goal would provide the information necessary to understand the chemical and/or structural differences between Ti-Cote C coatings with high and low erosion resistance. With this basic information in hand, an improved reactor can be designed and constructed that will achieve consistent Ti-Cote C quality.

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