17. DEVELOPMENT OF IMPROVED CERAMIC COATINGS TO INCREASE THE LIFE OF XLR99 THRUST CHAMBER (U)

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ABSTRACT

This report describes the coating development, laboratory testing, and engine testing program that was performed to solve the problem of premature failure of rocket-engine combustion chambers being experienced in operation of the X-15 system.

BACKGROUND

The XLR99 engine which powers the X-15 airplane, shown in figure 1 as viewed from the rear of the vehicle, is a liquid oxygen, anhydrous ammonia, regeneratively cooled engine. The combustion chamber or nozzle, shown with its characteristic star pattern, is a brazed assembly of 347 stainless steel tubes, formed to shape, through which the anhydrous ammonia flows longitudinally as a coolant. Figure 2 is a photograph of this section showing its construction. The interior surface of the chamber is coated to provide insulation and protection for the tubes from the 5,000° F flame. This coating is generally made up of 0.005 inch of a Nichrome flame-sprayed undercoat with 0.010 inch of Rokide Z flame-sprayed zirconia as an insulating, erosion-resistant top coating.

In service, the Rokide Z coating has been spalling or flaking due to thermal cycling from the large number of engine starts required or from vibration due to an unstable flame. The history of chamber failures is included as table I. The loss of the coating exposes the stainless steel tubes to the heat and erosive effects of the flame. As this exposure occurs, the ammonia within the tubes is overheated locally and boils so that the cooling of the tubes is reduced. The ammonia vapors then attack the tube, and a very brittle nitrided layer is formed. At the same time, the combustion gases begin to melt and erode the tube surface. As this condition persists, the effective thickness of the tube wall is gradually decreased until it finally bursts from cyclic internal pressurization. This situation occurs in the throat of the nozzle and produces a chamber failure with raw fuel leaking into the chamber from the cracked tube. This process is illustrated in figures 3 and 4.

APPROACH

In January 1961, Materials Central of the Aeronautical Systems Division (ASD) in cooperation with the X-15 Project Office of ASD initiated a study to determine the chamber failure mechanisms and to outline an approach to improve chamber durability. A program to improve the coatings system was developed since the primary cause of failure is loss of the coating. The two possible approaches were to improve the Rokide coating or to develop an improved coating system. Since it was believed that improvements in the Rokide Z coating system would be small and perhaps marginal, the emphasis was placed on the development of a new coating system. At that time, a program with the Plasmakote Corporation[1] already underway to exploit the concept of gradated coatings was oriented to solve this specific problem.

A gradated coating is a sprayed coating of metal and ceramic in which the composition changes from 100 percent metal at the substrate to 100 percent ceramic at the surface. In this way the weak, sensitive interface between the metal and ceramic layers is removed as illustrated in figure 5. These coatings were produced by spraying mixed powders with an arc-plasma jet and gradually changing the composition by changing the ratio of metal to ceramic powders. Most of the coatings investigated were basically combinations of zirconia with Nichrome, molybdenum, and tungsten. An existing program with the University of Dayton[2] was oriented to provide realistic techniques for laboratory evaluation for the coatings being developed. Several tests were developed to screen for the most promising coatings. A thermal shock test used 3- by 8-inch plate sections of actual chambers which had been coated with the desired compositions. The ends of this plate were potted in plastic as shown in figure 6 and water was run through the tubes as a coolant. The plate was then cycled ten times at each of nine levels of gradually increasing heat flux produced by the 1/2 inch flame of a nitrogen stabilized, 50 kilowatt arc-plasma jet (3,000° F - 8,000° F). The test in operation is shown in figure 7. Four to six tests were run on each panel and the results were recorded as the number of cycles to fail the coating. Single, 1/2-inch-diameter tubes were also coated and tested in a manner similar to the panel tests. Although these tests turned out to be much less severe than the panel test, these tubes were also used to obtain the relative insulating effect of the coatings by using the tube as a calorimeter and measuring the heat transferred through the coating.

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[1] Contract AF 33(616)7323.
[2] Contract AF 33(616)7838.

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RESULTS OF LABORATORY EVALUATION

Most of the initial studies were concerned with two gradated coating systems, as described in table II. A great number of additional systems have been evaluated to determine trends or potential of new systems; however, an insufficient number of tests were run to consider the results statistically significant.

It should be noted that the only difference between the two gradated coatings is the primer used over the stainless steel tubes. The thermal shock-test results, in which the two gradated coatings were compared with Rokide Z, are illustrated in figure 8 as the number of cycles to failure.

The extreme spread in life of the Rokide Z system and the high concentration of early failures agreed with engine experience and perhaps indicates nonuniformity in the coating itself. Coating A appears to offer some improvement in life. This can be thought of as an improvement due to coating technique since the materials are the same. However, with coating B a significant improvement is obtained. There were no failures below 43 cycles. This improvement over coating A can only be due to the use of molybdenum as a primer which apparently results in a more adherent, shock-resistant coating.

These same test results are plotted in figure 9 to indicate probability of failure at any given number of cycles.

ENGINE TEST PROGRAM

An engine test program was undertaken to evaluate the most promising coatings under actual engine operating conditions. Coating B, which consists of a molybdenum primer with Nichrome gradated to zirconia, was chosen for the first test.

A mock-up of the combustion chamber illustrated in figure 10 was used to determine deposition rates for the spraying process so that the desired coating thickness could be obtained on the actual hardware. The mock-up was constructed of aluminum with panels cut from an old chamber inserted at three positions. This assembly is coated in the same manner as an engine and chamber, and coating thicknesses were measured. The coating thicknesses on the smooth surface are compared with those on the corrugated panels. Proper spraying parameters can then be determined for coating a combustion chamber.

A special fixture was built at NASA Flight Research Center for coating a fully assembled engine. This fixture and the coating operation on the first test engine are shown in figure 11. This figure shows the engine mounted in rings so that it can be rotated. Figure 12 is a rear view of this operation.

The fixture rotates the engine at various speeds and programs the arc spray gun in and out of the engine from a pantograph arrangement. This procedure allows control of engine rotation and gun position necessary to provide a uniform coating deposit.

The chamber available for the first engine test had failed previously and had one cracked tube, which was welded over. As can be seen from the previously mentioned photomicrographs of failed tubes (figs. 3 and 4), producing a sound, reliable weld in these areas is very difficult because of heavily nitrided layers on the internal cracks.

The gradated coating system applied was chemically similar to the original Rokide Z in that its surface was zirconia backed up by Nichrome. It was therefore assumed that interaction between the coating and combustion products would be similar. In normal operation of this engine, 12 "hot streaks" occur longitudinally through the engine, producing the star pattern mentioned previously. Characteristically, these hot streaks have a white, chalk like surface which may be due to thermal shock of the zirconia particles or hydrogen reduction of the surface with subsequent reoxidation. Several "top coats" of various materials were applied in two circumferential strips just aft of the throat. These were used to determine if the exhaust gases were locally oxidizing and if a more erosion resistant material than zirconia could be used in the engine. These strips consisted of overcoats of tantalum carbide, titanium carbide, titanium nitride, zirconia with 10-percent molybdenum, and zirconia with one percent nickel. Figure 13 is a photograph of the coated chamber, as viewed from the exit cone, showing these test strips.

Prior to the testing of the gradated coating system, a used chamber with a new Rokide Z coating was tested in an old engine to provide directly comparable coating life data. The firing procedure designed for coating evaluation is included in table III. The test data from firing this engine are included in table IV. Loss of the Rokide Z coating in the throat was visible after the second run and progressed until after the seventh start and a total running time of about $5\frac{1}{2}$ minutes. A total of 25 square inches of coating was lost during the test. This progression is illustrated in figures 14 to 16.

The gradated coating was then tested in a similar manner to produce comparable results. The test data from the firing of the gradated coating system are included in table V. As was mentioned previously, this chamber had been leaking and the cracked tubes were welded. After the second run two leaks were evident with no coating loss. Subsequent runs produced some coating loss around previously leaking areas but none in nonleaking throat areas. After six starts and a total of $5\frac{3}{4}$ minutes, 3 square inches of coating were lost from the leaking areas, slight erosion was evident in nonleaking areas, and chipping of coating surface was evidenced upstream of the throat. This progression can be seen in figures 17 and 18. Due to difficulties, the tests on this engine were stopped.

Figure 19 shows this engine after the test series and illustrates the blackening of the coating that was initiated during the first run. This blackening appeared to be Nichrome "bleed through," since the coating was found to be electrically conductive along its surface. Figure 19 also shows that one top coat, the titanium nitride, did protect the zirconia surface by stopping the chalking action.

A metallographic study was made of sections of this chamber to determine the effectiveness of the top coats and whether there was metal bleed through in the coating. Figure 20 illustrates the character of the original two-layer Rokide Z coating from an old engine. Figure 21 is a section from the throat of the test engine showing the molybdenum primer and Nichrome gradated to a zirconia surface. The top coat of zirconia appears somewhat thin but there is no evidence of metal bleed through. Figure 22 shows the gradated systems with a top coat of zirconia and 10-percent molybdenum used to determine whether molybdenum would oxidize or react in this environment. There is no evidence of attack indicated and the system appears compatible.

Figure 23 shows the gradated system with the titanium nitride top coat which appeared to offer some protection for the zirconia. It can be seen from these photomicrographs that the zirconia had turned black, including areas under the top coats, with no evidence of metal bleed through. It is known, however, that zirconia is easily reduced by hydrogen which causes it to turn black. Moreover, zirconia will dissolve up to 1-percent chromium and in doing so will turn black and become electrically conductive. This would account for the electrical conductivity of the coating and its blackness without any evidence of metal bleed through.

CONCLUSIONS FROM ENGINE TEST

The first engine test has essentially substantiated the results of the coating development program, in that the gradated Nichrome zirconia coating with a molybdenum primer has been demonstrated to be a significant improvement over the original Rokide Z coating system. The evaluation of the several types of top coats indicated that the combustion products were not reactive with the molybdenum zirconia system or the titanium nitride system. These results allow the development of potentially improved coating systems by replacing Nichrome with molybdenum and through the use of nonreactive top coats.

The metallographic study of the coating after test indicated that the surface blackening had no apparent effect on the usefulness of the coating. Therefore, except for the area of loss, the usefulness of the gradated coating was unimpaired except, perhaps, for some slight surface loss. Although the bulk-fuel temperature-rise data shown in table IV were scanty and will not identify local overheating, there is no indication that the insulation provided by the gradated coating is significantly different from the original Rokide Z system.

It is apparent from the early ruptures of fully coated tubes during the engine test that it will be extremely difficult or impossible to reclaim failed chambers. This fact also points out the importance of early replacement of the coating to prevent internal attack of the tubes. Repeated exposure of uncoated tubes will produce internal and external attack and eventual tube rupture. Therefore, even if a tube is recoated before it leaks, it may easily contain sufficient internal attack to rupture on subsequent pressurization.

FUTURE

The results of the first engine test were encouraging but not completely convincing since the test time was relatively short and long time effects on the coating over a large period of time could not be determined. Nevertheless, due to the urgent need for improved chamber life and because the gradated coating demonstrated a significant improvement for at least 5 minutes, two new chambers have been coated for use in the program. The coating system used is the molybdenum primer and Nichrome gradated to zirconia as in the test engine except that the zirconia top coat thickness has been increased from 0.004 inch to 0.006 inch, and 0.002 inch of titanium nitride has been added as a top coat. An additional old chamber was stripped and recoated with two gradated coating systems and two top coats for the second phase of the engine testing. This testing is currently underway. The coatings in this chamber are molybdenum gradated to zirconia and tungsten gradated to zirconia with top coats of titanium nitride and zirconium diboride. Portions of the chamber were covered during spraying so that each of the coatings with and without top coats will be exposed in the throat area. Longitudinal sections, rather than the circular strips of the previous tests were used so that exposure conditions will be as similar as possible. The compositions of these coatings were chosen for two reasons: First, it was necessary to evaluate quickly the usefulness of top coats in the throat area and to evaluate the effect of replacing Nichrome with a refractory metal; and second, it was necessary to validate the laboratory tests before proceeding to coating optimization.

The result of the first engine test indicated that the use of high melting-point compounds as top coats could possibly stop the gradual erosion or chalking of the zirconia surface. Titanium nitride stopped the chalking in an area where conditions are much less severe than the throat, and therefore it must be further evaluated to determine its usefulness. Zirconium diboride was also included as typical of another family of compounds which may offer this protection.

Refractory metals were used instead of Nichrome to determine their usefulness under engine conditions. In the first engine test, the top coat which contained 10-percent molybdenum showed no apparent attack or oxidation. It can, therefore, be assumed that the exhaust products are not excessively oxidizing. A refractory metal instead of Nichrome would appear desirable since, in the event of erosion or loss of the coating surface, a refractory metal would offer some protection to the tubes, whereas the Nichrome would very likely melt. By following this reasoning, heavy undercoats of 0.030-inch molybdenum and tungsten were used in the throat of this chamber.

There is some question as to the validity of the thermal shock test for evaluating the top coats or the refractory-metal systems, because the flame can be much hotter than that in the engine and there is some oxidation due to entrainment of air in the flame. The first engine test confirmed the use of thermal shock as a judge of coating capability for the early coatings investigated; however, in subsequent tests on systems with top coats all samples performed poorly. This poor performance may be a result of an inherent shock sensitivity in the system, or it may be that the test is overly severe. The shock-test results on coatings containing refractory metals have been very disappointing. The test results on samples of zirconia gradated with molybdenum have been scattered with a number of early failures. The few samples tested containing tungsten have all shown early failures. This may be due to the fact that the test is somewhat oxidizing because of air entrainment in the nitrogen flame. The titanium nitride top coat was used in the two new chambers because, although the tests indicated early failures were to be expected, they also indicated that only the top coat failed and the failure did not affect the performance of the basic coating. Therefore, the laboratory thermal-shock test results would indicate that the top coats and the coatings themselves that are in the current test engine would all fail very quickly. This engine is being run to determine the validity of these tests and to avoid overlooking promising coating systems because of an overly severe laboratory test.

The direction for further coating development work, shown schematically in figure 24, will be dependent upon the outcome to the current engine test. If the coatings perform satisfactorily, the laboratory tests must be modified to be more realistic, and coating development work will be to optimize a system containing molybdenum or tungsten gradated to zirconia with a top coat. If the coatings perform very poorly the thermal shock test will be considered valid and coating development work will be to optimize the earlier type coatings without top coats, and the test will be used to choose the best system. The climax to this program will be an additional engine test of an optimized coating system. This system will then be incorporated into the program for new chambers and for maintenance of existing chambers.

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TABLE I

XLR99 CHAMBER HISTORY

Serial number	Cycles at crack	Time to failure, min:sec
Failed chambers		
102	86	14:00
42		18:39.7
29		36:47.6
113	85	35:28.5
120		18:45.1
28		
Chambers exceeding rated life		
40	117	46:36.0
116	56	71:52.0
111	206	122:51.0

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TABLE II

IDENTIFICATION OF COATING SYSTEMS

Coating designation	Primer	Graduation 1	Graduation 2	Graduation 3	Insulating layer
Rokide Z	0.004-inch Nichrome				0.010-inch Rokide Z (ZrO_2)
Coating A (Plasmakote)	0.003-inch Nichrome	0.003-inch 70% Nichrome 30% ZrO_2	0.003-inch 30% Nichrome 70% ZrO_2	0.003-inch 10% Nichrome 90% ZrO_2	0.004-inch ZrO_2
Coating B (Plasmakote)	0.003-inch Molybdenum	0.003-inch 70% Nichrome 30% ZrO_2	0.003-inch 30% Nichrome 70% ZrO_2	0.003-inch 10% Nichrome 90% ZrO_2	0.004-inch ZrO_2

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TABLE III

XLR99 COATING TEST PROCEDURE FOR ENGINE SERIAL NUMBERS 101 AND 6

Run type	Throttle setting, percent	Time at throttle setting, sec
Oxygen-fuel ratio calibration of sea-level orifices	70	Start
	50	5
	90	5
	Off	
Engine calibration and functional	70	Start
	50	5
	50	5
	70	5
	80	5
	90	5
	100	5
	50	5
	100	5
	50	5
	Off	
Controllability and restart	70	Start + 5
	50	5
	Off	10
	70	Restart
	100	5
	50	5
	Off	
Restart series test no. 1	70	Start + 10
	Off	10
	70	Restart
	50	10
	Off	10
	70	Restart
	100	10
	Off	10
	70	Restart + 10
	Off	10
	70	Restart
	50	10
	Off	
Chamber durability (minimum thrust)	70	Start
	50	100
	Off	
Chamber durability (maximum thrust)	100	Start + 60
	Off	
Maximum thrust restart	70	Start
	50	10
	Off	10
	100	Restart + 40
	Off	
Restart series test no. 2	70	Start
	50	5
	Off	10
	70	Restart
	50	
	Off	10
	70	Restart
	50	5
	Off	10
	70	Restart
	50	5
	Off	10
	70	Restart
	50	5
	Off	

[redacted]

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TABLE IV

XLR99 CHAMBER COATING TEST DATA FOR CHAMBER SERIAL NUMBER 40 OF ENGINE SERIAL NUMBER 101 RECOATED WITH ROKIDE Z

[46 min 41 sec operating time before recoating]

Run number	Oxygen-fuel ratio	Run time, min:sec	Total time on coating, min:sec	Rokide Z loss in throat area, sq in.	Run type	Remarks
28-101	1.252	0:5.0	0:5.0	0	Oxygen-fuel-ratio calibration at sea level	Lost data.
29-101	1.252	0:7.9	0:12.9	$\frac{1}{2}$	Oxygen-fuel-ratio calibration at sea level	Faint chalky areas formed in hot streaks.
30-101	1.252	1:09.5	1:32.4	2	Calibration and functional	Chalk growing heavier; 50-percent thrust, [1]$\Delta T = 74^\circ$ F; 70-percent thrust, $\Delta T = 72^\circ$ F; 100-percent thrust, $\Delta T = 69^\circ$ F.
31-101	1.252	0:33.8	2:06.2	$8\frac{1}{2}$	Controllability and restart	Several tubes in most severe lower hot streaks are exposed for about 6 inches to Nichrome; 70-percent thrust, $\Delta T = 65^\circ$ F; 100-percent thrust, $\Delta T = 56^\circ$ F.
32-101	1.252	1:02.3	3:08.5	21	Restart series no. 1	Hot streaks now very well defined with heavy chalk and dark brown fringes. Chalk extends 12 inches downstream from throat. Rokide erosion visible at throat plane over entire circumference. Brown hot streaks extend all way to exit skirt.
33-101	1.252	1:15.5	4:24.0	21	Chamber durability	Ammonia exhaustion shutdown after 76 seconds of run. Short fuel supply due to improper propulsion-system test stand operation; 50-percent thrust, $\Delta T = 90^\circ$ F.
34-101	1.252	1:8.7	5:32.7	25	Chamber durability (maximum thrust)	

[1] ΔT is the temperature rise between fuel pump discharge and jacket outlet banjo.

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TABLE V

XLR99 CHAMBER COATING TEST DATA FOR CHAMBER SERIAL NUMBER 120 OF ENGINE SERIAL NUMBER 6 RECOATED WITH COATING SYSTEM NUMBER 1

(GRADATED ZrO_2 AND NICHROME)

[18 min 45.1 sec operating time before recoating]

Run number	Oxygen-fuel ratio	Run time, min:sec	Total time on coating, min:sec	Coating loss in throat area, sq in.	Run type	Remarks
37-006	1.200	0:24.5	0:24.5	0	Oxygen-fuel-ratio calibration at sea level	No coating loss visible. Entire chamber is blackened by apparent Nichrome bleed for about 18 inches downstream of throat plane. Blackened areas extend to exit in hot-streak zones. Chalk has formed in the throat.
38-006	1.250	1:11.5	1:36.0	0	Combined oxygen-fuel calibration, engine calibration, and functional	Two chamber leaks detected, one in number 1 and one in number 9 streak. Neither leak is liquid yet. Blackening may have receded slightly. Small chips have come off over leaks.
39-006	1.250	0:32.2	2:08.2	1	Restart series number	Leak in number 1 streak now liquid. Strip loss on tube crowns in loss area starting from leak chips; 50-percent thrust, [1] $\Delta T = 65^\circ$ F; 100-percent thrust, $\Delta T = 62^\circ$ F.
40-006	1.250	1:45.1	3:53.3	2	Chamber durability (minimum thrust)	Still no loss in areas other than in leak area. Orange tinge on TiN patch is due to NH_3 leaks; 50-percent thrust, $\Delta T = 72^\circ$ F; 100-percent thrust, $\Delta T = 69^\circ$ F.
41-006	1.250	1:04.9	4:58.2	2	Chamber durability (maximum thrust)	Still no noticeable loss in areas other than leak areas. Green tinge in numbers 1 and 9 streaks due to NH_3 leaks. Restart series postponed in interest of safety. Leak appears to have stabilized. Continuity test indicates that black chamber discoloration is electrically conductive; 100-percent thrust, $\Delta T = 62^\circ$ F.
42-006	1.250	0:46.0	5:44.2	3	Restart series number for three restarts	Slight crown erosion in other hot streak areas beside leak streaks. Restart series apparently more severe test than durability type. Hydrogen peroxide drain fire on third restart. Engine pulled for chamber replacement and propulsion-system-test-stand repair.

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[1] ΔT is the temperature rise between fuel pump discharge and jacket outlet banjo.

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REAR OF X-15 AIRPLANE WITH SLR99 ENGINE

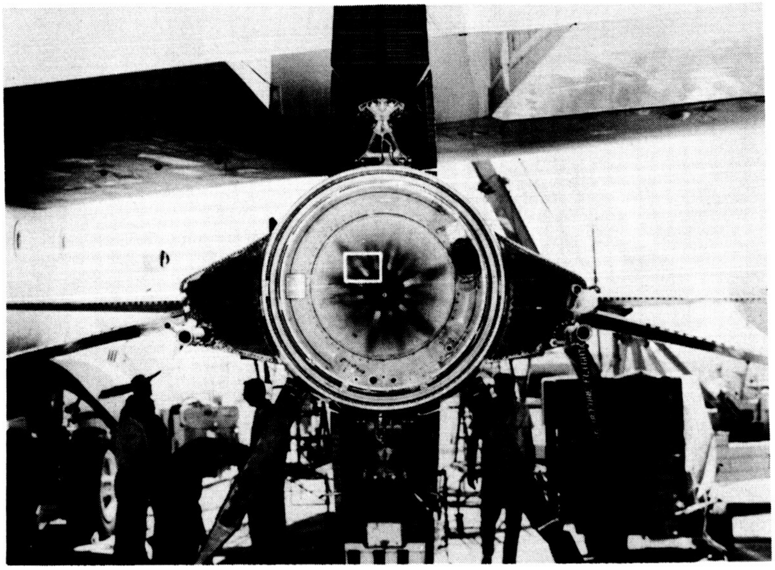

Figure 1

CLOSEUP OF SECTION OF CHAMBER

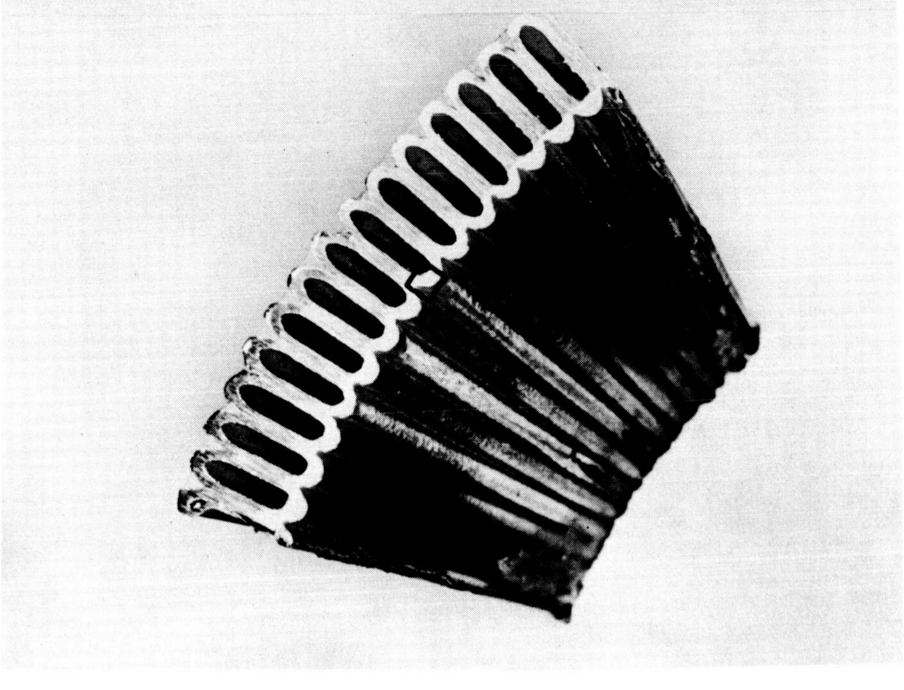

Figure 2

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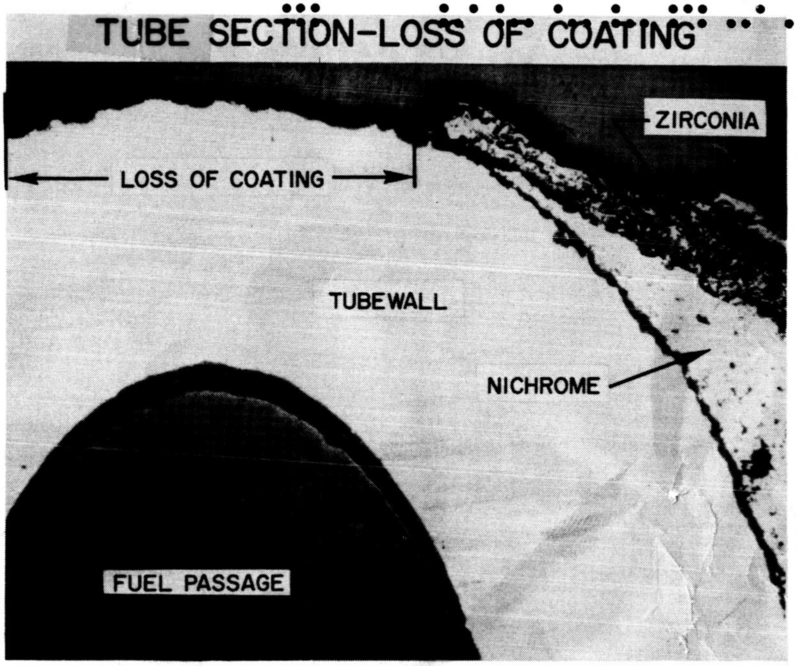

Figure 3

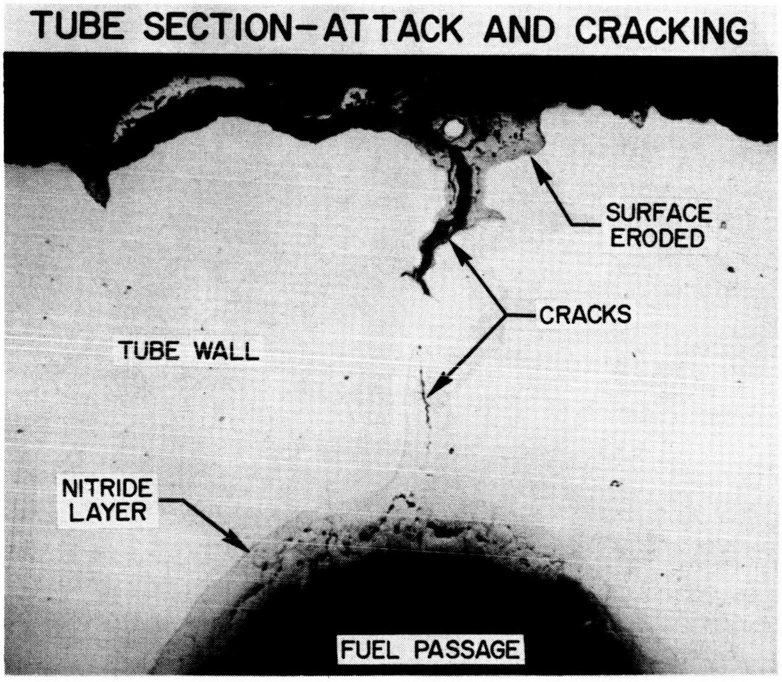

Figure 4

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GRADATED COATINGS

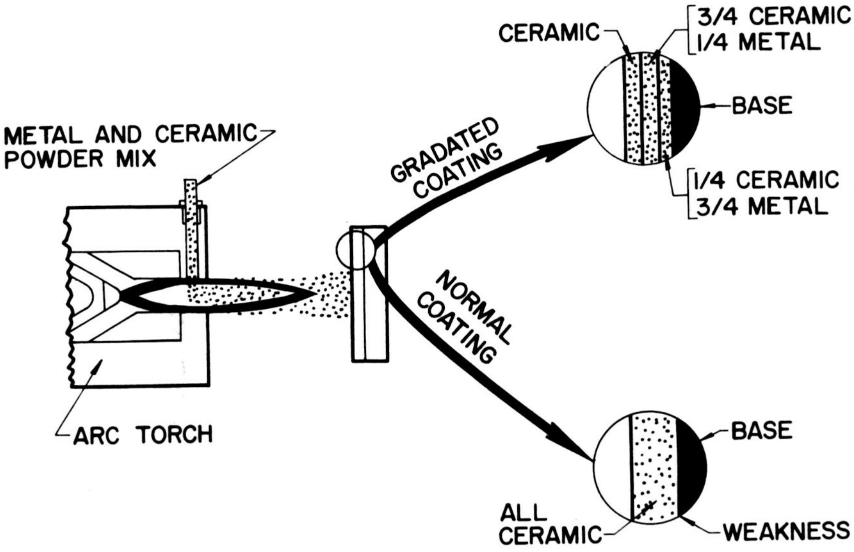


Figure 5

COATED PANEL FOR THERMAL SHOCK TEST

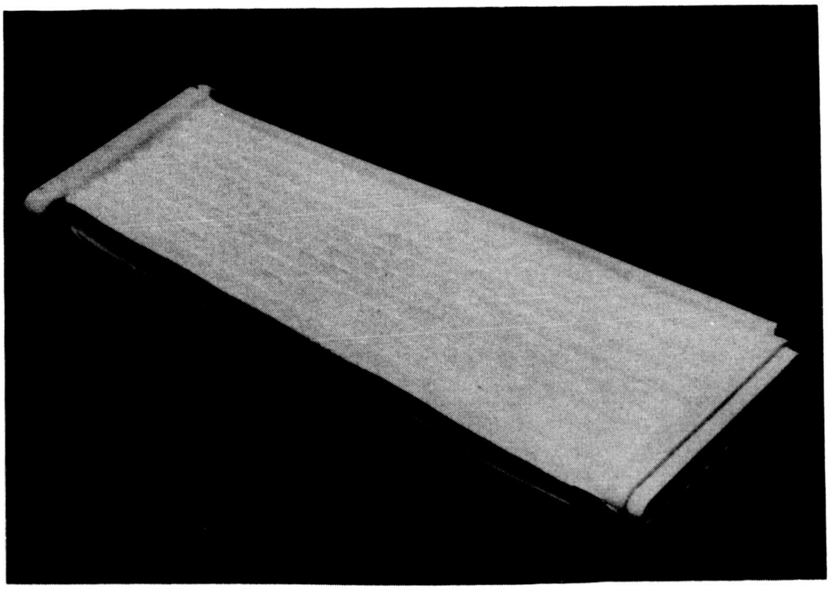
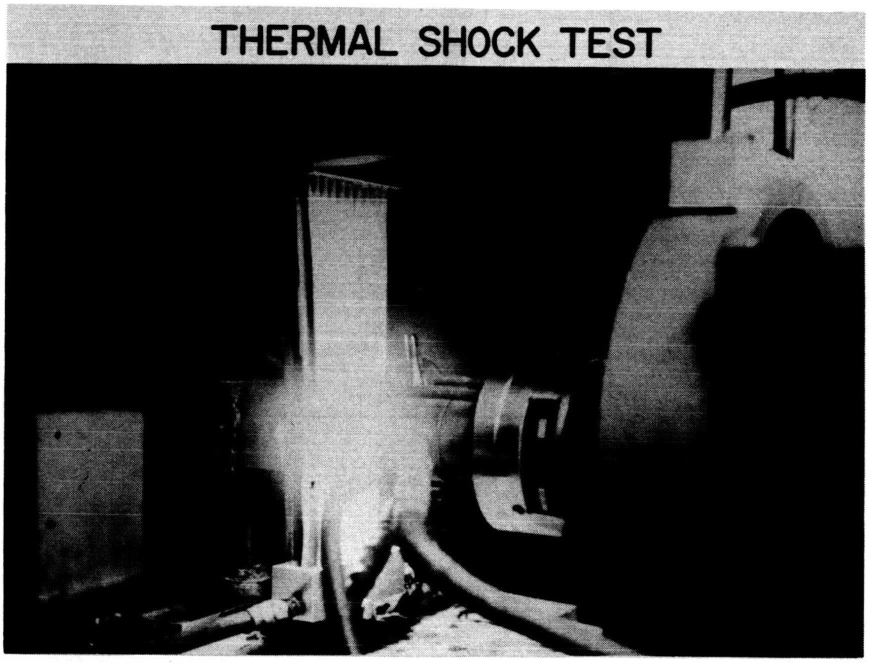


Figure 6

[redacted]



THERMAL SHOCK TEST

Figure 7

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THERMAL SHOCK-TEST RESULTS

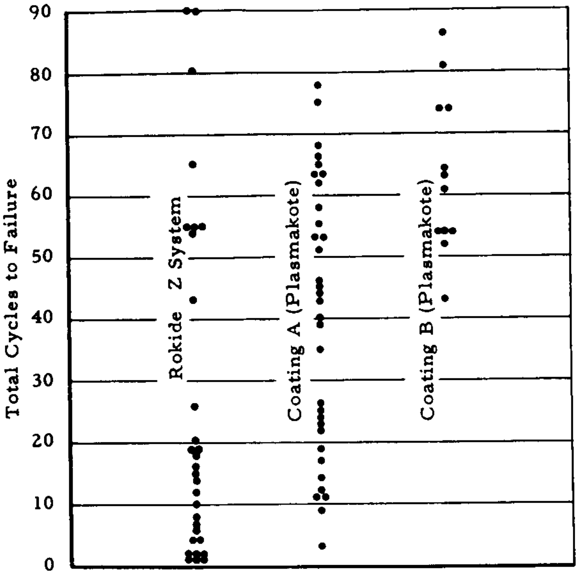

Figure 8

PROBABILITY OF THERMAL-SHOCK FAILURE

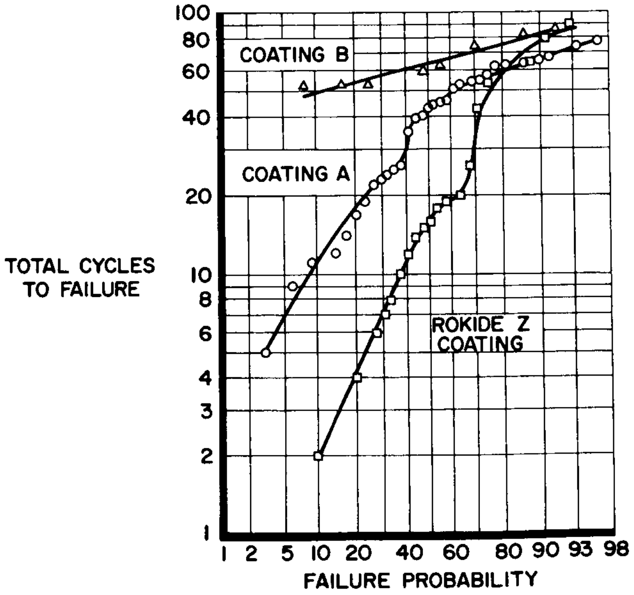

Figure 9

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MOCK-UP OF COMBUSTION CHAMBER

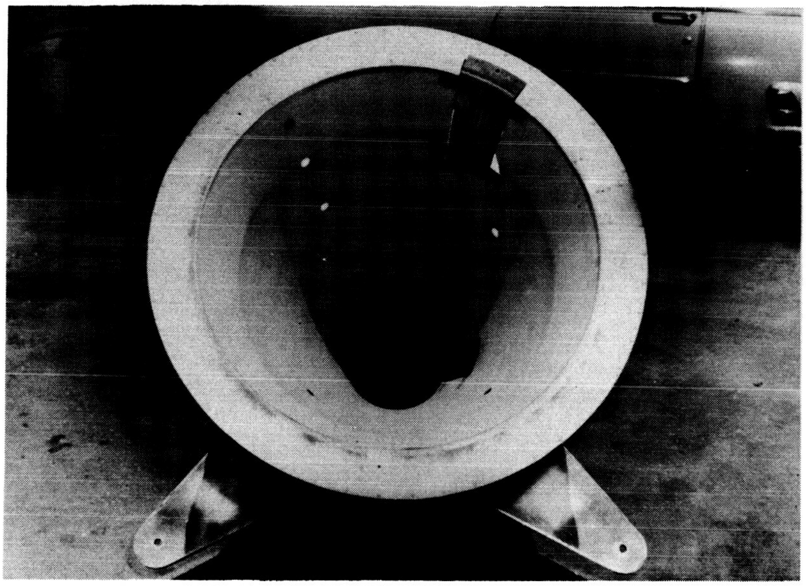

Figure 10

COATING OPERATION - SIDE VIEW

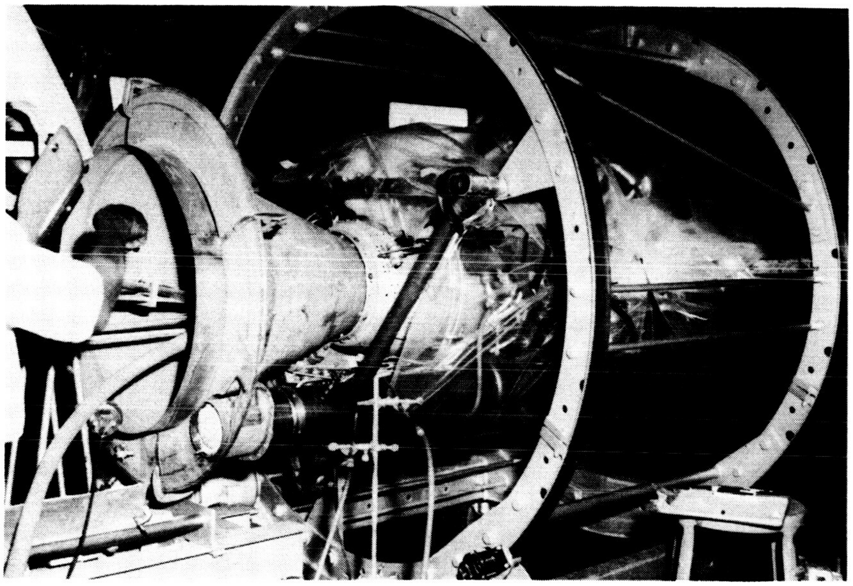

Figure 11

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COATING OPERATION - REAR VIEW

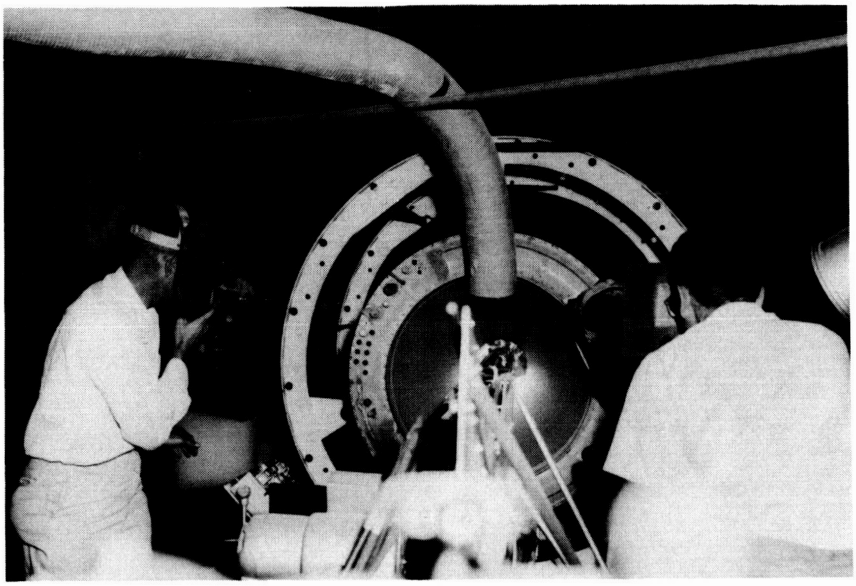

Figure 12

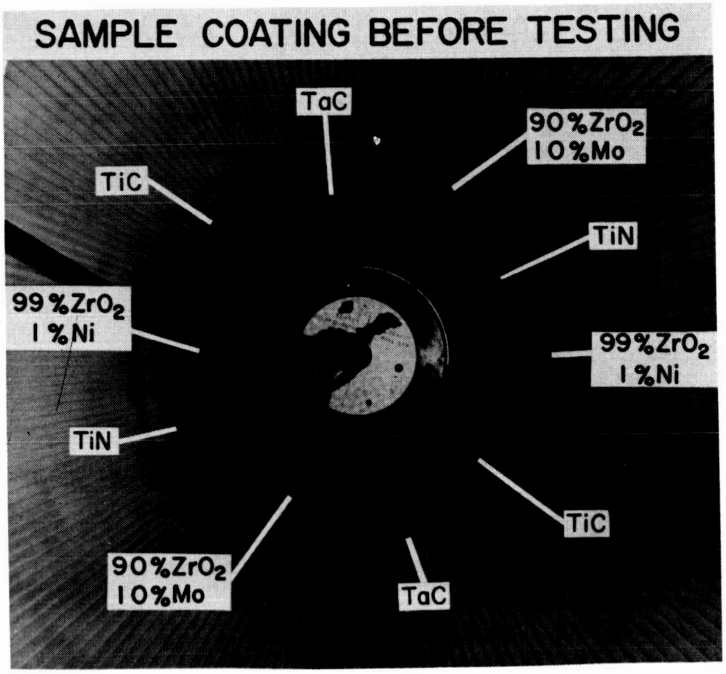

Figure 13

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ROKIDE Z COATING AFTER THREE STARTS AND 1-1/2 MINUTES
(2 SQ IN. OF ROKIDE Z LOST)

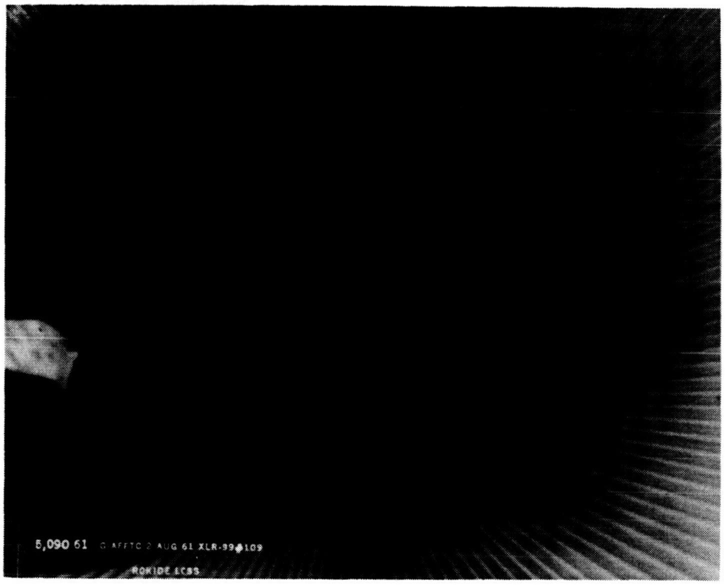

Figure 14

ROKIDE Z COATING AFTER FOUR STARTS AND 2 MINUTES
(8-1/2 SQ IN. OF ROKIDE Z LOST)

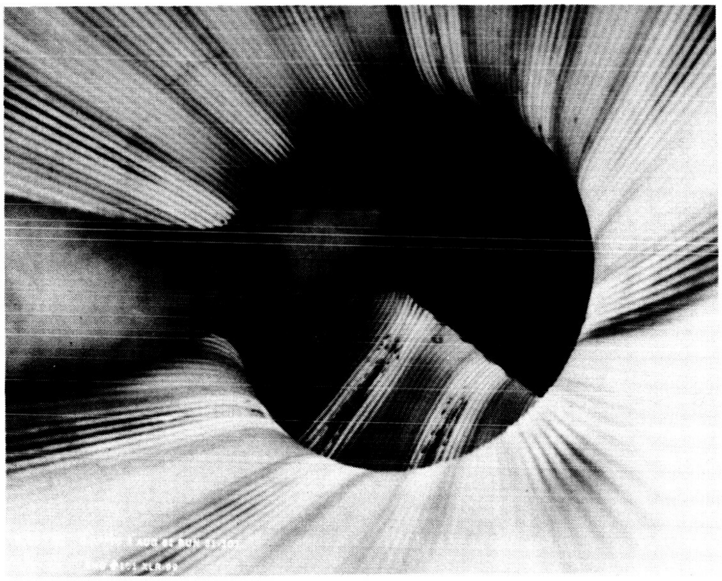

Figure 15

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ROKIDE Z COATING AFTER TEST - SEVEN STARTS AND
5-1/2 MINUTES
(25 SQ IN. OF ROKIDE Z LOST)

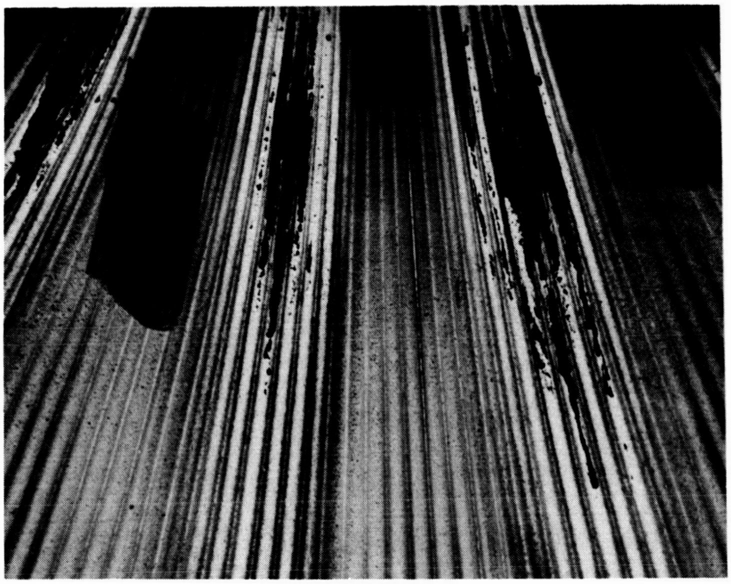

Figure 16

[redacted]

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GRADATED COATING AFTER THREE STARTS AND 2 MINUTES
(1 SQ IN. OF COATING LOST)

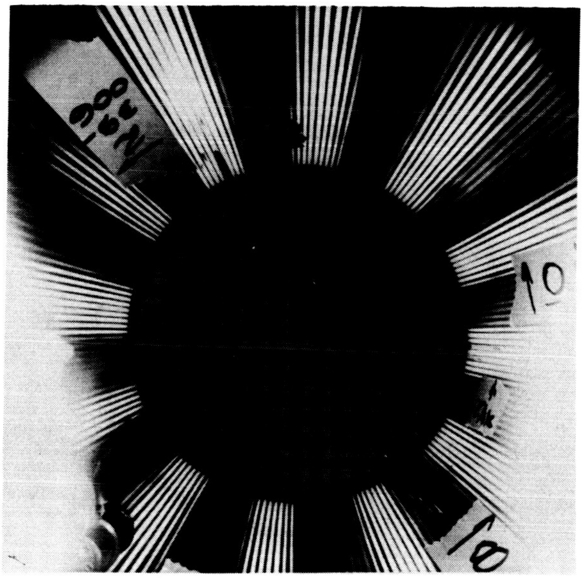


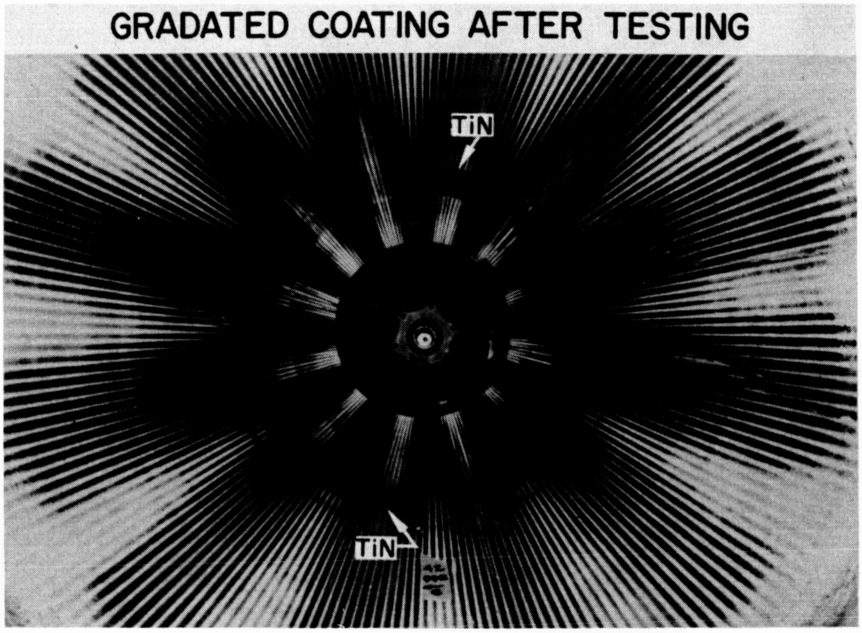
Figure 17

GRADATED COATING AFTER TEST - SIX STARTS AND 5-3/4 MIN
(3 SQ IN. OF COATING LOST)

Figure 18

[redacted]

[redacted]



GRADATED COATING AFTER TESTING

Figure 19

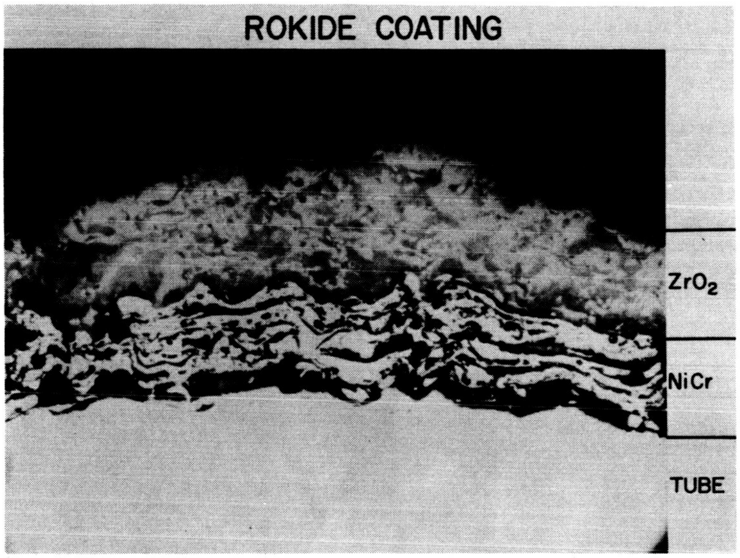


Figure 20

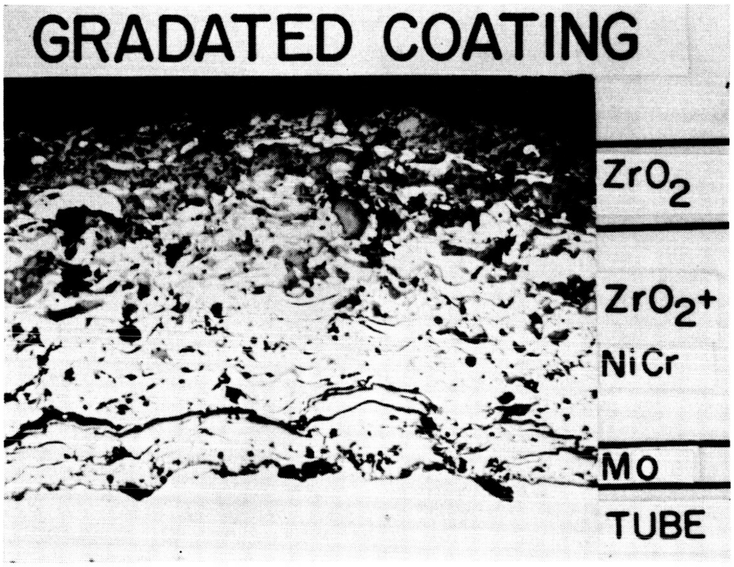


Figure 21

[redacted]

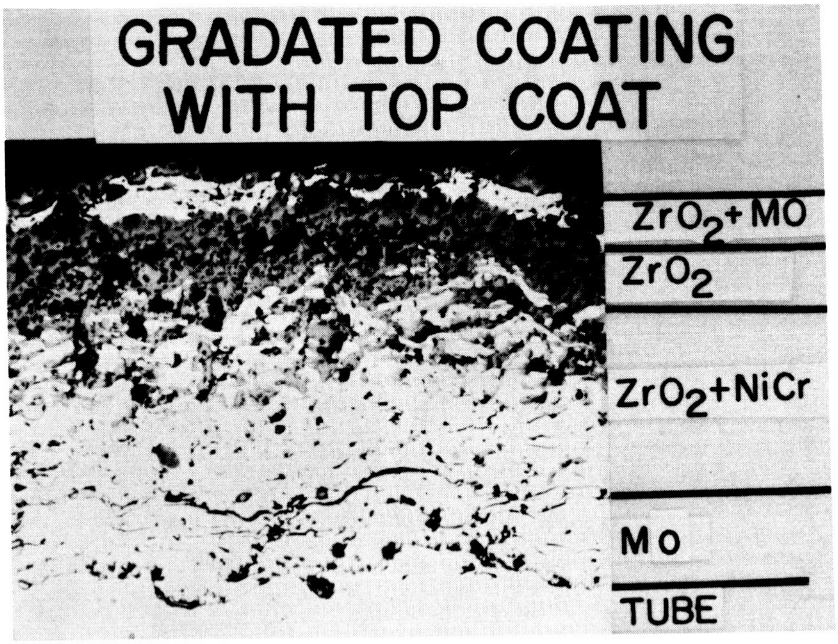


Figure 22

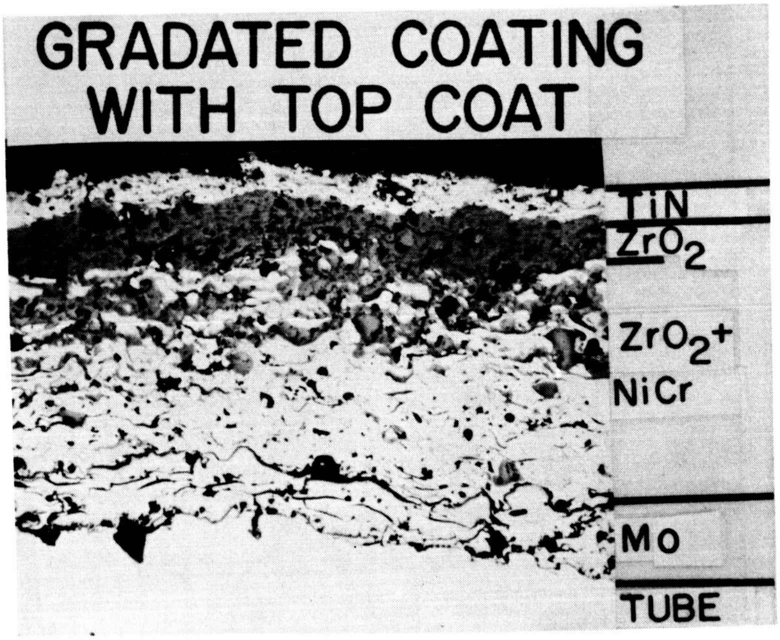


Figure 23

[redacted]

[redacted]

FUTURE OF COATING DEVELOPMENT

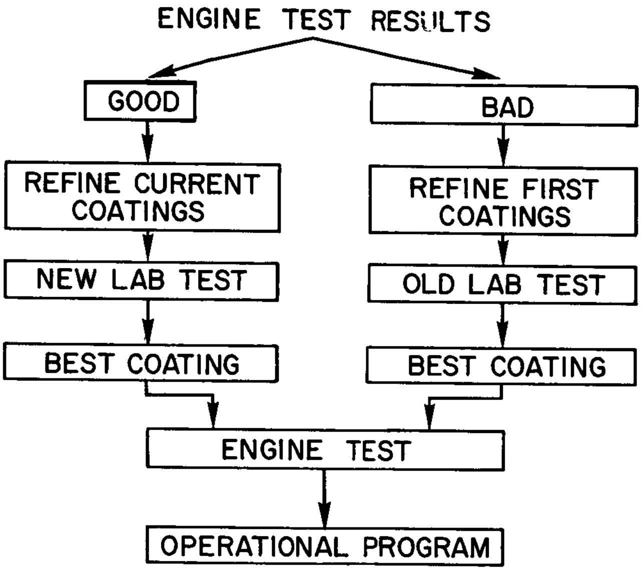


Figure 24

[redacted]