WADC TECHNICAL REPORT 54-492
PART III

OXIDATION-RESISTANT COATINGS
FOR MOLYBDENUM

D. V. Doane

Climax Molybdenum Company of Michigan

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Wright Air Development Center
Air Research and Development Command
United States Air Force
Wright-Patterson Air Force Base, Ohio

i

FOREWORD

This is the third and final part of a report of research on "Oxidation-Resistant Coatings for Molybdenum" by the Climax Molybdenum Company of Michigan, Detroit, Michigan, under USAF Contract No. AF 33(616)-2488, Task 70646, "Corrosion and Heat Resisting Alloys," Project 7351, "Metallurgy and Metallic Materials." This report serves as the final report for the contract. The contract was administered under the direction of the Aeronautical Research Laboratory, Directorate of Research, Wright Air Development Center. Lt. Attwell M. Adair served as Task Scientist during the period since Part II of this report was issued.

The majority of the work at Climax Molybdenum Company of Michigan was performed by J. R. Blanchard, Project Leader, and W. L. Milhem, Laboratory Technician, under the supervision of D. V. Doane, Metallurgical Supervisor, and G. A. Timmons, Vice President and Director of Research. The metallographic studies were performed by W. C. Coons, Project Leader.

Included in this report are the results of evaluation tests on chromium-nickel electrodeposits prepared by the National Bureau of Standards, under the supervision of Dr. Abner Brenner, with the sponsorship of the Bureau of Aeronautics, Department of the Navy. The nickel-clad specimens evaluated in this report were prepared at Battelle Memorial Institute under the supervision of M. LaChance.

ABSTRACT

Since Part 2 of this technical report was issued in June 1955, tests to evaluate the ductility and relative resistance to oxidation, thermal cycling, ballistic impact and erosion were completed on specimens of unalloyed molybdenum and 0.5% titanium-molybdenum alloy coated with the following materials:

1. aluminum-chromium-silicon sprayed-metal coating
2. nickel-chromium-boron sprayed-metal coatings
3. nickel-silicon-boron sprayed-metal coating
4. composite coating of 1 and 3
5. electroplated chromium
6. electroplated chromium-nickel composite
7. nickel cladding.

The evaluation tests were conducted at 1800^OF. Other tests included determination of ambient temperature ductility of coated molybdenum and oxidation tests at temperatures up to 3000^OF. The reported "self-healing" characteristics of aluminum-chromium-silicon coatings were investigated. Modifications to promising coating compositions were explored.

The results of evaluation tests and auxiliary metallographic studies provided a basis for a study of the "Nature of Promising Coatings" which constitutes the final section of this report. The pertinent findings of the investigation are presented in the following Summary page.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

Leslie B. Williams
Colonel, USAF
Chief, Aeronautical Research Laboratory
Directorate of Research

WADC TR 54-492 Pt 3   iii

SUMMARY

This report serves to record the results of research toward several objectives in the study of oxidation-resistant coatings for molybdenum. The following brief statements summarize the highlights of these studies:

1. The ballistic-impact resistance of electrodeposited chromium was shown to be quite satisfactory.

2. Although the tapered grip ductility specimen was not as satisfactory as the creep-rupture specimen previously employed, tests did indicate the ability of Cr-plate, Al-Cr-Si, Ni-Cr-B, Ni-Si-B coatings and a composite coating of Ni-Si-B and Al-Cr-Si to withstand 2% elongation at 1800°F without failure.

3. In an erosion test at 1800°F (essentially a controlled hot grit blast) all of the previously mentioned coatings and an Al-Ni-Si coating withstood the erosive action for at least 25 minutes.

4. Thermal shock tests of composite and modified coatings revealed encouraging results for porous chromium electrodeposits spray coated with Al-Cr-Si; since Cr alone is resistant to ballistic impact, but not to thermal shock, the composite warrants further investigation.

5. In all tests except the thermal cycling test, Cr-Ni electrodeposits on Mo exhibited equivalence or superiority to other coatings tested at this laboratory. The thermal cycling test revealed a specific limitation to this coating; the nickel separated from the underlying chromium.

6. Pure nickel cladding showed satisfactory ballistic-impact resistance, potential for greater resistance to thermal cycling than other nickel-base coatings, but less resistance to oxidation than nickel-base coatings containing chromium and silicon. Improvements in edge protection must be achieved before it will be possible to evaluate completely the effectiveness of the cladding itself or the effectiveness of spray coating clad molybdenum.

7. The ambient temperature ductility of molybdenum in bend tests and in special tup-type impact tests was reduced in the presence of the Al-Cr-Si and Ni-Cr-B coatings, although specimens as-coated with Al-Cr-Si showed more ductility than specimens as-coated with Ni-Cr-B. The ductility of the base 0.5% titanium-molybdenum alloy was unaffected by exposure for 500 hours at 1800°F plus 25 hours at 2000°F.

8. Oxidation tests at temperatures up to 3000°F established the following tentative temperature limits for promising sprayed-metal coatings for molybdenum:

$$Al-Cr-Si \quad 2600°F$$
$$Ni-Cr-B \quad 2200°F$$
$$Ni-Si-B \quad 2200°F$$

Tests of coatings comprising composites or mixtures of aluminum and aluminum oxide did not reveal any advantages for these coatings at high test temperatures.

9. Exploratory experiments, in which attempts were made to introduce a diffusion-barrier layer of copper between the molybdenum and nickel-base coatings, were not successful.

10. The results of experiments conducted to evaluate the "self-healing" of Al-Cr-Si coatings indicate that under some test conditions the flow of a eutectic phase from the coating can re-establish a coating where mechanical damage exposes small areas of molybdenum.

11. It is possible to summarize the behavior and nature of the general types of coatings studied under this contract in the following statements:

   a. Al-bonded coatings. These coatings are characterized by excellent bonding to base molybdenum through formation of a Mo$_3$Al-type layer which delays oxidation of underlying molybdenum. In evaluation tests at 1800°F, the coatings exhibit good resistance to oxidation and thermal shock, moderate resistance to erosion, but poor resistance to ballistic impact.

   b. Ni-base coatings. These are ductile coatings which serve well until cracks occur, then oxidation through cracks results in formation of nickel molybdate which accelerates failure under thermal cycling conditions. In evaluation tests at 1800°F, the coatings exhibit good resistance to oxidation and ballistic impact, and moderate resistance to erosion and thermal shock.

   c. Cr and Cr-Ni electrodeposited coatings. Cracks in the chromium promote pit-type attack on underlying molybdenum. The presence of a nickel overlayer delays this attack. In tests at 1800°F, these coatings exhibit good resistance to ballistic impact and erosion, erratic behavior in oxidation test, and poor resistance to thermal shock.

WADC TR 54-492 Pt 3   v

TABLE OF CONTENTS

WADC TR 54-492 Pt 3   vi

TABLE OF CONTENTS
(continued)

LIST OF ILLUSTRATIONS

LIST OF TABLES

OXIDATION-RESISTANT COATINGS FOR MOLYBDENUM

INTRODUCTION

This report, Part 3 of WADC Technical Report 54-492, constitutes the final report under Contract No. AF 33(616)-2488. In addition to presenting the results of investigations conducted since Part 2 was issued, an attempt will be made to summarize the knowledge gained from a six-year study of oxidation-resistant coatings for molybdenum.

Part 1, issued in December 1954, outlined the equipment and procedures used in applying sprayed-metal coatings on molybdenum. The oxidation test, thermal cycling test and ductility test were described in this report. The results of an exploration of coating compositions using sprayed-metal techniques were reported, as were the results of extensive tests on three compositions considered most promising. The importance of processing control in the application of sprayed-metal coatings was demonstrated. Seventy-five consecutive oxidation test specimens, prepared under careful but practical control procedures, sustained exposure to air for 500 hours at 1800^0F without failure; whereas without such control, the frequency of failure prior to 500 hours, using the same coating composition, was 15 in 20 specimens. Molybdenum bars electroplated with low contraction chromium exhibited considerable promise in oxidation test.

The report issued as Part 2 of WADC TR 54-492 in June 1955 described ballistic impact test equipment; summarized further studies of variables in the spray-coating process; presented the results of evaluation tests using coatings comprising composites of promising sprayed-metal compositions, and the results of thermal cycling tests with electroplated chromium, nickel, and nickel-chromium coatings. Also presented was a study of the changes in the nature of the aluminum-chromium-silicon coating during exposure to air at 1800^0F, as exhibited by weight changes, x-ray diffraction studies, and metallographic examination.

During the period since Part 2 was issued, coating research under this contract has been directed toward several objectives. Evaluation tests were completed using specimens of chromium-plated molybdenum, and of molybdenum coated with several sprayed-metal compositions, on which some tests were reported in Part 2. Since it had been found that no one coating exhibited outstanding performance in both impact and thermal shock tests at 1800^0F, a program was conducted to explore modifications of the chemical compositions of promising coatings. Through the cooperation of the National Bureau of Standards and the Navy Bureau of Aeronautics, specimens of molybdenum were electroplated with chromium plus nickel for evaluation tests in comparison with promising sprayed-metal coatings. Nickel-clad molybdenum was evaluated, and overlayers of sprayed-metal coatings were applied in the hope of extending service

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WADC TR 54-492 Pt 3   1

life in some of the tests. Exploration was made of "barrier-layer coatings", using copper to prevent (or minimize) diffusion, and overlayers of nickel and nickel-base alloys to develop higher melting points in the coating and to improve oxidation resistance. An investigation was made to determine the ductility and strain-rate sensitivity of coated molybdenum at temperatures near atmospheric, in answer to a need for quantitative comparisons with uncoated molybdenum. The useful temperature limits of several sprayed-metal coatings were determined in oxidation tests at temperatures up to 3000°F. An attempt was made to quantitatively define the reported "self-healing" characteristics of the aluminum-chromium-silicon coating.

The base metal used in the majority of the research on coatings during the period since issuing the last Technical Report, has been arc-cast 0.5% titanium-molybdenum alloy. This change was made because of the increased use of this alloy for its high strength and high recrystallization temperature. The use of the alloyed base metal has influenced coating behavior in some instances, and these influences will be reviewed in the report. An attempt will be made to specify the base material throughout the report, but unless otherwise stated, it may be assumed to be the 0.5% titanium-molybdenum alloy.

In addition to the specific objectives referred to above, each of which will be discussed in separate sections of this report, a broader objective of this final phase of coating research under Air Force sponsorship comprised a study of the nature of promising coatings. The mode of failure of coatings in the several evaluation tests was examined critically for clues as to failure mechanism. The changes in microstructure resulting from exposure to thermal cycling tests at 1800°F and exposure to oxidation tests at higher temperatures provided additional clues. The summary of "The Nature of Promising Coatings" appears as the final section of this Technical Report.

WADC TR 54-492 Pt 3   2

SECTION 1

FURTHER EVALUATION TESTS ON COATINGS PREVIOUSLY TESTED

During the period since the issuance of Part 2 of WADC TR 54-492, tests were conducted to determine the oxidation resistance, ductility, ballistic impact resistance, and erosion resistance of molybdenum electroplated with chromium. Ductility and erosion tests were completed on the aluminum-chromium-silicon coating, the nickel-silicon-boron coating (Coast Metals modified 50 Alloy), the nickel-chromium-boron coating (Colmonoy No. 5 and No. 6), and a composite coating of nickel-chromium-boron and aluminum-chromium-silicon. The compositions of the coatings and descriptions of the oxidation and ballistic impact tests have been given in previous WADC Technical Reports; the erosion test and a modified ductility test will be described in this section.

Oxidation Tests of Chromium-Plated Specimens

A series of eleven oxidation test panels (2 in. by 2 in. by 0.055 in.) of unalloyed molybdenum was electroplated with low contraction chromium (United Chromium CR 110); the plating thickness was 0.004 inches. To suspend the specimens in the plating bath and to provide electrical contact, a nickel wire was pressed into a slot cut into the molybdenum panel. In the oxidation test*, in which ten specimens were exposed to moving air at $1800^{\circ}F$, all specimens failed during the initial 24 hours' exposure. The failure occurred in all cases at the point of attachment of the nickel wire to the molybdenum. The nickel wire was removed from the one oxidation test specimen which had not been tested, and the exposed molybdenum was metal spray-coated with a nickel-chromium-boron alloy (Colmonoy No. 5); the specimen was diffusion treated in an argon atmosphere for 24 hours at $2000^{\circ}F$. Upon exposure to air at $1800^{\circ}F$, the specimen resisted oxidation for 150 hours. This constituted a considerable improvement over the results with as-plated specimens, but since the as-plated specimens all failed at the attachment point, it is not possible to state whether diffusion treatment itself improved oxidation life.

Ballistic Impact Tests of Chromium-Plated Specimens

Three ballistic impact specimens (1-7/8 in. by 1 in. by 0.094 in.) of unalloyed molybdenum were electroplated with chromium in the same manner as reported above. The nickel attachment wires were removed from two of the three specimens and the two specimens were altered as described above, except that they were diffusion treated in an argon atmosphere for two hours instead of 24 hours. The third specimen was tested in the as-plated condition.

In the impact test** the three specimens, heated to $1800^{\circ}F$, sustained impacts of steel shot (0.173 in. diameter) projected at a velocity of 330 feet per second without chipping or obvious cracking of the chromium plate. In the subsequent oxidation test at $1800^{\circ}F$, the as-plated specimen failed after 26 hours' exposure, whereas the two repaired and diffusion treated specimens endured for 140 hours before failure. Failures of all three specimens were definitely not associated with the impacted areas, but occurred at the points of attachment of the nickel wires.

*Described in WADC TR 54-492, Part I, December 1954, page 9ff.
**Described in WADC TR 54-492, Part II, June 1955, page 13ff.

WADC TR 54-492 Pt 3   3

Description of Modified Ductility Test

Coated molybdenum is subjected to the ductility test to determine whether the coating has the capacity to sustain a small amount of plastic deformation and still provide protection of the molybdenum against oxidation at 1800°F. In the ductility test formerly employed, plastic deformation amounting to 2-5% elongation was produced in creep-rupture testing equipment during 100 or 500 hours of testing. This test was tedious and expensive to perform. Inasmuch as a precise measurement of the elongation of the specimen was not required, a simpler test was adopted. In this test a cylindrical specimen with tapered ends for gripping is employed. A sketch of the specimen is shown in Figure 1. Electroplated specimens are tested without further finishing of the specimen. Spray-coated specimens are coated on all surfaces. After the diffusion treatment, the coating is machine ground to a smooth finish. The flat ends of the specimen are ground parallel. The distance between the ends is measured. The specimen is then subjected to an oxidation test in air for 4 to 8 hours at 1800°F to expose gross flaws in the coating.

The specimen is mounted in a tensile testing machine and heated in still air in an electric muffle furnace at 1800°F without being loaded to any appreciable extent. After the specimen has been heated at 1800°F for about 30 minutes, the load is applied. The rate of loading is about 1000 psi per minute in the elastic range and at a rate to produce 4% elongation per hour in the plastic range.

The rate of elongation is estimated by measuring the movement of the cross-head with a dial gage during testing. After approximately 4% elongation is observed on the dial gage, the specimen is removed from the tensile machine, and the distance between the flat surfaces on the ends of the specimen is measured with a micrometer to determine the exact amount of elongation. Due to slippage in the grips, 4% elongation measured by the dial gage actually produces approximately 2% elongation in the specimen. The elongated specimen is subjected to the standard oxidation test at 1800°F, to determine if the plastic deformation of the coated specimen has caused ruptures in the coating sufficient to expose the underlying molybdenum to oxidation.

An additional test is employed, in which the coated specimen is elongated approximately 4% under tensile loading at room temperature. The elongated specimen is measured, then subjected to the oxidation test at 1800°F. This test is designed to evaluate the ambient temperature ductility of the coating.

Ductility Tests of Several Coatings

Ductility tests at 1800°F and room temperature were conducted with specimens of the type described above, fabricated from 0.5% titanium-molybdenum alloy, and coated with electrodeposited chromium and sprayed-metal coatings of aluminum-chromium-silicon, nickel-chromium-boron, nickel-silicon-boron, and a composite coating of nickel-chromium-boron plus aluminum-chromium-silicon.

Tests of Specimens Electroplated with Chromium. Six ductility test specimens (0.250 in. gage diameter with tapered ends) that had been electroplated with a layer of chromium 0.004 inch thick were heated in an argon atmosphere for two hours at 2000°F before testing. The treatment was performed to improve the bond between the chromium plate and the molybdenum by the formation of an interfacial layer of a chromium-molybdenum solid solution.

Three specimens were tested at room temperature; three specimens were tested at 1800°F. The specimens were elongated approximately 2% at the gage section at the test temperatures. After the specimens were elongated, they were removed from the tensile machine and exposed to moving air at 1800°F. The results of the oxidation tests are given in Table 1.

So much difficulty was encountered in conducting the ductility tests with the electroplated specimens that the tests do not represent a true appraisal of the capacity of the plating to withstand plastic deformation at room temperature and at 1800°F. In the first place, the specimens could not be removed readily from the grips due to seizure of the plating to the grips. It was more difficult to remove specimens after the 1800°F test than after the room temperature test; nevertheless, all specimens had to be forced out of the grips. Although none of these specimens were broken during removal from the grips, several spray-coated specimens did break in tests described later. Therefore, it was assumed that the electrodeposits may have been damaged imperceptibly, even though fracturing did not occur.

The second problem involved oxidation of specimens at the point where nickel wires were brazed to the specimens to facilitate electroplating. This problem was not restricted to the ductility test specimens, but was encountered in other test specimens electroplated with chromium.

Attempts were made to repair the plated specimens by spray coating the defective areas with the Al-Cr-Si or Colmonoy No. 5 compositions, but failures continued to develop at the repaired areas.

It was concluded, therefore, that the results of the ductility tests with chromium-plated specimens were not reliable and that further tests of chromium plating should await the solution to the two problems involved.

Tests of Sprayed-Metal Coatings. Ductility tests at room temperature and 1800°F with sprayed-metal coatings on 0.5% Ti-Mo alloy were completed. Six specimens of each of the following coating compositions were prepared for testing:

1. Al-Cr-Si (20% Al + 80% Cr-Si alloy)

2. Colmonoy No. 5 (Ni-Cr-B alloy)

3. Coast Metals 50 alloy (Ni-Si-B alloy)

4. Composite of Colmonoy No. 6 alloy and Al-Cr-Si
   Layer 1: 0.002 in. Colmonoy No. 6
   Layer 2: 0.008 in. Al-Cr-Si

After the spray-coated specimens were diffusion treated two hours at 2000°F in purified hydrogen, the coatings were machine ground to a thickness of 0.005 in. (0.010 in. on diameter) as measured by a micrometer. The measurement represented the increase in diameter of the specimen as a result of coating. Because of the interdiffusion of coating and base metal, the actual thickness of the coating was greater than the measured increase in the radius of the specimen.

WADC TR 54-492 Pt 3   5

TABLE 1

RESULTS OF DUCTILITY TESTS WITH COATED
0.5% Ti-Mo ALLOY SPECIMENS

Specimen No.	Coating	Test Temp. °F	Oxidation Test after Elongating Gage Section 2%		
			Life at 1800°F, hr	Location of Failure	Remarks
E-44	Cr-plate	75	123	grip section	*
E-46	"	75	149	" "	*
E-47	"	75	93	gage section	*
E-42	"	1800	195	" "	*
E-43	"	1800	78	grip section	
D-150	Al-Cr-Si	75	351	gage section	
D-152	"	75	348	" "	
D-153	"	75	108	" "	
D-151	"	1800	500+	none	
D-154	"	1800	500+	none	
D-155	"	1800	500+	none	
D-158	Colmonoy No. 5	75	500+	none	*
D-160	"	75	500+	none	
D-161	"	75	500+	none	
D-156	"	1800	500+	none	
D-157	"	1800	500+	none	*
D-159	"	1800	500+	none	
D-162	Coast Metals 50	75	500+	none	*
D-163	"	75	500+	none	
D-164	"	1800	281	grip section	
D-165	"	1800	500+	none	*
D-167	"	1800	500+	none	*
Two-Layer Composite Coating - Colmonoy No. 6 + Al-Cr-Si					
D-437		75	23	gage section	coating cracked
D-438		75	23	" "	" "
D-439		75	46	" "	" "
D-440		1800	276	" "	*
D-441		1800	46	" "	*
D-442		1800	500+	none	*

* Repaired on flat ends or on tapered section by spray coating.

WADC TR 54-492 Pt 3   6

The data obtained and summarized in Table 1 show that all coatings had the capacity to sustain a 2% elongation in air at $1800^{O}F$ and provide protection for the underlying 0.5% titanium-molybdenum alloy for 500 hours in air at $1800^{O}F$ in the subsequent test. The results at $1800^{O}F$ with the composite coatings, however, were not consistent. It is suggested that forced removal of the specimens from the grips after testing in the tensile machine (encountered with all specimens) could have damaged the gage sections of these specimens sufficiently to reduce the life of the coating.

Erosion Test

An erosion test patterned after a test developed by the Aircraft Gas Turbine Division, General Electric Company, has been devised and standardized at this laboratory. The test is designed to simulate the effect of abrasive particles in the inlet air passing through the combustion chamber of the gas turbine and impinging on the turbine buckets. Admittedly, the laboratory test is severe, but it may serve to evaluate the relative abrasion resistance of coatings.

Description of Apparatus. The apparatus is essentially a device for hot grit blasting a coated molybdenum specimen heated to the testing temperature ($1800^{O}F$ for this investigation). The specimen is clamped in a vertical position, as shown in the sketch of the apparatus in Figure 2. Colmonoy Spraywelder, normally used for spray coating with powdered metals, blows the grit (No. 90 white aluminum oxide grit) through an oxy-acetylene flame onto the specimen, which is located at a distance of four inches from the nozzle of the Spraywelder. The hot grit particles impinge on the specimen at an angle of 45 degrees, and are concentrated on a small area about one inch below the top of the specimen. The flame of the Spraywelder heats the specimen to about $300^{O}F$; therefore, an auxiliary gas burner is used to supply the additional heat required to raise the temperature of the specimen near $1800^{O}F$ for the test. The auxiliary heat is applied to the rear surface of the specimen; this is shown in the sketch of the apparatus, Figure 2, and in a photograph of the test in operation, Figure 3.

The standard specimen for the erosion test is a panel 3 in. by 1 in. by 0.050-0.060 in. coated on all surfaces. Other sizes of specimens, however, can be tested with minor modifications to the clamping device.

Testing Procedure. The coated specimen is subjected to an oxidation test in air for eight hours at $1800^{O}F$ before erosion testing to ensure that there are no gross flaws in the coating.

The specimen is clamped in the vise shown in Figure 2 at a distance of four inches from the nozzle of the Spraywelder. The auxiliary burner is ignited and the gas-air ratio is adjusted to obtain an oxidizing flame at an air pressure of 24-25 psi.

The Spraywelder is ignited and clamped into position. Gas pressures used are:

Air	35 psi
Acetylene	12 psi
Oxygen	17 psi

The flame from the auxiliary burner is adjusted again so that the specimen is heated by the two heat sources to about 1780^OF, as measured with an optical pyrometer.

Approximately 1,200 grams of No. 90 aluminum oxide grit, which has been dried thoroughly by heating in an oven at 250^OF for at least 24 hours, is weighed and then placed in the hopper of the Spraywelder.

The valve regulating the flow of grit through the Spraywelder is opened to the proper position to obtain a flow of 30-35 grams of grit per minute.

The temperature of the specimen is measured with an optical pyrometer after the specimen has been blasted with grit for a few minutes. It has been found that the hot, impinging grit raises the temperature of the specimen about 30 to 40^OF. The auxiliary burner is adjusted, if necessary, so as to maintain the specimen at a temperature in the range 1800-1820^OF. A specimen being hot-grit blasted is shown in Figure 3.

At the end of each five-minute interval during testing, the flame and the flow of grit from the Spraywelder are shut off and the specimen, still heated to about 1500^OF by the auxiliary burner, is examined visually for evidence of failure; i.e., evolution of molybdic oxide vapors. If failure is not detected, the test is continued.

At the end of each ten-minute interval, the aluminum oxide grit is removed from the hopper and weighed so that the rate of flow of grit can be measured; the grit control valve is adjusted, if necessary. Grit is used only once as it had been found that reclaimed grit was not so abrasive as new grit. About 350 grams of grit are used in ten minutes of the test.

The procedure is continued until the substrate molybdenum is exposed and molybdic oxide vapor emanates from the eroded area upon inspection. Each end of the specimen is tested. The two eroded areas on one specimen are shown in Figure 4.

Erosion Tests of Several Coatings

Erosion tests at 1800^OF were conducted in the manner described above on three specimens of unalloyed molybdenum coated with the following materials:

1. electrodeposited chromium
2. aluminum-chromium-silicon sprayed-metal coating
3. nickel-chromium-boron sprayed-metal coating
4. nickel-silicon-boron sprayed-metal coating
5. aluminum-nickel-silicon sprayed-metal coating
6. a composite of 2 and 3.

The results of the tests are given in Table 2. All specimens were oxidation tested in air at 1800^OF for eight hours before the erosion test. Two of the four specimens coated with aluminum-chromium-silicon were exposed to moving air at 2000^OF for 200 hours in addition to the regular 1800^OF treatment. It is shown in Table 2 that the 2000^OF treatment improved the erosion resistance of the aluminum-chromium-silicon coating.

WADC TR 54-492 Pt 3   8

The consistency of the results obtained with each particular coating composition is an indication that the testing procedure for the erosion test is satisfactory. Failures of the four coating compositions occurred in 25 to 65 minutes. The Colmonoy No. 5 coating endured the longest; the aluminum-chromium-silicon coating that was exposed only eight hours at 1800^OF before testing had the least resistance to erosion.

The severe abrasiveness of new aluminum oxide grit is demonstrated in the test with the Colmonoy No. 5 coating. The end of the specimen that was hot grit blasted with reclaimed grit endured about twice as long as the end of the specimen that was hot grit blasted with new grit.

TABLE 2

RESULTS OF EROSION TESTS AT 1800^OF WITH COATED
MOLYBDENUM SPECIMENS 3 IN. BY 1 IN. BY 0.055 IN.

Specimen No.	Coating Composition	Life of Coating, minutes	
		End A	End B
D-131	Al-Cr-Si	30	25
D-132	Al-Cr-Si	25	25
D-271	Al-Cr-Si*	45	40
D-273	Al-Cr-Si*	45	40
D-245	Colmonoy No. 5	65	110**
D-246	Colmonoy No. 5	60	60
D-247	Colmonoy No. 5	60	55
D-248	Coast Metals 50	40	50
D-249	Coast Metals 50	50	50
D-250	Coast Metals 50	50	40
D-251	Al-Nisiloy	35	35
D-252	Al-Nisiloy	35	30
D-253	Al-Nisiloy	30	40
D-443)	(Composite of	35	55
D-444)	(Colmonoy No. 6	45	35
D-445)	(plus Al-Cr-Si	30	55
D-186	Cr Plate	30	35
D-187	Cr Plate	25	25
D-188	Cr Plate	25	30

* Exposed 200 hours to air at 2000^OF in addition to the eight-hour exposure at 1800^OF before testing.

** Reclaimed grit employed in test of End B.

WADC TR 54-492 Pt 3 9
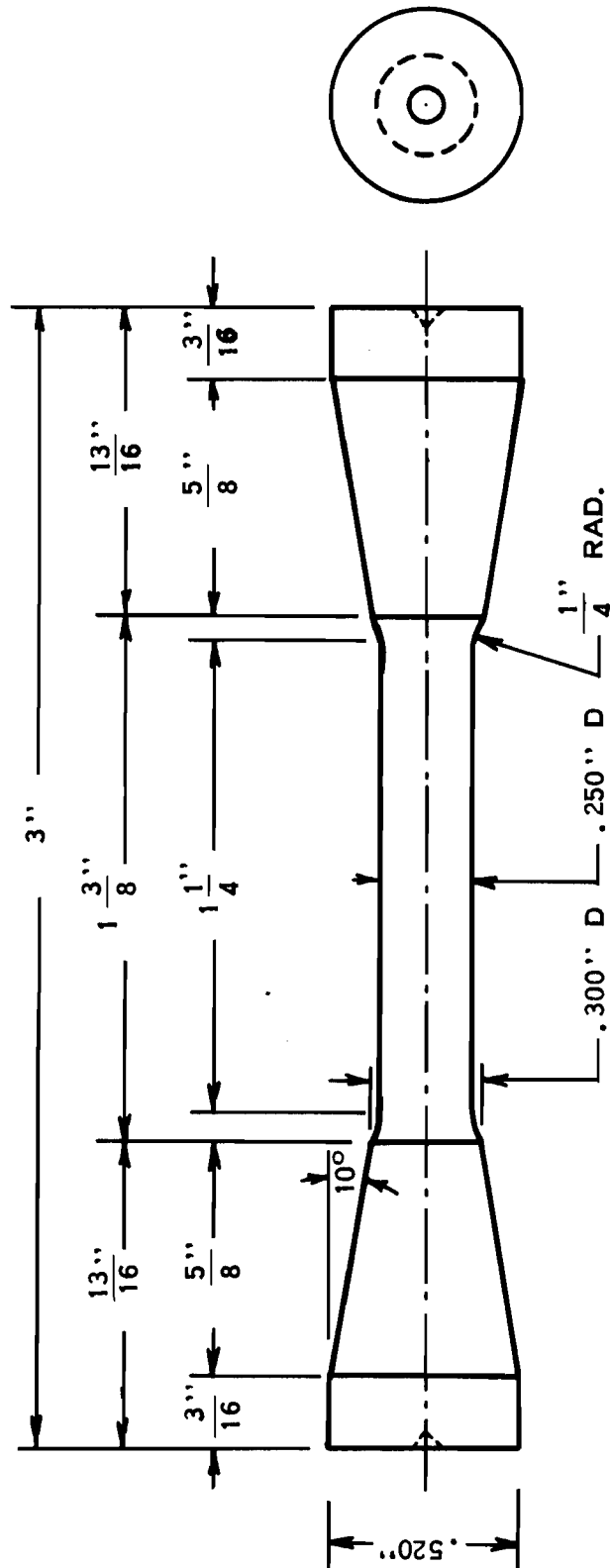
FIGURE 1 (917) – DUCTILITY TEST SPECIMEN WITH TAPERED ENDS

FIGURE 2

APPARATUS FOR EVALUATING EROSION RESISTANCE OF COATED MOLYBDENUM SPECIMENS AT 1800 F

CLIMAX MOLYBDENUM CO. 972
NOVEMBER 9, 1955

WADC TR 54-492 Pt 3

11
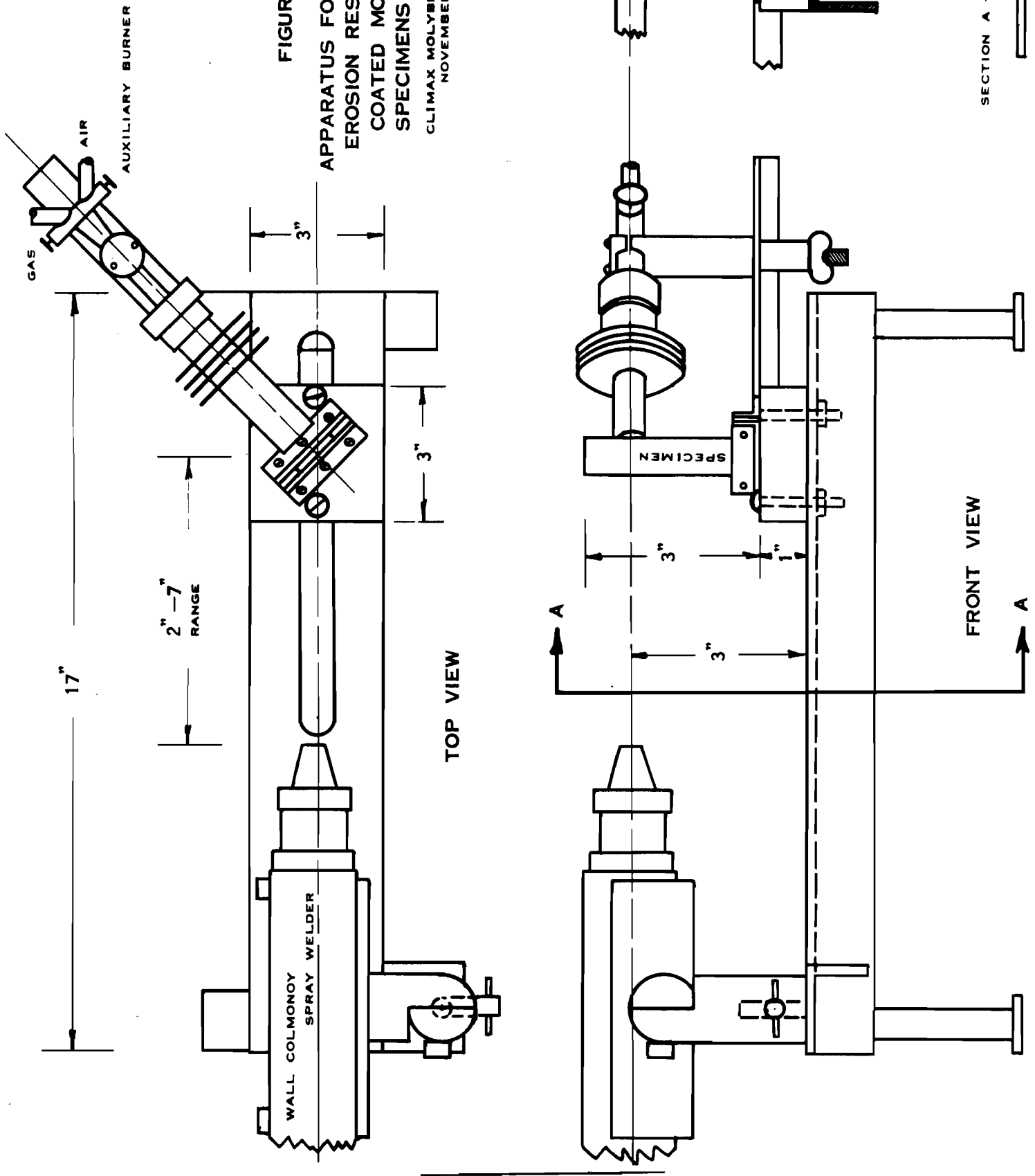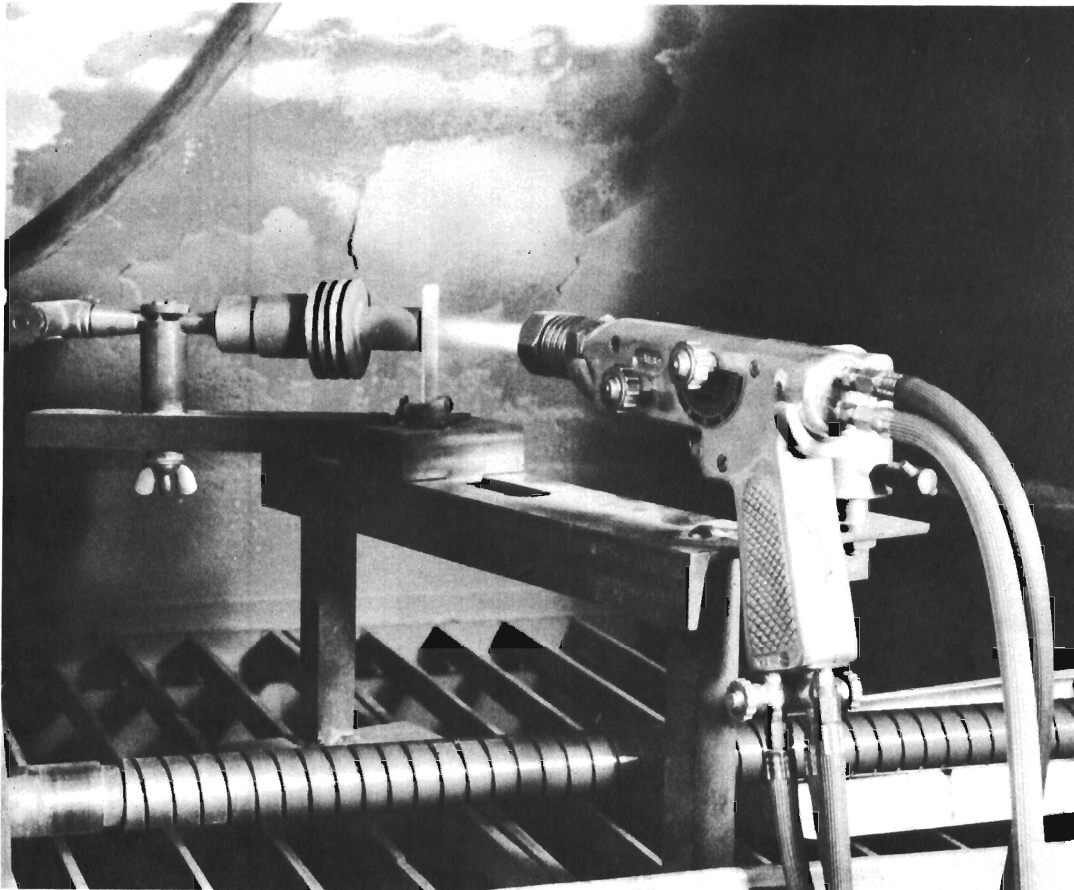
FIGURE 3 (P1267) - HOT GRIT BLASTING OF COATED MOLYBDENUM SPECIMEN
USING EROSION TEST APPARATUS
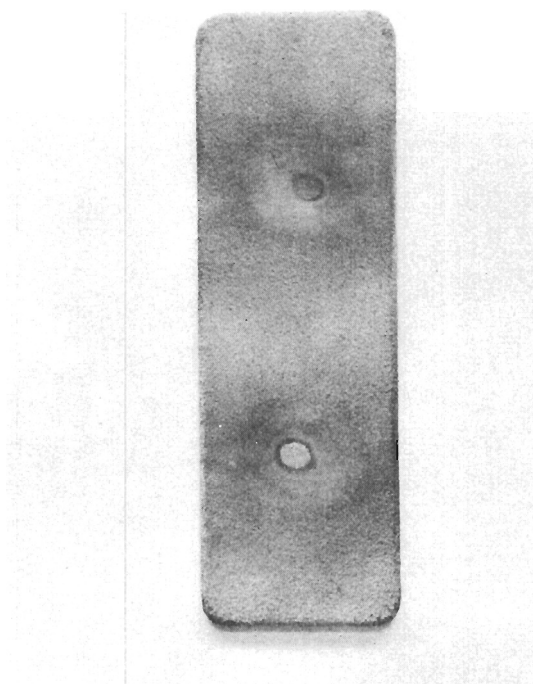
FIGURE 4 (P1325)   FULL SIZE

COATED MOLYBDENUM SPECIMEN SHOWING THE TWO
ERODED AREAS OBTAINED IN TWO EROSION TESTS
AT 1800°F (Al-Cr-Si Coating)

WADC TR 54-492 Pt 3   13

SECTION 2

EXPLORATION OF MODIFIED SPRAY COATING COMPOSITIONS

At the time of writing Part 2 of WADC TR 54-492, it had been found that no single coating exhibited outstanding results in both impact and thermal shock tests at 1800°F, even though the coatings tested had satisfactorily resisted oxidation at 1800°F for 500 hours, plus an additional 100 hours' exposure to oxidation at 2000°F. One composite coating of nickel-chromium-boron and aluminum-chromium-silicon compositions applied with metallizing equipment exhibited thermal shock resistance as satisfactory as the aluminum-chromium-silicon composition alone, and better resistance to ballistic impact. This behavior indicated promise in modifying or combining sprayed-metal coating compositions. This section of the report presents the several modifications attempted and the results of preliminary evaluation tests.

Additions of Molybdenum to Nickel-Base Coatings

In an attempt to increase the melting point and reduce the thermal expansion characteristics of nickel-base coatings, molybdenum was added in varying amounts to the nickel-chromium-boron (Colmonoy) and the nickel-silicon-boron coatings. Molybdenum powder was mixed mechanically with the alloy powders to provide mixtures containing 10, 20 and 30% molybdenum by weight. Three oxidation test panels of unalloyed molybdenum were spray coated with each mixture, using the usual procedures described in previous reports. In oxidation tests at 1800°F, the panels coated with mixtures containing 10% molybdenum powder endured for 500 hours without failure. The coatings containing 20 and 30% molybdenum became powdery during exposure and failed in 180-436 hours.

Three molybdenum thermal shock specimens were coated with 10% molybdenum plus 90% Colmonoy No. 5, and three similar specimens were coated with 10% molybdenum plus 90% Coast Metals 50 alloy. Thermal shock tests with these specimens resulted in failures in the range 87-123 cycles. These results did not constitute an improvement over the results obtained without the molybdenum addition. Therefore, experiments with additions of molybdenum to nickel-base alloys were discontinued.

Composite Coatings of Aluminum-Bonded and Nickel-Base Alloys

In tests at 1800°F, aluminum-bonded coatings have been found to be superior to nickel-base coatings in the thermal shock test, but inferior to nickel-base coatings in the ballistic-impact test. In the latter test, the nickel-base coatings exhibit a definite superiority in that they do not spall under the impact of a steel shot with a velocity of 330 feet per second. The aluminum-bonded coating spalls at this velocity of impact. The superiority of the nickel-base coatings in this test is attributed to the fact that the nickel-base coatings are more ductile than the aluminum-bonded coatings at 1800°F.

WADC TR 54-492 Pt 3   14

Previous experiments to improve the ballistic-impact resistance of aluminum-bonded coatings by applying a nickel-base coating 0.002 in. thick beneath the aluminum-bonded coating did not achieve the desired increase in ductility, as the composite coating failed within 22 hours' exposure to air at 1800°F after impacting.

Since the impact resistance of the Al-Cr-Si and aluminum Alloy 13 coatings was not increased appreciably by the Colmonoy inner layer, it was thought that the desired plasticity of composite coatings at 1800°F might be attained if Colmonoy or another ductile metal comprised the outer layer of the composite.

Oxidation tests at 1800°F with each of four different composite coatings, in which aluminum Alloy 13 or the Al-Cr-Si coating served as inner layers, and Colmonoy No. 6 or pure nickel served as outer layers, indicated that the Al-Cr-Si plus nickel coating had sufficient promise to warrant further testing. The other three coatings either separated in the diffusion treatment or could not sustain 500 hours' exposure to air at 1800°F without failure.

Ballistic impact tests and thermal cycling tests were conducted at 1800°F with a sprayed-metal composite coating comprising a layer 0.007 in. thick of the aluminum-chromium-silicon composition, diffusion treated two hours at 2200°F in dry argon, and a layer 0.003 in. thick of nickel, diffusion treated two hours at 2000°F in dry argon. In the ballistic impact test, the specimens subjected to impact velocities of 330 feet per second (the standard test) did not fail immediately, but exhibited failure in a subsequent oxidation test after 23 hours' exposure.

In thermal cycling tests with specimens prepared as described above, the nickel layer peeled immediately, but the underlying Al-Cr-Si layer endured for more than 1,000 cycles. The exceptional life in the thermal cycling test was attributed to the high temperature diffusion treatment of the Al-Cr-Si layer. Confirming tests will be presented in a later section of this report.

Although the nickel layer over the Al-Cr-Si coating apparently absorbed some of the energy in the ballistic impact test and prevented immediate failure, the improvement over the Al-Cr-Si coating alone was only slight; when failure occurred, nickel molybdate was formed, which spalled on cooling. The immediate peeling in the thermal cycling test indicated an inadequate bond between the two coating layers. Further work with composite coatings was discontinued.

Aluminum-Chromium-Silicon Coatings of High Aluminum Content

In an attempt to improve the plasticity of the outer portion of the aluminum-chromium-silicon coating, and thus improve the ballistic impact resistance of the coating, the following coatings of high aluminum content were investigated:

1. 0.010 in. single layer 50% aluminum plus 50% chromium-silicon alloy

2. Layer 1: 0.008 in. 20% aluminum plus 80% chromium-silicon alloy
   Layer 2: 0.002 in. aluminum Alloy 13

WADC TR 54-492 Pt 3   15

3. 0.010 in. single layer aluminum Alloy 13.

Ballistic impact tests were conducted with these coatings. All coatings failed immediately at the impacted area under impact velocities of 130 and 330 feet per second.

Porous Chromium Plate Spray Coated with Aluminum-Chromium-Silicon

Thermal shock tests with unalloyed molybdenum specimens electroplated with various types of chromium plate showed, in prior work*, that the coatings endured for a maximum of 60 cycles before failure occurred. These results were considerably inferior to those obtained with sprayed coatings of Al-Cr-Si. The latter coatings have the capacity to sustain 400-500 cycles before failure occurs.

In the group of chromium-plated specimens were three thermal shock specimens plated with porous chromium.** They were prepared in order to facilitate the application of a sprayed metal coating over chromium plate to enhance the oxidation protection afforded by chromium. Other types of chromium plate were found to be exceedingly difficult to spray coat. In previous tests, porous chromium was as resistant to thermal shock as the other types of chromium plate tested.

A layer of Al-Cr-Si 0.010 in. thick was sprayed on three thermal shock specimens plated with porous chromium. They were not grit blasted prior to spraying.

After diffusion treating in dry argon for two hours at 2000°F, two specimens were oxidation tested for eight hours in air at 1800°F. One specimen was exposed at 1800°F until failure, which occurred when a small flaw was detected at an edge after 200 hours of testing. The first two specimens were subjected to a thermal shock test at 1800°F. All three specimens were given an erosion test at 1800°F.

The results obtained in these tests are shown in Table 3 and indicate that the sprayed coating was beneficial. The performances, however, did not exceed those obtained with the Al-Cr-Si coating alone.

In the thermal shock tests failures occurred after 230-330 cycles, whereas the plating alone failed in 60 cycles. The specimen that had been exposed to air for 200 hours at 1800°F before testing failed in 40-55 minutes in the erosion test; the other two specimens failed in 35-40 minutes. Previously the maximum life in the erosion test exhibited by chromium plate was 30 minutes.

The results of these tests indicated that spray coating with Al-Cr-Si improved the performance of porous chromium plate in thermal shock and erosion tests at 1800°F. The life in the thermal shock test was not as long as obtained with straight Al-Cr-Si coatings. However, the thermal shock test is considered very severe; thus, the minimum life of 290 cycles obtained with the specimens is an indication

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*WADC TR 54-492, Part 2
**CR110 chromium plate with reverse current at end of plating cycle

WADC TR 54-492 Pt 3   16

that the composite coating has fair thermal shock resistance and might, therefore,
be acceptable. Since tests to date indicate that electroplated chromium satisfact-
orily withstands the ballistic impact test, it is conceivable that the composite will
exhibit an acceptable combination of properties. It is recommended, therefore,
that future investigations incorporate tests for the further evaluation of the porous
chromium plus Al-Cr-Si composite coating.

TABLE 3

RESULTS OF THERMAL SHOCK AND EROSION TESTS WITH SPECIMENS
ELECTROPLATED WITH POROUS CHROMIUM AND SPRAYED WITH Al-Cr-Si

Coating Composition		Thermal Shock Test Cycles to Failure		Erosion Test Minutes to Failure	
		A	B	A	B
Porous Chromium, as-plated, 0.003 in. thick					
	Specimen 1	60	50		
	Specimen 2	60	55		
	Specimen 3	60	50		
0.003 in. Porous Chromium +	0.010 in. Al-Cr-Si				
	Specimen E-25*	-	-	55	40
	Specimen E-26	290	333	35	35
	Specimen E-27	234	290	40	40

* Specimen E-25 was subjected to oxidation test in air at 1800^OF for 200 hours
  before erosion test was conducted.

SECTION 3

EVALUATION OF AN ELECTROPLATED CHROMIUM-NICKEL COATING

Over the past several years, this laboratory has obtained and evaluated many specimens of molybdenum electroplated with chromium. It is believed that chromium offers considerable promise as a coating for molybdenum due to its low coefficient of thermal expansion and high degree of oxidation resistance. Results to date have been erratic; some specimens exhibited excellent resistance to oxidation; others failed disappointingly in a few hours of exposure. Failures apparently occurred by oxidation of molybdenum through pores in the electrodeposit or through cracks generated by thermal cycling. The National Bureau of Standards recently developed a chromium-nickel electrodeposit for molybdenum in which chromium is deposited on molybdenum and nickel is deposited over the chromium to provide a ductile sealing layer. Oxidation tests by the Bureau showed that this electrodeposited composite coating provided consistent protection against oxidation of the base molybdenum.

As a part of this contract, the Wright Air Development Center arranged through the Navy Bureau of Aeronautics, which has sponsored the research at the National Bureau of Standards, for the latter Bureau to provide coated molybdenum specimens for evaluation tests at this laboratory. Accordingly, oxidation, ductility, thermal cycling, ballistic impact, and erosion test specimens of 0.5% titanium-molybdenum alloy were furnished to the Bureau for electroplating.

Electroplating Procedure

A nickel wire was attached to the molybdenum specimens using a nickel-chromium-boron brazing alloy. The wire was used to avoid the problem of defects in the electrodeposit at contact points required by the plating procedure. The plating comprised a layer of chromium 0.001-0.002 in. thick adjacent to the molybdenum and a layer of nickel 0.006-0.008 in. thick on the chromium. The Bureau reported the following steps in the plating procedure:

1. Degrease.
2. Clean anodically in 70% sulfuric acid.
3. Rinse.
4. Etch in potassium ferricyanide 300 g/liter, sodium hydroxide 100 g/liter, 80-90°C for 1 to 2 minutes. Agitate bath.
5. Rinse.
6. Chromium plate (into the bath with current on) 120 amps/dm^2, 75-80°C. Chromium thickness 0.001-0.002 in.
7. Etch in hydrochloric acid (1:1) until vigorous gassing occurs and transfer without rinsing to a nickel strike, consisting of $NiCl_2.6H_2O$, 200 g/liter, dissolved in dilute hydrochloric acid (1:10). Strike at 10 to 15 amp/dm^2 for a few minutes.
8. Transfer to a Watts nickel bath without rinsing and nickel plate a coating 0.007±0.001 inch thick.

After plating, the Bureau annealed the specimens in helium for about 30 minutes at 1380-1470°F. A cross section through the chromium-nickel plating on an as-received specimen is shown in Figures 5 and 6. The thicknesses of the plating are shown in Figure 5. The structure of the plating at the nickel-chromium interface is shown in Figure 6; a small amount of interdiffusion between chromium and nickel had been produced by the treatment at 1380-1470°F.

Oxidation Tests

Oxidation tests were conducted with specimens in the as-received condition and after diffusion treating in dry argon for 24 hours at 2000°F.

Specimens were received from the Bureau in two groups. The oxidation test specimens received in the first group were tested in the as-received condition. Four of the five specimens appeared to be in excellent condition after exposure to air for 500 hours at 1800°F. The fifth specimen did not fail but exhibited blisters of oxide that spalled from the nickel layer during exposure. In subsequent oxidation tests at 2000°F, three of the five specimens failed within 138 hours' exposure. Two specimens were unfailed after 117 and 138 hours' exposure (see Table 4-A).

The six specimens received in the second group were oxidation tested after diffusion treating in dry argon for 24 hours at 2000°F. Only three specimens of this group sustained 500 hours' exposure to air at 1800°F without failure. These three specimens sustained an additional exposure of 173 hours at 2000°F without failure; however, nickel oxide formed on each specimen and flaked off during the 1800 and 2000°F tests.

Thermal Shock Tests

Two specimens in the as-received condition were subjected to the thermal shock test in the thermal cycling apparatus. Blisters appeared in both specimens after about 25 cycles. Evidence of failure at the blistered area was detected after 130 cycles for one sample and 158 cycles for the other. Cracks in the plating at the blistered area are clearly visible in the photographs of the specimens shown in Figure 7. Metallographic examination of a section through the blistered area of specimen E-81 disclosed that the nickel layer had separated from the chromium to form a blister. The chromium layer still adhered to the base metal, but contained cracks; the molybdenum alloy exhibited oxidation at the base of cracks, as shown in Figure 8. A transverse section through the blister of specimen E-81 had the same appearance as the specimen shown in Figure 9.

To eliminate blistering, an attempt was made to increase the strength of the bond between the chromium and the nickel layer by diffusion treating an as-received specimen in dry argon for 24 hours at 2000°F. The desired effect was not achieved; the specimen blistered in the thermal shock test after 60 cycles and failed after 146 cycles. A section through the blistered area is

WADC TR 54-492 Pt 3   19

shown in Figure 9. The nickel layer separated from the chromium layer to form a blister. The chromium layer still adhering to the base metal at the blistered area is shown in Figure 10.

The results obtained with the chromium-nickel plated specimens in the thermal shock test (shown in Table 4-B) were decidedly inferior to those obtained with sprayed-metal coatings, particularly the aluminum-chromium-silicon coating. The latter coating exhibited the capacity to protect molybdenum against oxidation for 400-600 cycles in the thermal cycling apparatus, whereas the chromium-nickel plated specimens exhibited blisters in the plating after 15-60 cycles, and the molybdenum beneath the blisters began to oxidize after 67-158 cycles. Metallographic examination showed that the plating, in forming the blisters, separated at a line of inclusions in the chromium-rich layer. Couch, Shapiro and Brenner*, in their work with similar chromium-nickel electroplated specimens, suspected these inclusions to be Cr_2O_3.

Ballistic Impact Test

One chromium-nickel plated specimen in the as-received condition and two specimens diffusion treated 24 hours at 2000°F in argon were subjected to the ballistic impact test at 1800°F. After impacting, the specimens sustained 500 hours' exposure to oxidation at 1800°F, plus 118 hours' exposure at 2000°F, without failure. These results are shown in Table 4-C.

Erosion Test

Only one specimen was subjected to the erosion test at 1800°F. This was a specimen that had been used for the thermal shock test of the plating in the as-received condition. An area of this specimen remote from the section exposed to thermal shock was used for the erosion test. The plating resisted the severe abrasive action of the grit for 95 minutes (Table 4-D). Compared to the results obtained with other coatings, this is considered to be excellent. In erosion tests with sprayed-metal coatings, it was reported previously that the Colmonoy No. 5 alloy coating resisted erosion for 60 minutes.

Ductility Test

The ductility test was performed at 1800°F with one chromium-nickel plated specimen. In this test the nickel plate flowed under stress at the tapered section in the grips of the tensile machine, so that it was necessary to remove the speci-men from the grips forcibly. In the subsequent oxidation test at 1800°F the spe-

*D. Couch, H. Shapiro and A. Brenner, "Researches on Protection of Molybdenum from Oxidation at Elevated Temperatures". National Bureau of Standards Project 0506-10-3218, Report 4484, January 1, 1956.

WADC TR 54-492 Pt 3   20

cimen failed at the tapered section and at the gage section after 210 hours' exposure (Table 4-E). Similar behavior was experienced with other specimens, tested both at room temperature and at 1800^{0}F. Therefore, no conclusions can be made relative to the ductility of the chromium-nickel plate as evaluated by the ductility test.

Summary

In all tests except the thermal cycling test, chromium-nickel electrodeposits on molybdenum exhibited equivalence or superiority to other coatings tested at this laboratory. The thermal cycling test revealed a specific limitation to this coating; the nickel separated from the underlying chromium.

TABLE 4

RESULTS OF OXIDATION, BALLISTIC IMPACT, THERMAL SHOCK AND DUCTILITY TESTS WITH SPECIMENS OF 0.5% Ti-Mo ALLOY ELECTROPLATED WITH 0.001 IN. Cr PLUS 0.007 IN. Ni BY NATIONAL BUREAU OF STANDARDS

A. Oxidation Test (2 in. by 2 in. by 0.050 in. specimen)

1. As-Received

Specimen No.	Life in Oxidation Test, Hr		Location of Failure
	1800°F	2000°F	
E-61	500 plus	138	face
E-62	500 plus	138	edge
E-63	500 plus	138 +	none
E-64	500 plus	114	face*
E-65	500 plus	117 +	none

2. Diffusion Treated in Dry Argon for 24 Hours at 2000°F

E-66	283	-	face
E-67	500 plus	173 +	none
E-68	500 plus	173 +	none*
E-69	166	-	at wire attachment
E-70A	500	-	edge
E-70B	500 plus	173 +	none*

B. Thermal Shock Test (4 in. by 1 in. by 0.050 in. specimen)

Specimen No.	Condition	Cycles to Failure**	Remarks
E80	As-received	130	Blisters appeared in plating after 15-25 cycles
E81	As-received	158	"
E82A	24 hr at 2000°F argon	146	Blisters appeared in plating after 60 cycles
E82B	"	95	
E82C	"	67	Blisters appeared in plating after 17 cycles

C. Ballistic Impact Test (1-7/8 in. by 1 in. by 0.094 in. specimen)

Specimen No.	Condition	Exposure in Oxidation Tests After Impacting, Hr***	
		1800°F	2000°F
E71	As-received	500 plus	118 (unfailed)
E72	24 hr at 2000°F argon	500 plus	118 (unfailed)
E73	24 hr at 2000°F argon	500 plus	118 (unfailed)

*Nickel oxide flaked off during test.

**Cycles to failure indicate time when molybdenum began to oxidize.

***Impacted at 1800°F with steel shot; velocity 330 ft/sec.

WADC TR 54-492 Pt 3

TABLE 4
(continued)

D. Erosion Test at $1800^{O}F$

Specimen No.	Condition	Life of Coating, minutes
E80	As-received	95

E. Ductility Test (gage section 1/4 in. diameter by 1-1/4 in. long)

Specimen No.	Oxidation Test after Elongating Gage Section 2% Life at $1800^{O}F$, Hr	Remarks
E77	210	Failed at tapered end and at gage section

Ni

Cr

0.5% Ti-Mo Alloy

FIGURE 5 (M6091)   X100
Etchants: (1) Polish-Etch-Buff
           (2) Carapella's Reagent
           (3) NaOH +K$_3$Fe(CN)$_6$

CHROMIUM-NICKEL PLATING ON 0.5% Ti-Mo ALLOY IN
AS-RECEIVED CONDITION

Ni

C^L
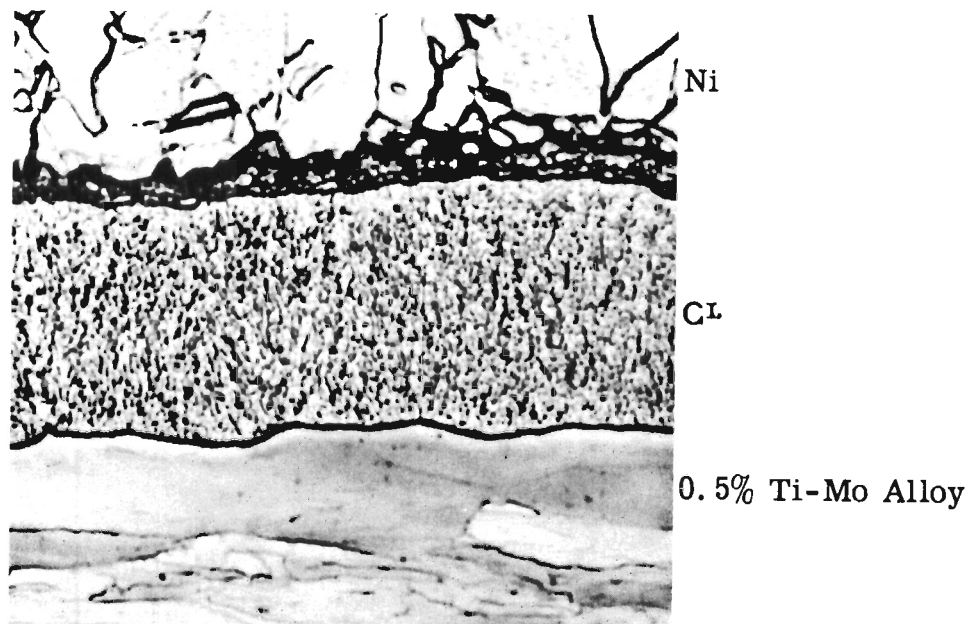
0.5% Ti-Mo Alloy

FIGURE 6 (M5940)   X750
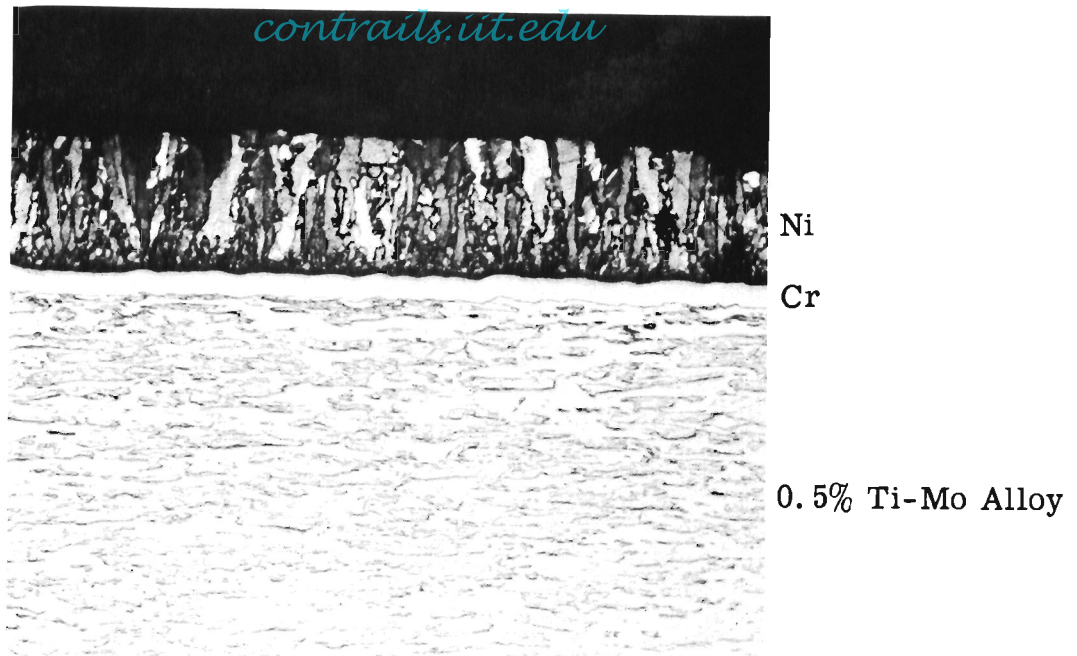Etchants: (1) Polish-Etch-Buff
              (2) Electrolytic Polish
              (3) Carapella's Reagent
              (4) NaOH+ K$_3$Fe(CN)$_6$

CHROMIUM-NICKEL PLATING ON 0.5% Ti-Mo ALLOY
IN AS-RECEIVED CONDITION

NO. OF CYCLES TO FAILURE	130	158
SAMPLE NO.	E80	E81
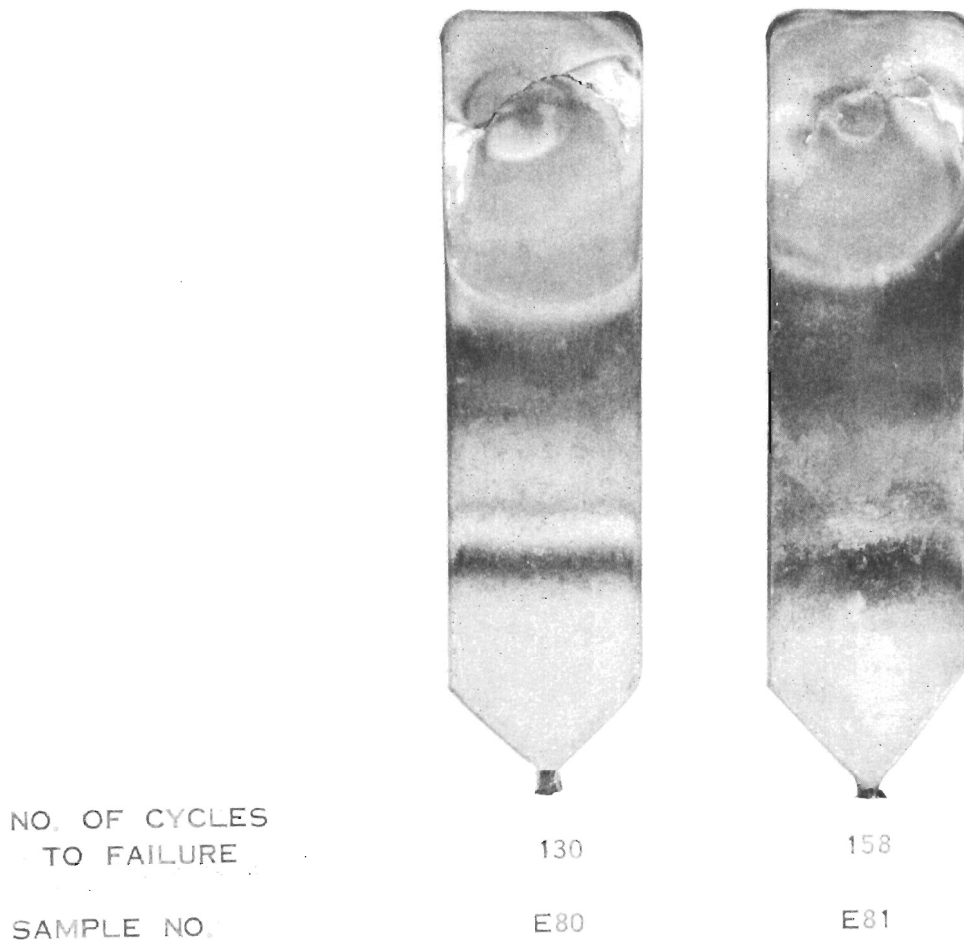
FIGURE 7 (P1411)   FULL SIZE

APPEARANCE OF CHROMIUM-NICKEL PLATED SPECIMENS AFTER THERMAL
SHOCK TEST (TESTED IN AS-RECEIVED CONDITION)

WADC TR 54-492 Pt 3   25

Cr

0.5% Ti-Mo Alloy
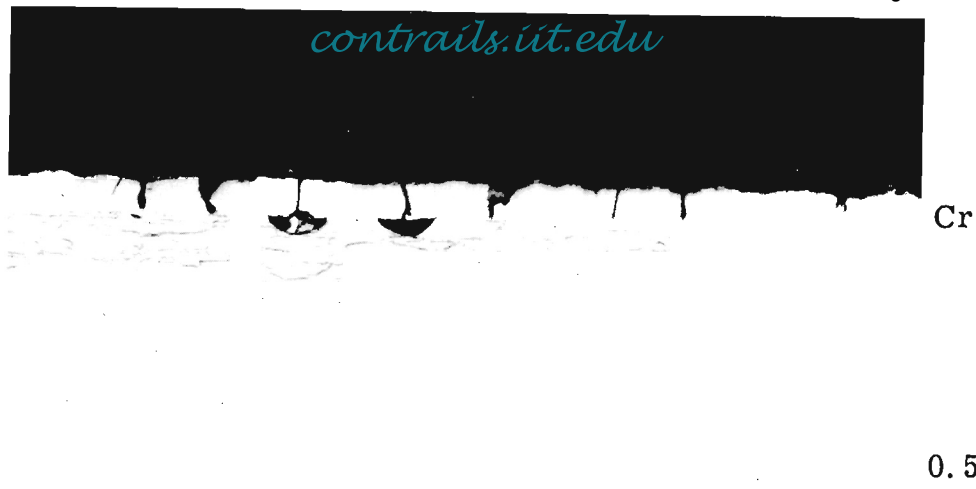
FIGURE 8 (M6102)   Polish-Etch-Buff   X100

SECTION THROUGH BLISTER IN PLATING OF THERMAL
SHOCK SPECIMEN E81 TESTED IN AS-RECEIVED CONDITION
SHOWING CHROMIUM PLATE ADHERING TO MOLYBDENUM

FIGURE 9 (P1428)   X2

SECTION THROUGH BLISTER IN PLATING OF THERMAL
SHOCK SPECIMEN E82A TESTED AFTER DIFFUSION
TREATING 24 HOURS AT 2000°F IN DRY ARGON

WADC TR 54-492 Pt 3   26

Cr

0.5% Ti-Mo Alloy

FIGURE 10 (M6123)   Polish-Etch-Buff   X100

SECTION THROUGH BLISTER IN PLATING OF THERMAL SHOCK
SPECIMEN E82A TESTED AFTER DIFFUSION TREATING 24
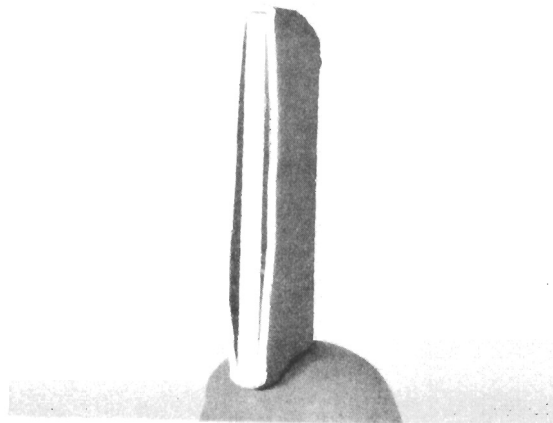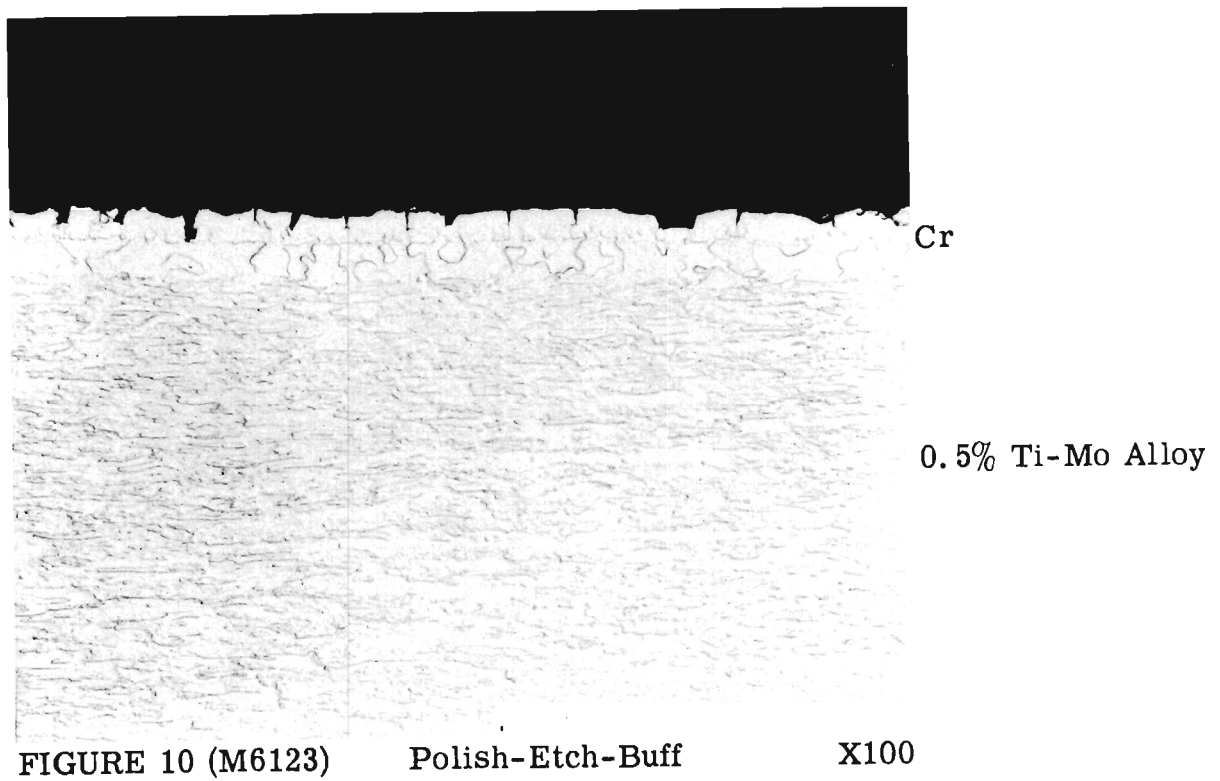HOURS AT 2000°F IN DRY ARGON SHOWING CHROMIUM
PLATE ADHERING TO MOLYBDENUM

WADC TR 54-492 Pt 3   27

SECTION 4

EVALUATION OF NICKEL-CLAD MOLYBDENUM

Molybdenum specimens, nickel-clad by Battelle Memorial Institute, were evaluated in thermal shock, oxidation, ballistic impact, and erosion tests. One phase of the program was to determine whether the oxidation resistance of the clad specimens under the various evaluation test conditions could be improved by metal-spray coating over the cladding. As will be explained in the following paragraphs, difficulty with the edges of the clad specimens precluded a definitive evaluation of the effectiveness of the spray-coated overlayer. The test program did provide an indication of the protective value of nickel cladding as compared to other coatings.

Description of Processing and Specimens Produced

Unalloyed, recrystallized molybdenum stock, 0.250 in. and 0.450 in. thick, was supplied to Battelle Memorial Institute for nickel cladding. Battelle prepared the following nickel-clad specimens:

11 oxidation test specimens	- 2 in. by 2 in. by 0. 060 in.	
4 thermal shock specimens	- 4 in. by 1 in. by 0. 060 in.	
4 erosion test specimens	- 3 in. by 1 in. by 0. 060 in.	
6 ballistic impact specimens	- 1-7/8 in. by 1 in. by 0. 096 in.	

The clad specimens were prepared by the method described by LaChance and Jaffee.* Sections of the submitted 0.250 in. and 0.450 in. thick stock, in nickel envelopes, were reduced in nine rolling passes at $2190^{\circ}F$ to clad sections 0.060 in. and 0.096 in. thick, respectively. After rolling, the sections were annealed at $1800^{\circ}F$ for 30 minutes.

A section through a specimen of the 0.096-in.-thick clad stock showing the structure of the molybdenum and the cladding is presented in Figure 11. The nickel is 0.005 in. thick. The bond between the nickel and the molybdenum is shown in Figure 12. According to D. C. Goldberg, who discussed the paper by LaChance and Jaffee*, the structure at the interface comprises "α Ni-Mo and ϵ Mo-Ni solid solutions and a film of the hard brittle δ compound (50-50 atomic % Ni-Mo) at the interface."

The required sizes of specimens were cut from the annealed stock. The edges were ground on an emery belt; the corners were belt-ground to a 3/32 in. radius. The edges of the specimens were protected by applying an overlay of INCO "61" nickel with a heliarc torch. A fairly heavy weld bead resulted. This is illustrated in Figure 13.

Thermal Shock Tests

To establish a basis for determining the effectiveness of spray coating in improving the oxidation protection of the nickel cladding, one as-clad specimen was tested in the

*M. H. LaChance and R. I. Jaffee, "Fabrication and Evaluation of Thin Clad Sheets of Molybdenum", Trans. ASM, vol 48, 1956, pp 595-626.

WADC TR 54-492 Pt 3   28

thermal cycling apparatus. The specimen failed in two tests after 85 and 110 cycles. Failure occurred at the weld bead. It appeared that oxidation of the molybdenum base occurred through cracks that were generated in the bead. Figure 13 shows the thermal shock specimen after testing. The failure areas and cracks in the weld bead can be seen at stained areas in the four corners of the specimen. A section of the specimen at the tested area is shown in Figures 14 and 15. The massiveness of the weld bead, the large grain size, and the intergranular cracks of the weld metal are illustrated.

The application of a layer of aluminum-chromium-silicon 0.004 in. thick on top of the cladding and weld bead did not improve the results. Reduction of the thickness of the bead by hand filing provided a slight increase in the life of the specimen in the thermal shock test.

Since it was the purpose of the work to attempt to improve the nickel-clad coating by applying a spray coating, several such experiments were conducted. Details of the experiments, which were concerned chiefly with edge protection, are given in Table 5-A.

Efforts to improve the edge protection by spray coating the molybdenum with Colmonoy No. 5, Coast Metals 50 alloy or aluminum-chromium-silicon were futile. It was possible to determine the thermal shock resistance of the nickel cladding itself by recoating the edges of a specimen after failure at the edges, and re-exposing the specimen to the thermal shock test. This was performed with specimen E158. After two repairs, the specimen failed on the flat surface after a total of 316 cycles at one end of the specimen, and 396 cycles at the other end.

Oxidation Tests

In oxidation tests with as-received panels, the nickel cladding failed after a maximum of 286 hours' exposure to air at 1800°F. Removing excess weld metal at the edges and spray coating the edges with aluminum-chromium-silicon was detrimental, rather than beneficial. Metal at the welds appeared to melt and crack during diffusion treatment at 2000°F. The test results are given in Table 5-B.

Ballistic Impact Tests

The results of ballistic impact tests with three nickel-clad specimens are reported in Table 5-C. The as-clad specimen (in which the weld bead had been filed to a smooth contour) exhibited the ability to resist the impacting without failure. Specimens in which the heavy weld bead was replaced with sprayed-metal coatings failed at the impacted area.

Erosion Tests

In the erosion test, a fair appraisal of the effect of the sprayed coating was not obtained, since only one of the clad specimens was spray coated. The test results obtained on one as-clad specimen and one clad specimen to which the spray coating

WADC TR 54-492 Pt 3   29

was applied indicated that the erosion resistance of the clad specimen was slightly improved by the aluminum-chromium-silicon overlayer. The test results are reported in Table 5-D.

Summary

It was concluded from the tests with nickel-clad molybdenum that improvement in edge protection must be achieved before it will be possible to evaluate further experiments with spray coating clad molybdenum. The nickel-cladding shows satisfactory ballistic impact resistance and potential for greater resistance to thermal cycling than other nickel-base coatings. The oxidation resistance of nickel-clad molybdenum is not as good as nickel-base coatings containing chromium or silicon.

TABLE 5

RESULTS OF OXIDATION, BALLISTIC IMPACT, THERMAL SHOCK AND EROSION TESTS WITH SPECIMENS OF UNALLOYED MOLYBDENUM ROLL-CLAD WITH NICKEL BY BATTELLE MEMORIAL INSTITUTE

A. Thermal Shock Test (4 in. by 1 in. by 0.060 in. specimen)

Specimen No.		Condition	Cycles to Failure End A	Cycles to Failure End B	Remarks
E156		As-received	85	110	failed at weld bead
E157		Coated with Al-Cr-Si	62	80	failed at weld bead
E158	(1)	Filed weld section to smooth contour	146	196	failed at weld bead
	(2)	Removed weld metal; coated edges with Colmonoy No. 5	120	130	failed at weld bead
	(3)	Removed Colmonoy No.5 coated edges with Coast Metals 50	50	70	failed at flat surface
		Total Cycles (E158)	316	396	
E170		Removed weld; coated all over with Al-Cr-Si	89	110	failed at edge

B. Oxidation Test (2 in. by 2 in. by 0.060 in. specimen)

Specimen No.	Condition	Life in Oxidation Test at $1800^{O}F$, hr	Remarks
E160	As-received	262	Nickel oxide flaked
E161	As-received	286	off continuously.
E162	As-received	286	Failures of all speci-
E163	As-received	286	mens were on flat sur-
E164	As-received	286	faces.
E165	Weld beads filed. Al-Cr-Si		The coatings on all
E166	coating 0.005 in. thick	23*	specimens cracked at
E167	applied over all surfaces.		the weld bead during
E168	Diffusion treated 2 hr at		diffusion treatment.
E169	$2000^{O}F$ in dry argon.		

*Failed at edges where coating had cracked.

TABLE 5
(continued)

C. Ballistic Impact Test at 1800^OF (1-7/8 in. by 1 in. by 0.096 in. specimen)

Specimen No.	Condition	Life in Oxidation Test at 1800^OF after Impacting, hr
E180	Weld bead hand filed to smooth contour	168 (failed at weld bead)
E184	Weld bead removed, edges coated with Colmonoy No. 5 alloy	41 (failed at impacted area)
E185	Weld bead removed, coated on all surfaces with Al-Cr-Si	47 (failed at impacted area)

D. Erosion Test at 1800^OF

Specimen No.	Condition	Life of Coating, Minutes	
		End A	End B
E179	As-received	60	60
E177	Coated with Al-Cr-Si	65	80

WADC TR 54-492 Pt 3

Ni

Unalloyed Mo
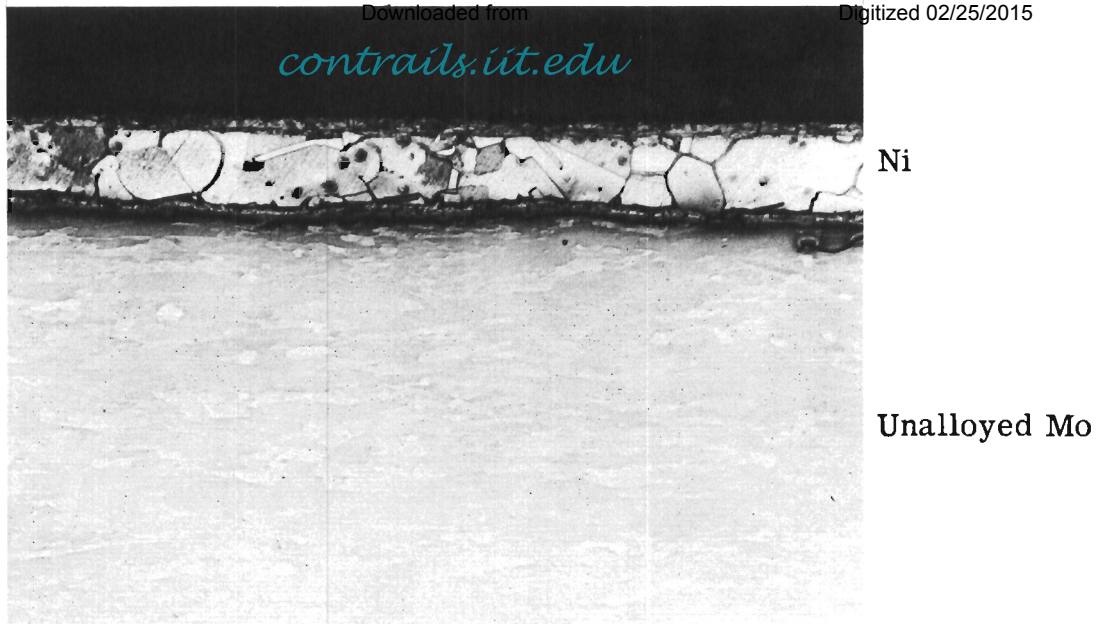
FIGURE 11 (M6084)   X100

Etchants: (1) Carapella's Reagent
             (2) NaOH $+K_3Fe(CN)_6$

STRUCTURE OF 0.096 IN. THICK Ni-CLAD MOLYBDENUM STOCK
AS-RECEIVED. NICKEL LAYER IS 0.005 IN. THICK.

Ni

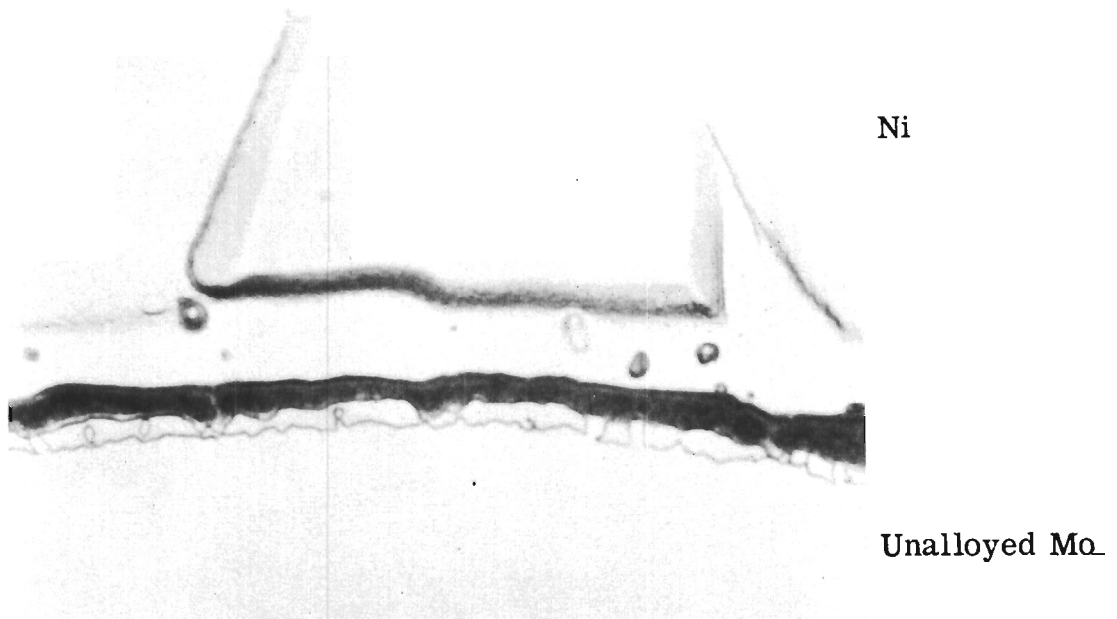Unalloyed Mo

FIGURE 12 (M6086)   X2000

Etchants: (1) Carapella's Reagent
             (2) Hot Tap Water

STRUCTURE OF 0.096 IN. THICK Ni-CLAD MOLYBDENUM STOCK
AS-RECEIVED SHOWING STRUCTURE AT Ni-Mo INTERFACE

WADC TR 54-492 Pt 3   33
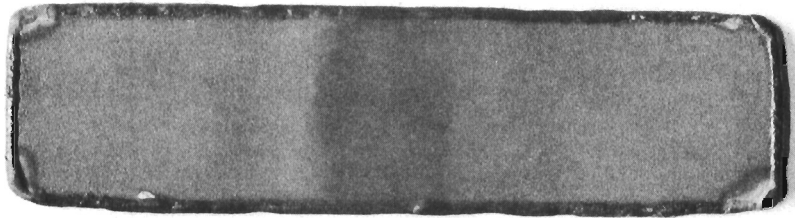
FIGURE 13 (P1414)   FULL SIZE

PHOTOGRAPH OF Ni-CLAD MOLYBDENUM THERMAL SHOCK
SPECIMEN E156 AFTER TESTING.   FAILURE OCCURRED
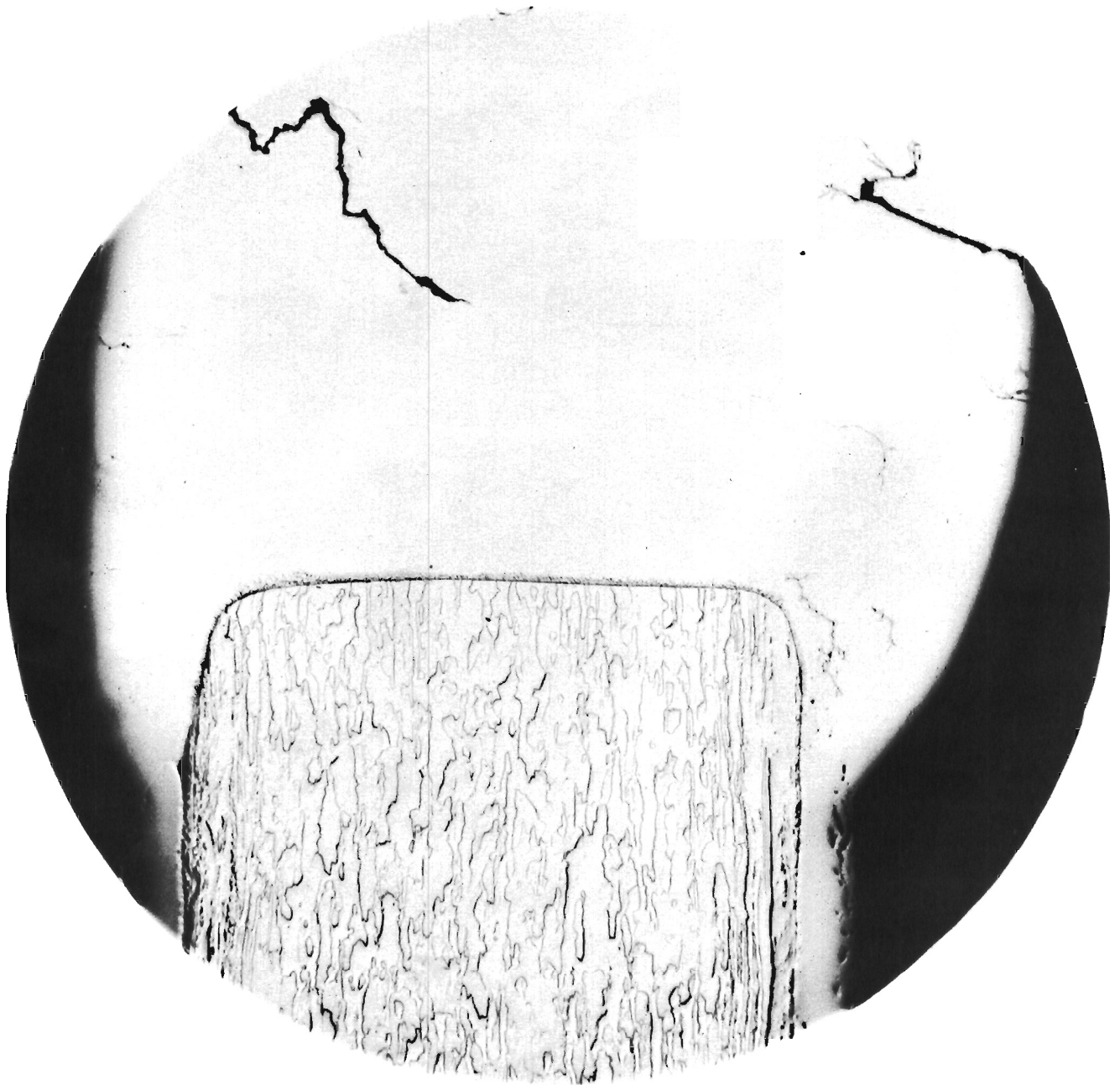AFTER 85 AND 110 CYCLES IN TWO TESTS.

WADC TR 54-492 Pt 3   34

FIGURE 14 (M6127)   Polish-Etch-Buff   X100

SECTION THROUGH WELD BEAD OF Ni-CLAD THERMAL SHOCK
SPECIMEN AFTER TESTING

WADC TR 54-492 Pt 3   35

FIGURE 15 (M6128)   X100

Etchants: (1) Carapella's Reagent
                (2) $NaOH + K_3Fe\,(CN)_6$

SAME AS SPECIMEN IN FIGURE 14

SECTION 5

DUCTILITY OF COATED MOLYBDENUM AT AMBIENT TEMPERATURES

Prompted by isolated shop experiences indicating apparent lack of room-temperature ductility of coated molybdenum, and by concern of those who have observed room-temperature brittleness in super-alloys after prolonged exposure to service temperatures, a series of controlled tests were initiated to compare, on a semiquantitative basis, the ductility of 0.5% titanium-molybdenum alloy in the following conditions:

1. as-rolled
2. as-coated and diffusion-treated
3. after extended exposure at 1800 and 2000°F,
    tested with and without coatings.

Two sprayed-metal coatings were investigated: the aluminum-chromium-silicon composition and the nickel-chromium-boron composition (Colmonoy No. 5).

Two types of tests were conducted: a bend test, using specimens fabricated from sheet molybdenum, and a drop-type impact test, using specimens fabricated from rolled bar stock. Since relative toughness could be measured most easily by varying temperatures rather than strain rate, a series of tests were conducted under constant strain rate conditions over a range of test temperatures.

Description of the Bend Test

The test consists of bending a sheet metal specimen in a jig having the working contour shown in Figure 16. A universal-type tensile-testing machine is used to move the plunger member toward the die member, causing the interposed specimen to bend. The two members of the jig are forced together at a rate of 0.030 in. per minute until the specimen fails, or until the specimen conforms to the V-shape of the jig.

The die member, the specimen, and the lower portion of the plunger member are submerged in suitable liquids which are heated or cooled for conducting tests above or below room temperature.

Preparation of Bend Test Specimens

Bend test specimens 1 in. by 3 in. by 0.055 in. were fabricated from 0.5% titanium-molybdenum alloy sheet. The corners and edges of each specimen were rounded with a file. Specimens received the following treatments preparatory to the bend test:

1. Four specimens were retained for testing in the <u>uncoated</u> condition.

WADC TR 54-492 Pt 3

2. Five specimens were coated with a <u>Ni-Cr-B alloy</u> (Colmonoy No. 5) 0.010 in. thick, and then diffusion treated in dry argon for two hours at 2000°F, preparatory to testing in the <u>as-coated</u> condition.

3. Five specimens, similarly coated with <u>Ni-Cr-B alloy</u>, were exposed to standard oxidation test conditions for 500 hours at 1800°F, plus an additional 25 hours at 2000°F, preparatory to testing in the <u>exposed</u> condition.

4. Five specimens were coated with <u>Al-Cr-Si alloy</u> (20% aluminum plus 80% chromium-silicon alloy) 0.010 in. thick, diffusion treated two hours at 2200°F in dry argon, preparatory to testing in the <u>as-coated</u> condition.

5. Five specimens, similarly coated with <u>Al-Cr-Si alloy</u>, were exposed to standard oxidation test conditions for 500 hours at 1800°F, plus an additional 25 hours at 2000°F, preparatory to testing in the <u>exposed</u> condition.

Results of Bend Tests

Bend tests were conducted with specimens in the "uncoated," "as-coated" and "exposed" conditions, at room temperature and at selected temperatures above or below room temperature, to define the temperature conditions for low and high bend ductility. Each specimen was maintained at constant temperature during the test, and application of the load was continued until fracture occurred (indicated audibly or by sudden decrease in load), or until the 150° angular limit of the equipment was reached. The maximum load was recorded, and the maximum bend angle was measured. The results of bend tests are presented in Table 6. The relationships between bend angle and test temperature are depicted graphically in Figure 17.

Description of the Impact Test

An impact test was developed by Thompson Products, Inc., for use with materials having impact resistance too low to be measured consistently in a test of the Charpy type. The test setup is illustrated in Figure 18, and the specimen dimensions are given in Figure 19. The specimen is clamped in a jig, which in turn is bolted to a solid support; in this case, the table of a milling machine. A one-pound tup is suspended over the specimen and held by means of a single-filament nylon fishing line. The tup is aligned above the specimen so that the point of impact is one-half inch from the specimen's free end. The specimen is clamped so that the center of the notch is one-half inch from the face of the clamp. Accurate alignment of the specimen beneath the tup was accomplished by horizontal adjustment of the mill table. The maximum falling distance for the tup ("H" in Figure 18) was approximately 96 inches, which represented 96 inch-pounds maximum impact-energy available.

The test program was divided into two categories:

      1. Room temperature tests.
      2. Tests at several elevated temperatures.

For tests in both these categories, the tup was stationed a desired distance (H) above the specimen; then the line was burned through, permitting the tup to fall. The tup was raised in one or two inch increments until the specimen either fractured or bent more than 5^0. Specimens fractured at the notch or jig face. Extreme care was taken to prevent misalignment, which would vary the point of impact, as would room air currents swinging the suspended tup.

For tests at elevated temperatures, the specimen was heated to the desired temperature by an oxy-acetylene torch, and the tup was released in the usual manner. For temperature measurement, a thermocouple was wired to the specimen face away from the flame, at a position near the notch. The elevated temperatures employed in these tests were selected so that the values obtained for the impact energy absorbed on each type specimen would provide a method of differentiating the influence of coating or heat treatment condition.

Preparation of Impact Test Specimens

Impact test specimens were fabricated from as-rolled 0.5% titanium-molybdenum alloy bar, 5/8 in. diameter. The specimens were machined to the dimensions shown in Figure 17, and received the following treatments prior to the special impact test:

1. Two specimens were machined and retained for testing in the as-rolled condition.

2. Five round bars, approximately 2-1/4 in. long, were coated with the Al-Cr-Si alloy and were exposed to standard oxidation test conditions for 500 hours at 1800^0F, plus an additional 25 hours at 2000^0F. The coating was removed and specimens were machined from each of these bars preparatory to testing in the exposed-coating removed condition.

3. Five specimens were coated with the Al-Cr-Si alloy, using the procedures described for the bend test specimens, preparatory to testing in the as-coated condition.

4. Five specimens, coated with the Al-Cr-Si alloy, were exposed to standard oxidation test conditions for 500 hours at 1800^0F, plus 25 hours at 2000^0F, preparatory to testing in the exposed condition.

5. Five specimens were coated with the Ni-Cr-B alloy, using the procedures described for the bend test specimens, preparatory to testing in the as-coated condition.

6. Five specimens, coated with the Ni-Cr-B alloy, were exposed to standard oxidation test conditions for 500 hours at 1800^0F, plus 25 hours at 2000^0F, preparatory to testing in the exposed condition.

Results of Impact Tests

The impact tests, as described above, were conducted with specimens in the "uncoated," "as-coated," "coated and exposed," and "exposed-coating removed" conditions. The results of the tests are presented in Table 7. Those specimens which bent 5° under the impact of the test were considered ductile; hence equivalent in "toughness" to the as-machined, uncoated specimens.

Summary

It will be recognized that these tests do not reflect any particular service condition. The test results do serve a purpose in measuring, on a semiquantitative basis, the influence of coatings and exposure at high temperatures on the ductility of commercial 0.5% titanium-molybdenum alloy.

In general, both tests indicate that the presence of coatings detracts from the ambient temperature ductility of molybdenum. The bend-test results indicate that the Ni-Cr-B (Colmonoy No. 5) coating reduces the ductility of molybdenum to a greater extent than the Al-Cr-Si coating. However, in the special impact test, the difference between the coatings is somewhat less obvious, although under these test conditions also, the specimens as-coated with Al-Cr-Si show more ductility than specimens as-coated with Ni-Cr-B.

An important result of this work is the indication, from the impact-test results, that exposure of the 0.5% titanium-molybdenum alloy for 500 hours at 1800°F, plus 25 hours at 2000°F, did not reduce the ductility of the material as compared to the as-rolled condition.

TABLE 6

RESULTS OF BEND TESTS ON SHEET SPECIMENS OF 0.5% Ti-Mo ALLOY

Test Temp, °F	Uncoated		Al-Cr-Si Coating				Ni-Cr-B Coating			
			As-Coated		Exposed		As-Coated		Exposed	
	Angle	Load	Angle	Load	Angle	Load	Angle	Load	Angle	Load
304							19	80		
255							13	58		
204					124/142	45	15	57	85	80
170					104	47			0	25
142					85	45	11	55	22	70
110					36	45			14	45
78	150	60	150	40	0	33	5	50	3	35
30			20	55						
20	150	70	70*	60*						
-10			29	65						
-40	125	75	0	27						
-80	110	90								

*Deflection rate very high

TABLE 7

RESULTS OF SPECIAL IMPACT TESTS
(Tests Conducted on Specimens Machined from 0.5% Ti-Mo Alloy Bar)

Test Temp, °F	Impact Energy to Fracture (Inch-Pounds)					
	Uncoated		Al-Cr-Si Coating		Ni-Cr-B Coating	
	As-Machined	Exposed	As-Coated	Exposed	As-Coated	Exposed
74	30	28	3	3	4	4
200		24*				
275		(30)**				
350	30	(26)**	14	5	6	14
400			14*			
425			14			
450		(26)**	(26)**	(26)**	10	(28)**
525					20	(30)**
600				(20)**	(22)**	

*Specimens fractured at these values at first drop of tup; therefore, impact energy to fracture may be less.

**Values in parentheses indicate energy which produced 5° bend rather than fracture of specimens.

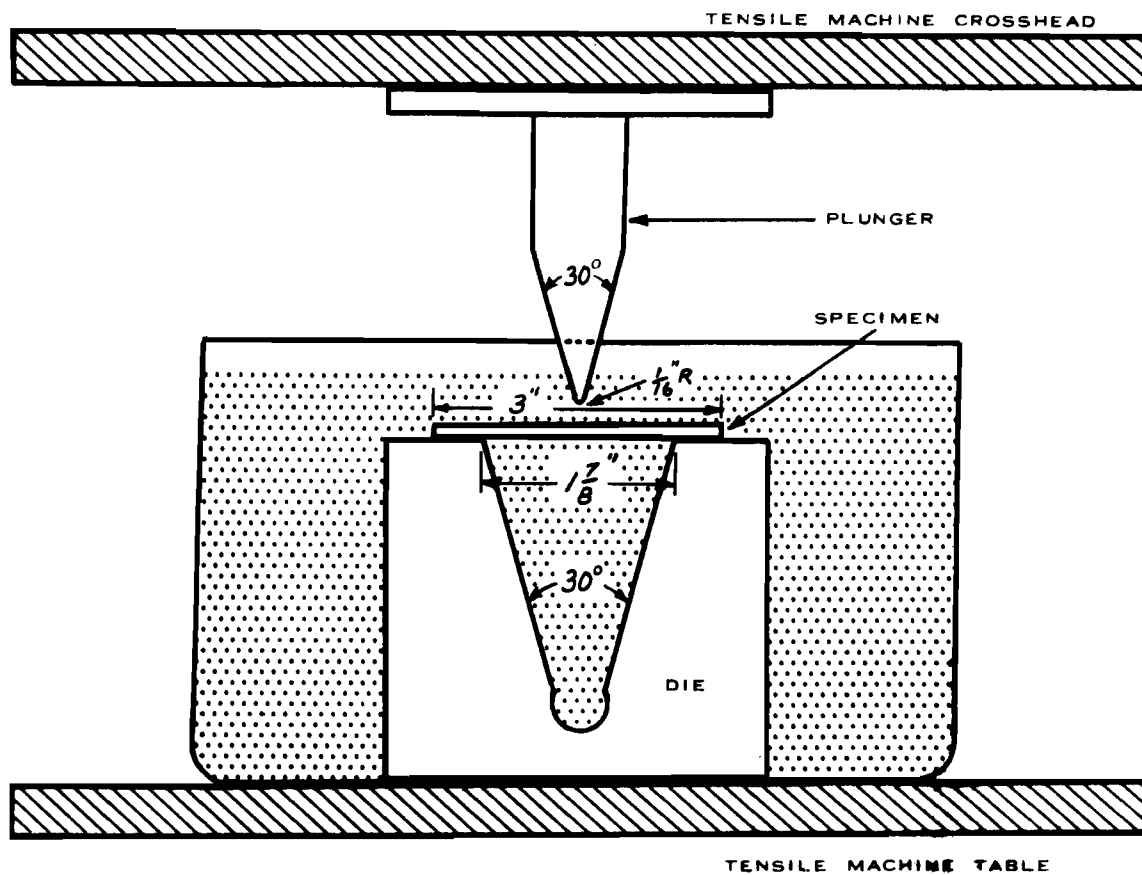CLIMAX MOLYBDENUM CO. OF MICH. 1354
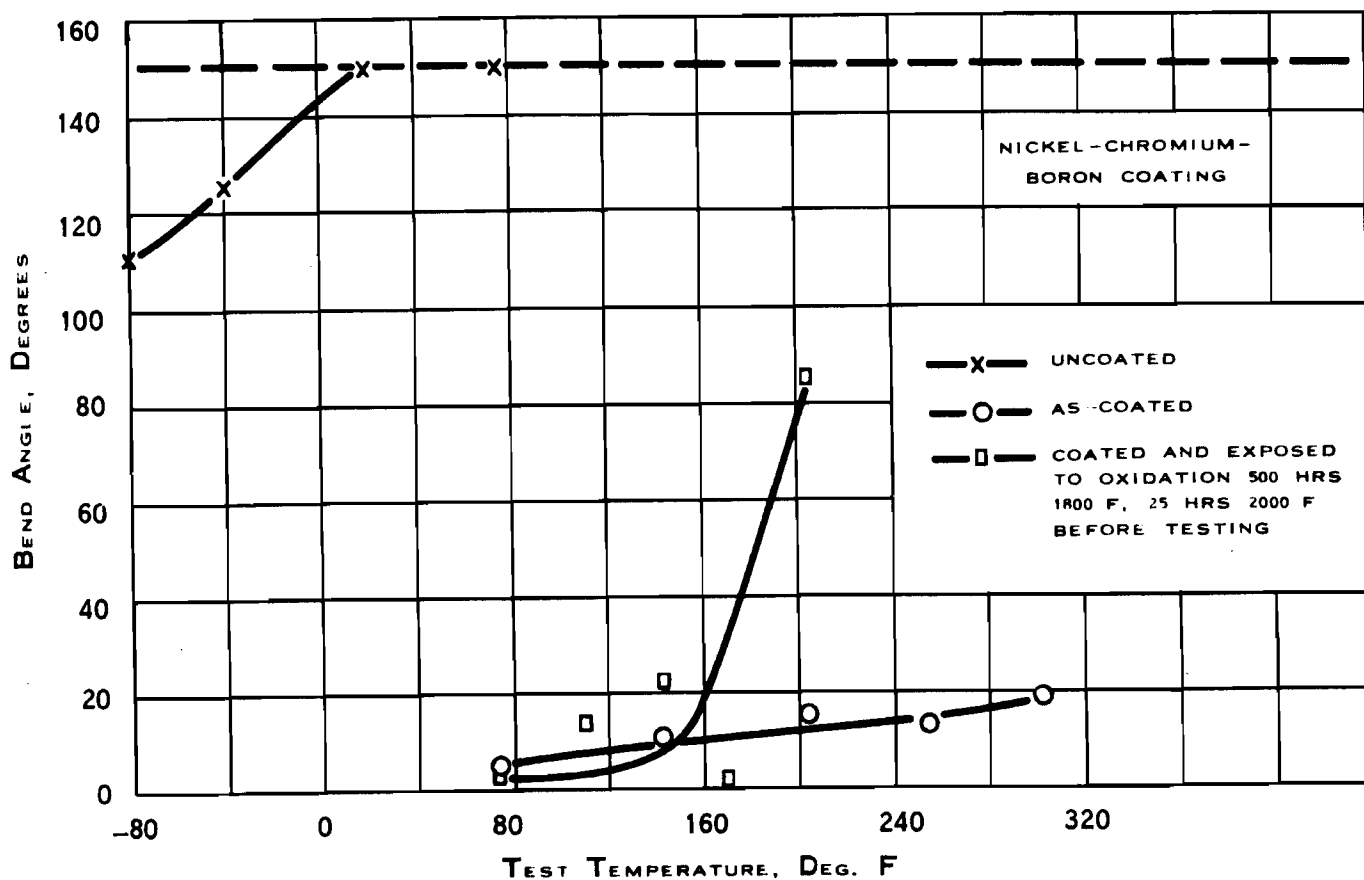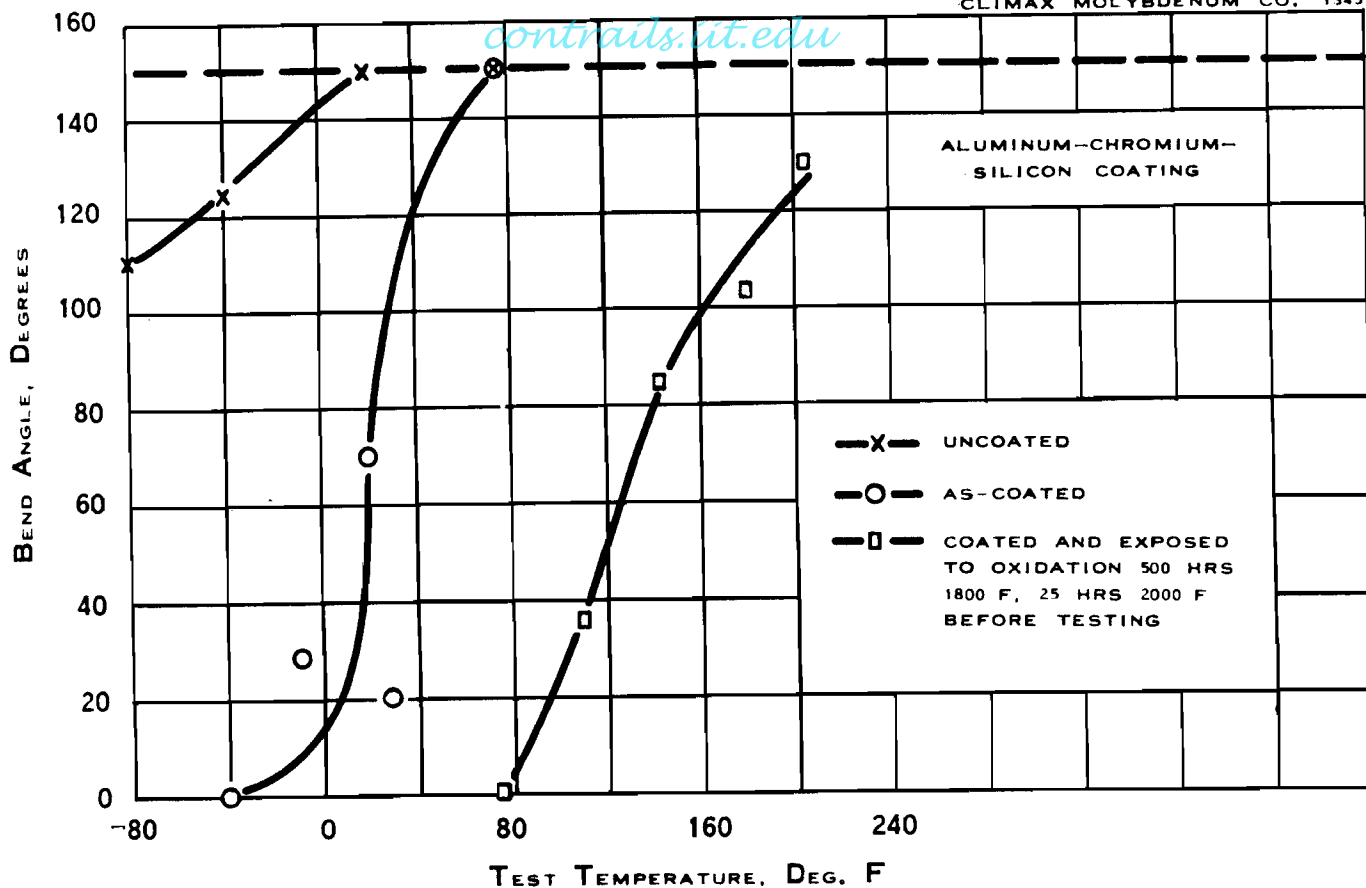

FIGURE 16 — SKETCH OF BEND TEST JIG

WADC TR 54-492 Pt 3   42

FIGURE 17 — RESULTS OF BEND TESTS

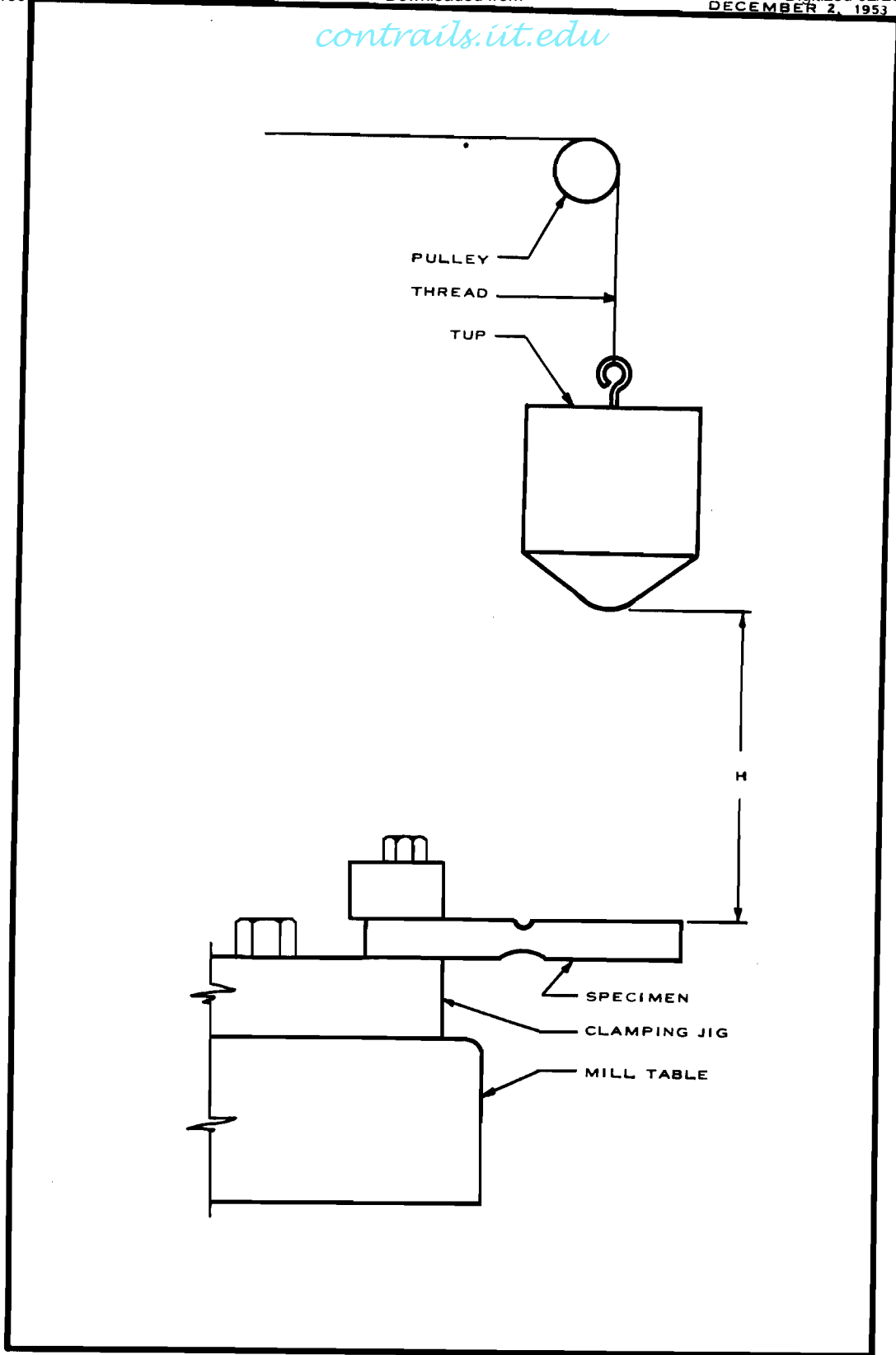**FIGURE 18 (482) – SCHEMATIC REPRESENTATION OF SPECIAL IMPACT TEST ASSEMBLY**

CLIMAX MOLYBDENUM CO. 481   DECEMBER 2, 1953
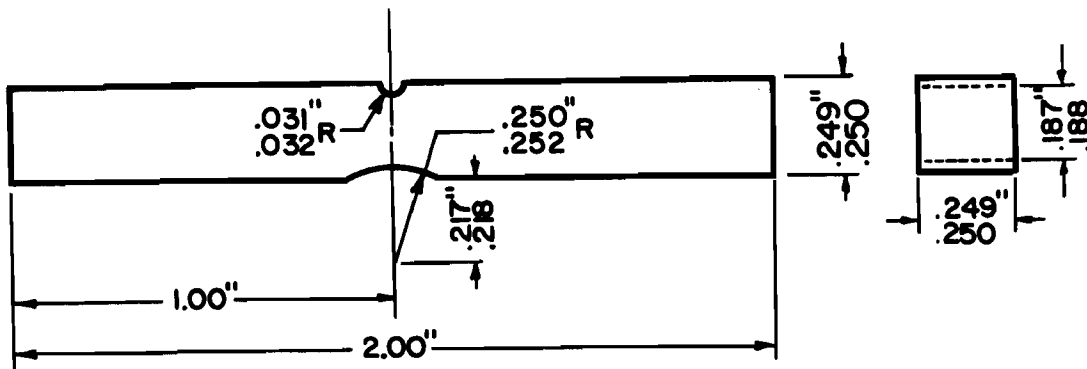

FIGURE 19 (481) - SPECIAL IMPACT SPECIMEN

SECTION 6

EXPLORATION OF COATINGS FOR SERVICE AT TEMPERATURES UP TO 3000°F

With the development of high efficiency heat engines for aircraft and missile application, a need has arisen for materials for relatively short-time service at temperatures in the range from 2000 to 3000°F. Molybdenum-base alloys which exhibit appreciable strength at temperatures up to 2400°F have been developed, and it is quite conceivable that, for many applications, molybdenum will exhibit usable strength at even higher temperatures. For these reasons, a program to explore possible coatings for these higher service temperatures was included as one object of the current contract. This program comprised three separate phases: first, the development of equipment for conducting reproducible oxidation tests at these higher temperatures; second, the testing of sprayed-metal coatings which exhibited promise in the temperature range 1800-2000°F; and third, the exploration of coatings considered specifically suited to the higher temperature service.

Oxidation tests at temperatures up to 3000°F were initiated to investigate the possibility of protecting molybdenum for even a few hours with sprayed-metal coatings at temperatures above 2400°F. It was not intended that the life of a coating be determined. In the majority of these tests the time of testing at any one temperature was limited to approximately four hours.

Description of Oxidation Test Equipment

For test temperatures up to and including 2400°F, the Climax laboratory had two Globar-heated muffle furnaces, with test chambers similar to those of the 1800°F oxidation test furnaces, which have been described in earlier reports.

Some exploratory tests were conducted at temperatures up to 3000°F by resistance heating coated molybdenum rods. These preliminary tests indicated promise for the aluminum-chromium-silicon coating, but only semiquantitative results were obtained due to nonuniform temperature distribution and local overheating. It was decided that considerable refinement would be required before such procedures could produce consistent results.

A gas-fired muffle furnace was constructed for oxidation tests of coated panels under more closely controlled conditions at temperatures in the range 2400-3000°F. The furnace comprised two test chambers placed in the center of a combustion chamber fired with three gas-air burners. The muffles were sealed at the ends so that the combustion atmosphere would not enter the test chambers. Air was introduced at the rear of each test chamber and was regulated to provide a flow of air comparable to that used in the oxidation tests at lower temperatures. Silicon carbide muffles were used for the first series of tests. It was found that silicon carbide reacted with air at temperatures above 2800°F; therefore, alundum tubes were used as muffles in the 2800°F and 3000°F tests. The furnace provided a uniform heating zone in both test

WADC TR 54-492 Pt 3   46

chambers. To increase the heating rate of the furnace and achieve a temperature of 3000°F, it was necessary to add tank oxygen to enrich the air entering the burners.

Tests of Aluminum-Chromium-Silicon Coating

Tests with the aluminum-chromium-silicon sprayed-coating composition at high temperatures included two procedures. For both procedures, standard test panels were first tested at 1800°F, chiefly to expose gross flaws in the coatings before proceeding with the higher temperature testing. With one group of specimens, oxidation tests were conducted by exposing specimens in pairs at successively higher temperatures starting at 2000°F and ending at 2600°, 2800° and 3000°F. Other specimens were exposed directly to oxidation at temperatures in the range 2200-3000°F. The results of these tests are presented in Table 8-A.

Exposures at temperatures below the ultimate test temperature were made to condition the coating before proceeding to a higher test temperature. The conditioning treatment increased the diffusion of molybdenum into the coating, thereby raising the solidus temperature of the coating. It also increased the thickness and refractory properties of the oxide film at the outer surface of the coating. Tests of several specimens showed that the aluminum-chromium-silicon coating protected the base molybdenum against oxidation for six hours at 2600°F, plus four hours at 2800°F, plus four hours at 3000°F. Visual examination revealed that the coating had flowed at the edges of the specimens after exposure at 2800°F. Flow of the coating increased during the 3000°F exposure, as shown in Figure 20.

The microstructures of the specimens after oxidation tests at these elevated temperatures are shown in Figures 22 through 27. Exposure for four hours at 2400°F resulted in considerable diffusion, as illustrated by the width of the "interfacial zone" in Figure 22. A eutectic phase was present in the microstructure of the specimen exposed for four hours at 2600°F (Figures 23 through 25). After exposure at 2800°F, the coating exhibited a metallic inner zone, evidence of a coarse eutectic zone, and formation of an oxide layer on the surface (Figure 26). At the 2800°F test temperature, the melting point of the coating was exceeded, and the molybdenum apparently dissolved in the coating at an increased rate, causing the irregular interface observed in Figure 26.

The coating on the 3000°F specimen was sufficiently hard to scratch glass. Metallographic examination of the specimen revealed the existence of two oxide phases at the surface of the specimen (Figure 27). X-ray diffraction patterns of the outer surface indicated a predominance of alpha corundum (a form of Al_2O_3). The porosity of the coating and the oxidation of the underlying molybdenum can be observed in the photomicrographs of Figure 27.

In the oxidation tests conducted without preconditioning, the specimens withstood direct exposure at 2400°F and 2600°F, but failed by blistering during direct exposure at 2800°F. The coating seemed to flow and protect the base metal longer during direct exposure at 3000°F than at 2800°F. Figure 21 is a photograph of the specimens after direct exposures at 2600°F, 2800°F and 3000°F.

The results of the oxidation tests indicated that it was advantageous to condition the aluminum-chromium-silicon coating by exposures at lower temperatures prior to exposure at 2800°F or 3000°F. Exposure can be made at temperatures up to 2600°F with or without preconditioning, with the expectation of at least four hours' protection.

Tests were conducted, under Climax sponsorship, to determine the life of the aluminum-chromium-silicon coating at 2400°F. A group of ten specimens, prepared in the standard manner, withstood exposure in the range 180-335 hours at 2400°F before failure.

Tests of Nickel-Chromium-Boron and Nickel-Silicon-Boron Coatings

The results of tests of specimens coated with the nickel-chromium-boron alloy (Colmonoy No. 5) and the nickel-silicon-boron alloy (Coast Metals 50) are presented in Table 8-B and C. Both coatings appear to withstand direct heating at 2000°F satisfactorily. One specimen coated with the nickel-chromium-boron coating failed after 27 hours' exposure at 2200°F. Another specimen coated with the nickel-silicon-boron coating failed after eight hours' exposure at 2200°F. Both coatings failed in a short time (less than 1-1/2 hours) when exposed to air at 2400°F, regardless of whether the coating was preconditioned or was exposed directly. After the 2400°F test, metallographic examination of a specimen coated with Colmonoy No. 5 revealed evidence of intergranular attack on the molybdenum by the coating, and of molybdenum grains "floating" to the surface of the coating (Figure 28).

Tests of Rokide "A" Coatings

Previous experiments had shown that Rokide "A" (alumina sprayed coating developed and applied by Norton Company), applied directly to molybdenum, was too porous to prevent immediate oxidation of molybdenum at 1800°F. Therefore, it was decided to utilize Rokide "A" in a composite coating comprising an inner layer 0.004 in. thick of aluminum Alloy 13, and an outer layer 0.004 in. thick of Rokide "A". One group of specimens having this two-layer coating was tested at temperatures up to 2800°F. The coating protected the base molybdenum against oxidation for four hours when specimens were exposed directly to air at 2600°F or 2800°F, as shown in Table 8-D (specimens E96, E97). Specimen E98, preconditioned at lower test temperatures, failed after four hours at 2400°F.

A group of specimens was coated with Alloy 13 and Rokide "A" for additional tests involving direct exposure to oxidation at 2400°F and 2600°F. The coating procedures were different from those used for the previous specimens in that after a 0.004-0.005 in. thick layer of Alloy 13 was applied, the panels were diffusion treated at 2200°F in tank argon to promote more diffusion of molybdenum into the coating. The Norton Company applied a Rokide "A" coating approximately 0.004 in. thick. Results of the tests on these specimens (E447 through E454) are recorded in Table 8-D. In these tests, an attempt was made to define the life of the composite coating. The life at 2400°F was considerably less than that obtained with the aluminum-chromium-silicon coating reported above.

Erosion Test of Rokide "A" Coating

It was postulated that a refractory coating might provide better resistance to erosion than the metallic coatings previously tested. One specimen, coated with a composite coating of Alloy 13 and Rokide "A", was subjected to an erosion test at 1800°F, following the usual test procedure. Failure at two locations on the specimen occurred after 30 minutes' exposure to the abrasive stream at 1800°F.

Tests of Mixtures of Aluminum and Aluminum Oxide

Experiments had indicated the feasibility of applying mixtures of aluminum and aluminum oxide with a Wall-Colmonoy Spraywelder. Powder mixtures can be aspirated through the oxy-acetylene flame, and the molten aluminum acts as a binder for holding the aluminum oxide in place on the molybdenum.

Oxidation tests were conducted at temperatures up to 3000° F with mixtures of aluminum plus aluminum oxide. Coatings comprising mixtures of either 10% or 20% aluminum have the capacity to sustain four hours' exposure at 2600°F, provided the coating is exposed at 2000°F and 2400°F for four hours prior to exposing at 2600°F, as shown in Table 8-E. All specimens failed within four hours when exposed directly at 2600°F.

Metallographic examination of a specimen after diffusion treatment revealed a thin coating of aluminum, bonded by diffusion to the underlying molybdenum, and mechanically entrapping a thin layer of aluminum oxide on the exterior surface. Apparently the aluminum oxide was "floated out" to the surface of the panel during diffusion treatment, and the majority of the oxide was nonadherent after the diffusion treatment.

Summary

Visual examination of specimens from high temperature oxidation tests indicates the ability of the Al-Cr-Si to protect the base molybdenum for periods up to four hours at 3000°F. However, metallographic examination indicates melting of the coating at 2800°F, and the practical temperature limit for this coating is considered to be 2600°F.

Melting of the Ni-Cr-B and Ni-Si-B alloys results in severe intergranular attack of the base molybdenum in oxidation tests at 2400°F. The practical temperature limit for these coatings is considered to be 2200°F.

Attempts to incorporate aluminum oxide in aluminum-bonded coatings as mixtures or as composites of aluminum and aluminum oxide did not reveal any advantages for such coatings in oxidation tests at high temperatures or in erosion tests at 1800°F.

WADC TR 54-492 Pt 3   49

TABLE 8

RESULTS OF OXIDATION TESTS IN AIR AT TEMPERATURES UP TO 3000°F
(2 in. by 2 in. by 0.050 in. specimen)

A. Al-Cr-Si Coating (20% Al + 80% Cr-Si Alloy)

Specimen No.	Time and Temperature of Exposure						Condition of Specimen after Exposure
	1800°F, hr	2000°F, hr	2400°F, hr	2600°F, hr	2800°F, hr	3000°F, hr	
E142	4	4	4				unfailed
E143	4	4	4				unfailed
E140	4	4	4	4			unfailed (Figure 20)
E141	4	4	4	4			unfailed
E138	4	4	4	5-1/2	4		unfailed; slight melting of coating (Figure 20)
E139	4	4	4	5-1/2	4		unfailed; slight melting of coating
E136	4	4	4	6	4	4	unfailed; considerable melting of coating (Figure 20)
E137	4	4	4	6	4	4	unfailed
E145	8		4				unfailed
E146	8		4				unfailed
E147	8			4			unfailed (Figure 21)
E148	8			4			unfailed
E149	8				1-1/2		failed (Figure 21)
E150	8				1-1/2		failed
E151	8					2	failed
E152	8					3	failed (Figure 21)

B. Colmonoy No. 5 Alloy Coating

Specimen	1800°F, hr	2000°F, hr	2200°F, hr	2400°F, hr	2600°F, hr	2800°F, hr	Condition
E223		575					unfailed (specimen distorted)
E224			27				failed
E225	8			1-1/2			failed
E226	8	4	4	1/2			failed
E227	8	4	4	1/2			failed

C. Coast Metals 50 Alloy Coating

Specimen	1800°F, hr	2000°F, hr	2200°F, hr	2400°F, hr	2600°F, hr	2800°F, hr	Condition
E228		500 +					unfailed (specimen distorted)
E229			8				failed
E230	8	4	4	1/2			failed
E231	8	4	4	1/2			failed
E232	8			1-1/2			failed

WADC TR 54-492 Pt 3

TABLE 8
(continued)

D. Aluminum Alloy 13 plus Rokide "A"* Coating

Specimen No.	1800°F, hr	2000°F, hr	2200°F, hr	2400°F, hr	2600°F, hr	2800°F, hr	Condition of Specimen after Exposure
E96						4	unfailed; slight melting of undercoat
E97					4		unfailed; no melting of undercoat
E98	8	4	4	4			failed at edge
E447					3		failed on one corner
E448					3		failed on face (blistered)
E449					14		failed on edge and face
E450					10		failed on face
E451				17			failed on edge and face
E452				17			failed on edge and face
E453				17			failed on edge and face
E454				16			coating cracked

E. Al-Al_2O_3 Coating (10% or 20% Al plus 90% or 80% Al_2O_3)

	1800°F, hr	2000°F, hr	2400°F, hr	2600°F, hr	2800°F, hr	3000°F, hr	
10% Al							
E207	8	4	4	62			failed
E208	8			6			coating blistered and peeled
E209	8			4			coating blistered and peeled
E203-E206	8	4	4	4			unfailed (3 specimens)
20% Al							
E220	8	4	4	62			failed
E221	8			6			coating blistered and peeled
E213	8			4			coating blistered and peeled
E216-E219	8	4	4	4			unfailed (3 specimens)

*Rokide "A": Al_2O_3 applied by Norton Company, Worcester, Massachusetts
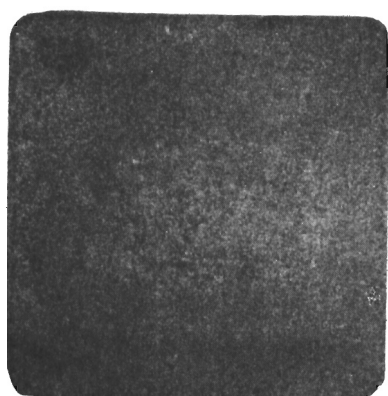
FIGURE 20 (P1479)

FULL SIZE

Specimen E140
4 hr at 1800°F
4 hr at 2000°F
4 hr at 2400°F
4 hr at 2600°F
Unfailed
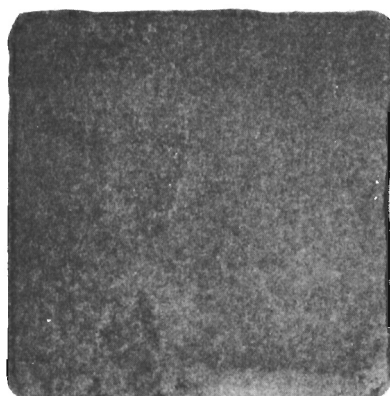
Specimen E138
4 hr at 1800°F
4 hr at 2000°F
4 hr at 2400°F
5-1/2 hr at 2600°F
4 hr at 2800°F
Unfailed
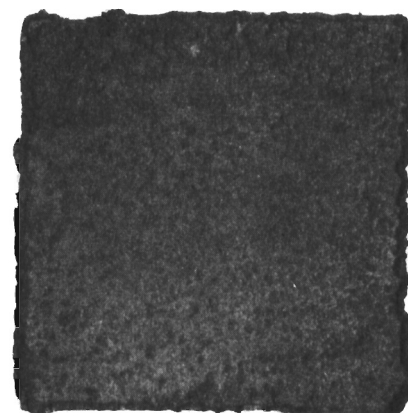
Specimen E136
4 hr at 1800°F
4 hr at 2000°F
4 hr at 2400°F
6 hr at 2600°F
4 hr at 2800°F
4 hr at 3000°F
Unfailed
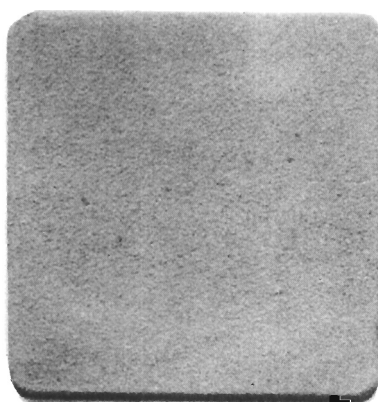
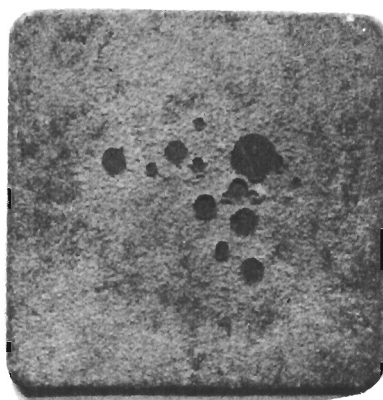**FIGURE 21 (P1488)**

FULL SIZE

Specimen E147
8 hr at 1800°F
4 hr at 2600°F
Unfailed

Specimen E149
8 hr at 1800°F
1-1/2 hr at 2800°F
Failed

Specimen E152
8 hr at 1800°F
3 hr at 3000°F
Failed

PHOTOGRAPHS OF PANELS OF 0.5% Ti-Mo ALLOY SPRAY COATED WITH
Al-Cr-Si AND OXIDATION TESTED AS INDICATED UNDER PHOTOGRAPH

(M6400)   Polish-Etch-Buff   X100

Interfacial Zone

Molybdenum

(M6401)   Polish-Etch-Buff   X1500
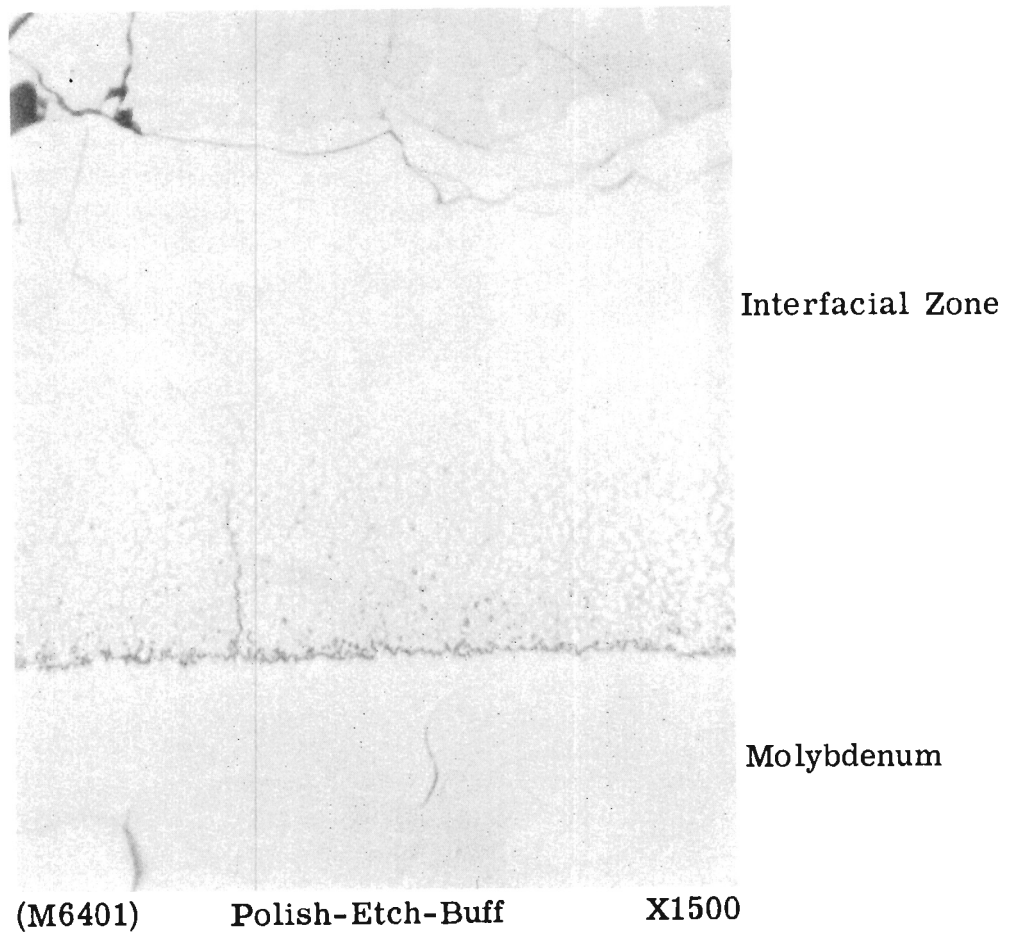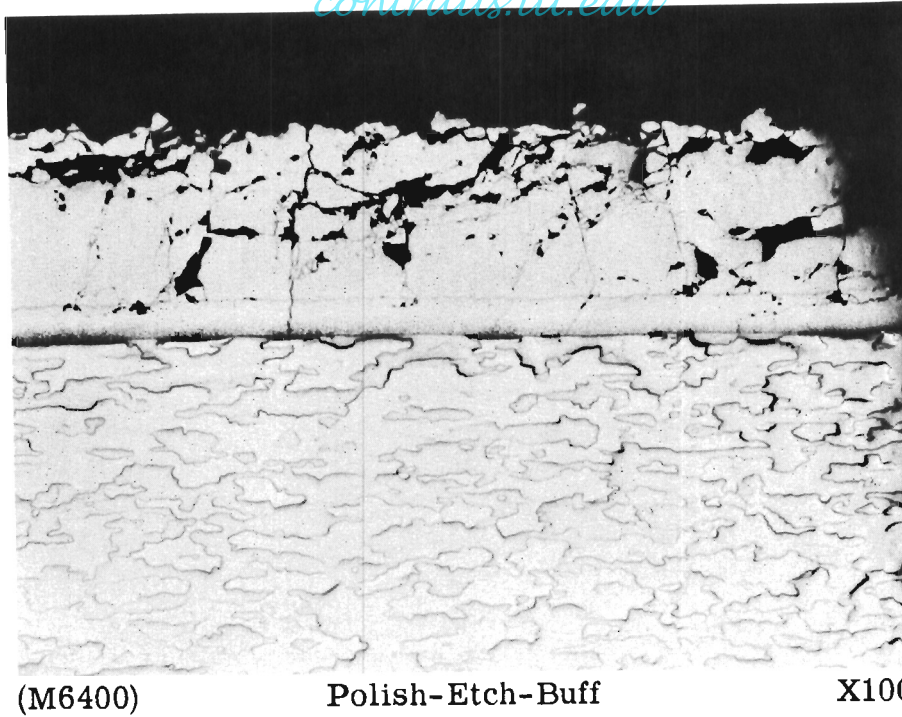
FIGURE 22 -   Specimen E144.   Al-Cr-Si on 0.5% Ti-Mo alloy.   Diffusion
treated 2 hours 2000°F in dry argon.   Oxidation tested
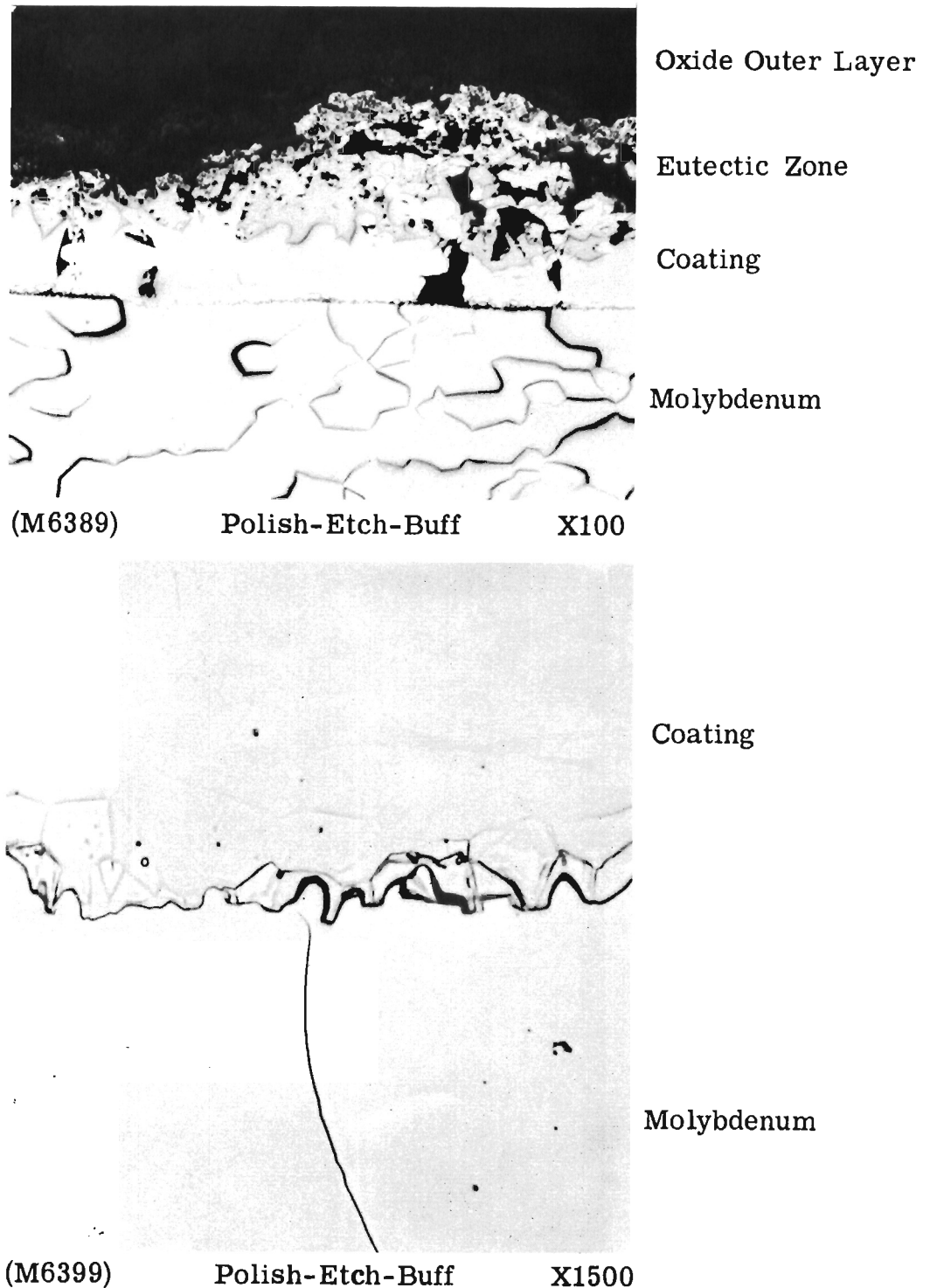4 hours 1800°F, 4 hours 2000°F, 4 hours 2400°F.

WADC TR 54-492 Pt 3   53
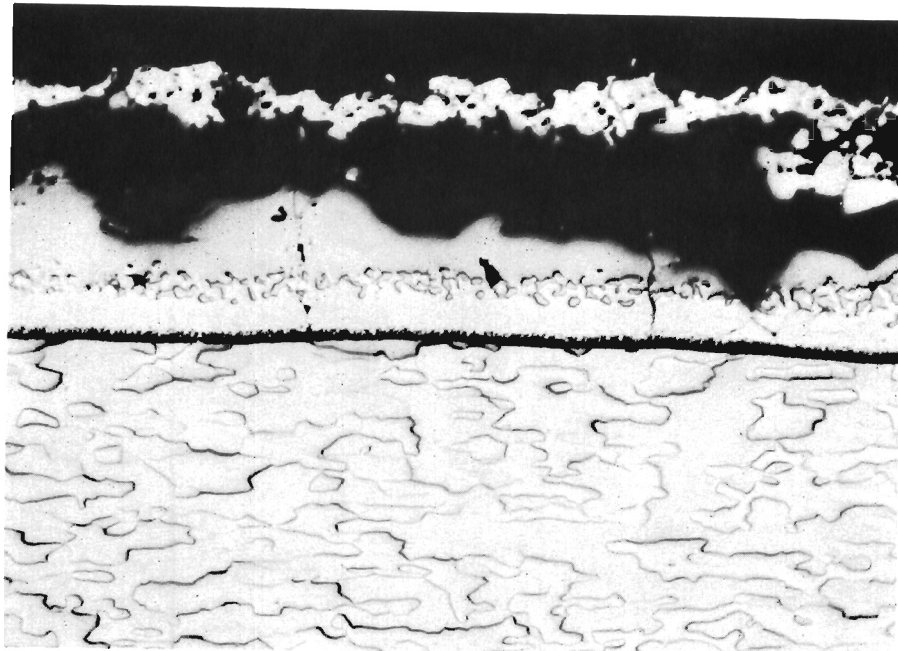
(M6384)   Polish-Etch-Buff   X100
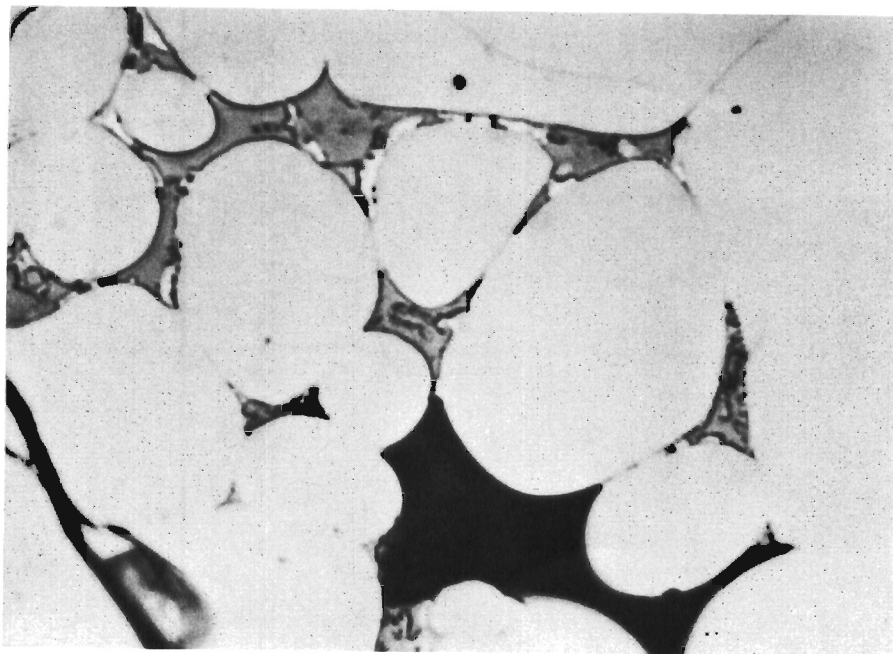
(M6388)   2% Hydrofluoric Acid   X2000
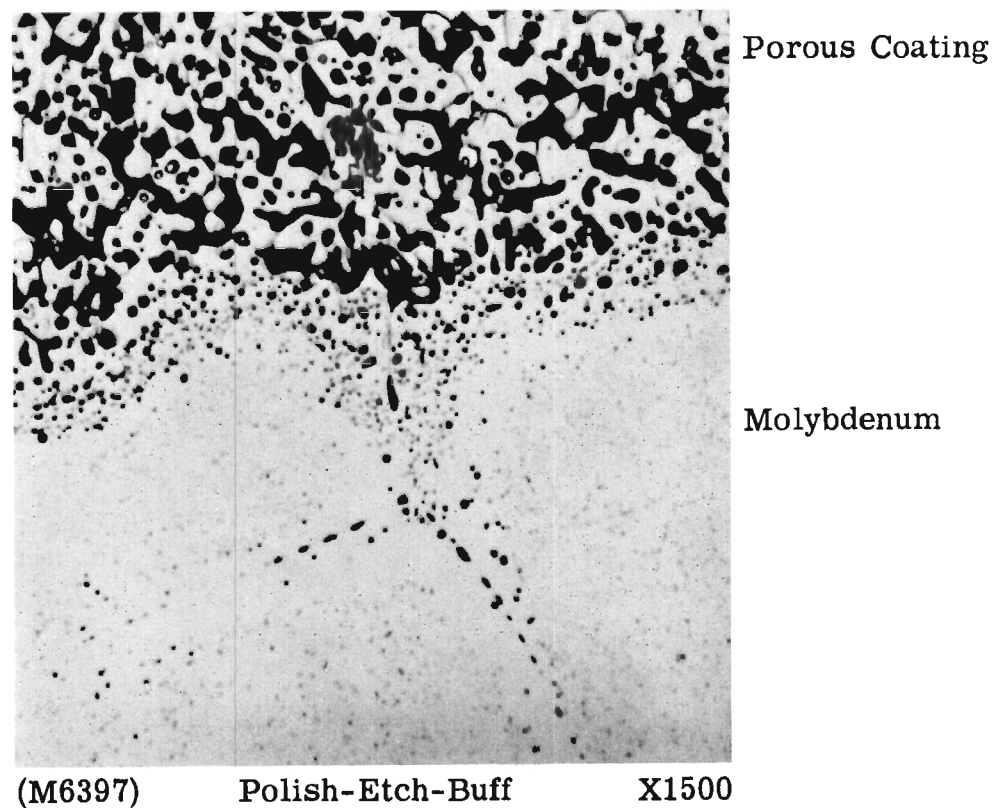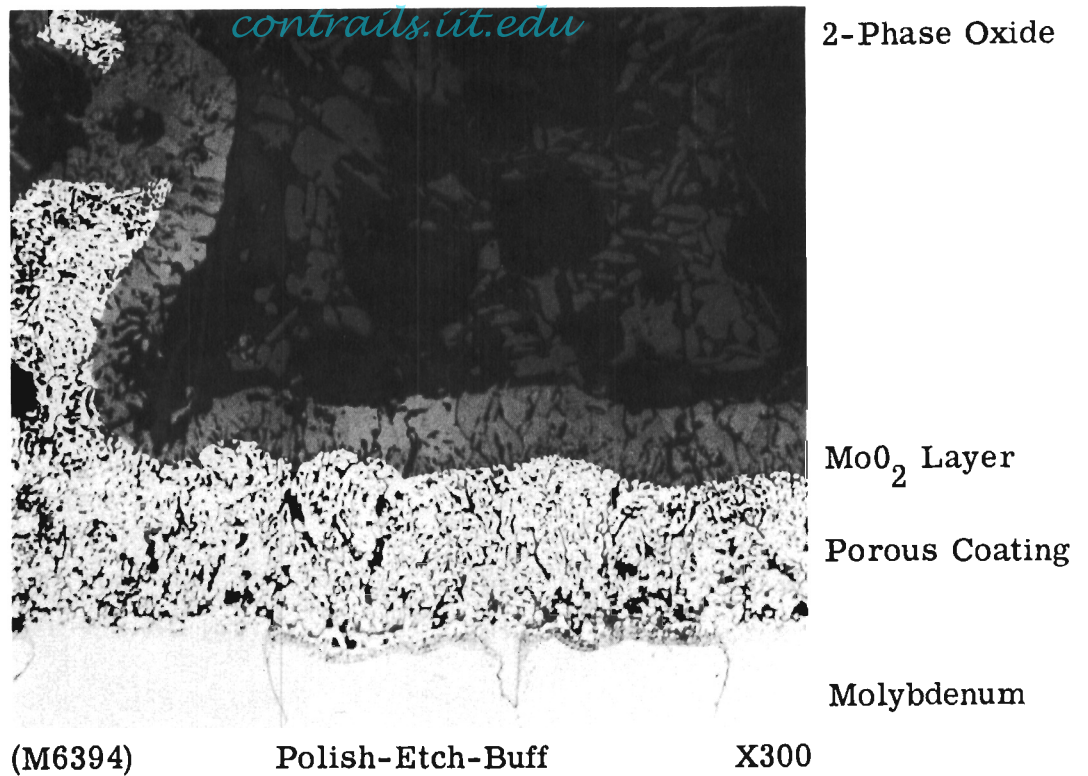
FIGURE 23 - Specimen E141. Al-Cr-Si on 0.5% Ti-Mo alloy. Diffusion
             treated 2 hours 2000°F in dry argon. Oxidation tested
             4 hours 1800°F, 4 hours 2000°F, 4 hours 2400°F, 4 hours
             2600°F. Evidence of eutectic phase in coating.
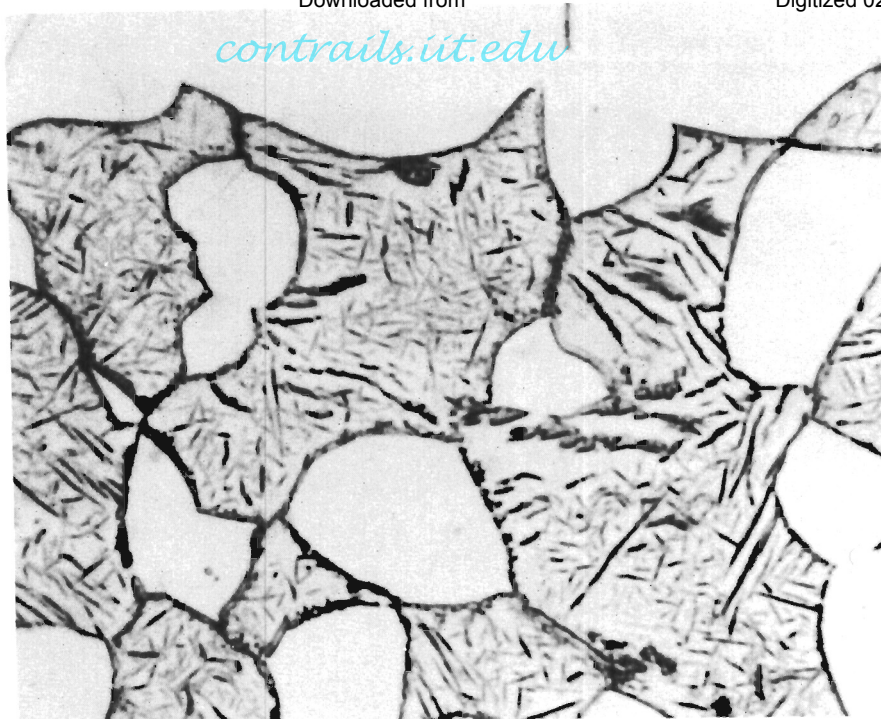
(M6387)   2% Hydrofluoric Acid   X2000

FIGURE 24 -   Specimen E141.   Additional evidence of
              eutectic phase in coating.
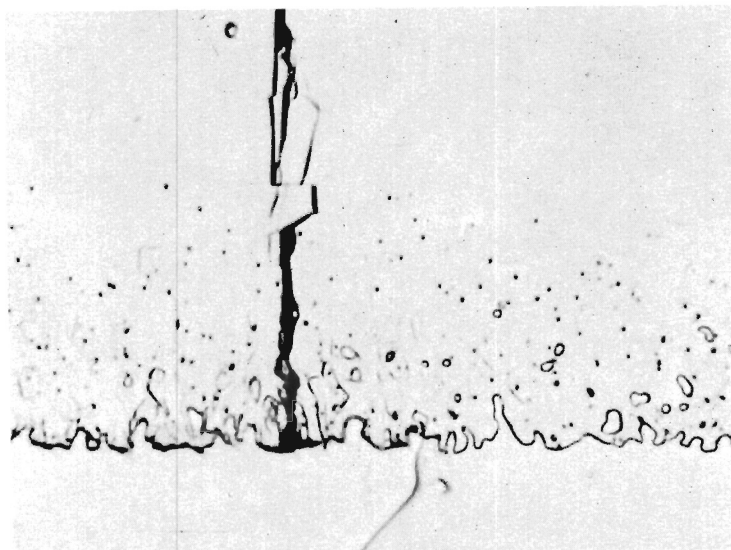
(M6398)   2% Hydrofluoric Acid   X2000

FIGURE 25 -   Specimen E141.   Indication of globules
              of undissolved molybdenum in interfacial
              zone of coating after 2600°F exposure.

(M6389)   Polish-Etch-Buff   X100

Oxide Outer Layer

Eutectic Zone

Coating

Molybdenum

(M6399)   Polish-Etch-Buff   X1500

Coating

Molybdenum

FIGURE 26 -   Specimen E139.   Al-Cr-Si on 0.5% Ti-Mo alloy.   Diffusion
treated 2 hours 2000°F in dry argon.   Oxidation tested
4 hours 1800°F, 4 hours 2000°F, 4 hours 2400°F, 5-1/2
hours 2600°F, 4 hours 2800°F.

2-Phase Oxide

MoO_2 Layer

Porous Coating

Molybdenum

(M6394)   Polish-Etch-Buff   X300

Porous Coating

Molybdenum

(M6397)   Polish-Etch-Buff   X1500

FIGURE 27 -   Specimen E137.   Al-Cr-Si coating on 0.5% Ti-Mo alloy.   Diffusion
treated 2 hours 2000°F in dry argon.   Oxidation tested 4 hours
1800°F, 4 hours 2000°F, 4 hours 2400°F, 6 hours 2600°F, 4 hours
3000°F.
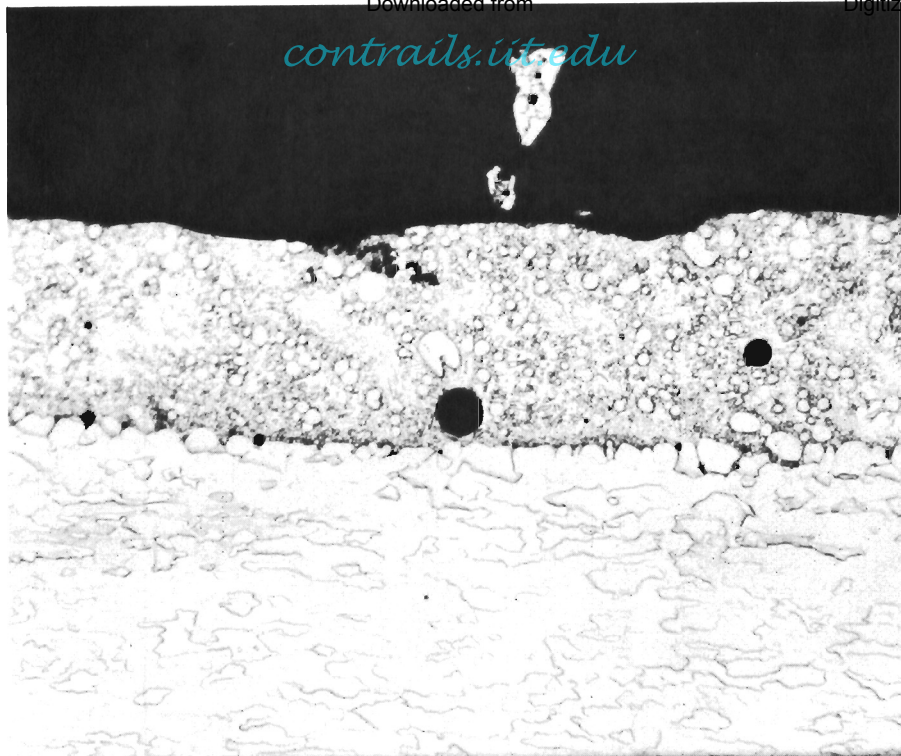
(M6949)   Polish-Etch-Buff   X100
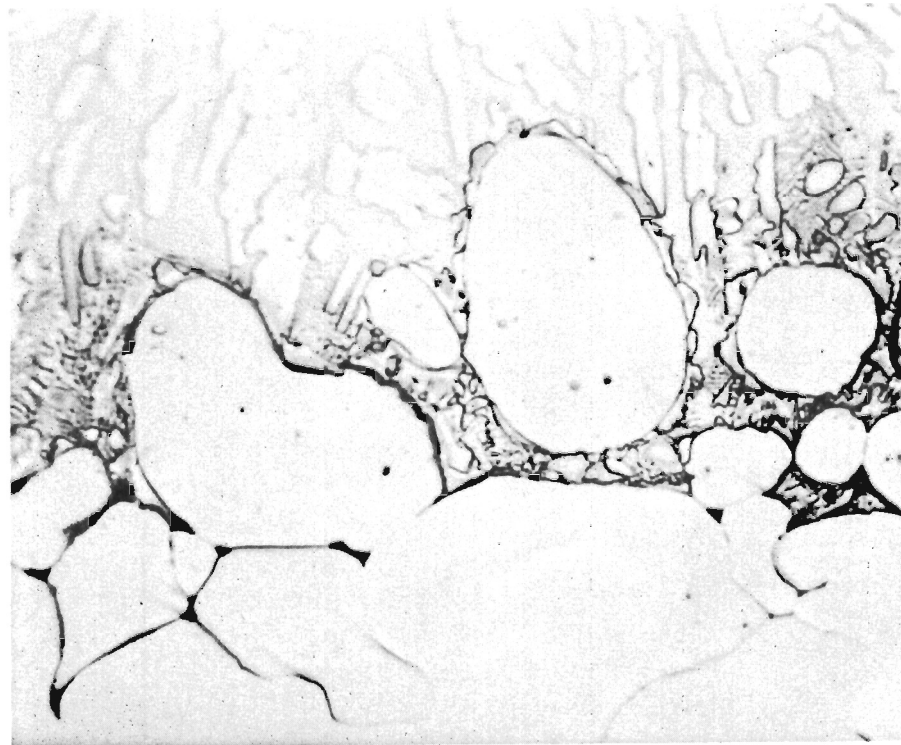
(M6950)   Polish-Etch-Buff   X1000

FIGURE 28 -   Specimen E227. Colmonoy No. 5 on 0.5% Ti-Mo alloy. Diffusion
treated 2 hours at 2000°F in dry argon. Oxidation tested 8 hours
1800°F, 4 hours 2000°F, 4 hours 2200°F, 1/2 hour 2400°F (failed).
Evidence of intergranular attack on molybdenum and "floating" of
molybdenum to surface.

SECTION 7

EXPLORATION OF BARRIER LAYER COATINGS

Consideration has been given to the incorporation of a diffusion barrier in nickel-base coatings, because of the tendency of such coatings to fail by formation of nickel molybdate when oxygen reaches the nickel-molybdenum interface. Also, diffusion of nickel into the base molybdenum results in a recrystallized layer in the molybdenum immediately under the coating; a diffusion barrier would reduce the rate of formation of this layer. Recent experiments have shown that under certain circumstances, copper, although essentially insoluble in molybdenum, will wet molybdenum and form an adherent bond. It was postulated that a copper layer adjacent to the molybdenum would prevent diffusion of molybdenum into a nickel-base coating applied over the copper, and might reduce the rate of diffusion of nickel into the underlying molybdenum. An additional advantage of using copper was the possible formation of copper molybdate if oxygen were to reach the molybdenum through breaks in the copper layer.

Evidence of a copper-molybdenum bond was found in the results of the following experiments:
1. Copper wire was metal-sprayed on a molybdenum surface and diffusion treated in hydrogen.

2. Copper was deposited as a weld-metal layer on molybdenum.

3. Copper oxide on a molybdenum surface was reduced by hydrogen.

In experiments with the weld-metal layer, attempts to remove the copper resulted in fracture in the underlying molybdenum, thus indicating a high-strength bond. A bond strength of 25,600 psi was determined in a tensile test of a composite specimen produced by casting copper against a molybdenum stool in a graphite mold.

In exploratory experiments in which copper was employed as a component of several composite coatings, diffusion treatments were incorporated to consolidate the coatings and to increase the melting point of the copper layer by diffusion of nickel into the layer. Each composite coating, approximately 0.010 inch thick, was metal-sprayed on five specimens of 0.5% titanium-molybdenum alloy 2 in. by 2 in. by 0.055 in. The coatings tested and the results obtained are given in Table 9.

The results were not promising for any of the composites tested, and no further work was undertaken.

TABLE 9

RESULTS OF OXIDATION TESTS WITH BARRIER LAYER COATINGS

Coating	Step	Thickness	Description	Life in 1800°F Oxidation Test, hr
A	1	0.005 in.	Cu, wire sprayed	
	2	0.005 in.	Ni, wire sprayed	
	3		Diffusion treated*	2
B	1	0.005 in.	Cu, wire sprayed	
	2		Diffusion treated	
	3	0.005 in.	Ni, wire sprayed	
	4		Diffusion treated	6
C	1	0.0055 in.	Cu, wire sprayed	
	2	0.0065 in.	Colmonoy No. 5, powder sprayed	
	3		Diffusion treated	13
D	1	0.0055 in.	Cu, wire sprayed	
	2		Diffusion treated	
	3	0.0065 in.	Colmonoy No. 5, powder sprayed	
	4		Diffusion treated	1
E	1	0.003 in.	Cu, wire sprayed	
	2	0.004 in.	Ni, wire sprayed	
	3	0.005 in.	Colmonoy No. 5, powder sprayed	
	4		Diffusion treated	22
F	1	0.003 in.	Cu, wire sprayed	
	2	0.004 in.	Ni, wire sprayed	
	3		Diffusion treated	
	4	0.005 in.	Colmonoy No. 5, powder sprayed	
	5		Diffusion treated	6

*All diffusion treatments comprised heating 2 hours at 2000°F in purified hydrogen.

SECTION 8

EVALUATION OF "SELF-HEALING" CHARACTERISTICS OF THE ALUMINUM-CHROMIUM-SILICON COATING

Several instances have been observed and reported in which molybdenum, imperfectly coated with an aluminum-chromium-silicon composition, has been subjected to oxidizing conditions, but has not exhibited rapid oxidation of the exposed molybdenum. Such observations have been intriguing, since, if the Al-Cr-Si coating is "self-healing," this would greatly increase confidence in using coated molybdenum commercially. It was decided to include under this contract a series of experiments designed to measure quantitatively the extent of "self-healing" of controlled defects under controlled oxidation conditions. An earlier observation of "self-healing" and the results of two types of controlled tests to explore "self-healing" are described in this section of the report.

Previous Evidence of Self-Healing

One example of apparent self-healing of aluminum-bonded coatings was observed in an oxidation test of a panel of unalloyed molybdenum coated with a 0.010" thick layer of Al-Cr-Mo-Si (20% aluminum plus 80% chromium-molybdenum-silicon alloy). The coated panel developed a blister at the edge of the panel after about 200 hours at 1700^OF. When the panel had been exposed for an additional 80 hours, the blister was intentionally broken to expose the base molybdenum sheet. After reheating this panel to 1700^OF, it was noted that the customary small amount of molybdic oxide vapors was evolved from the sample. After an additional 24 hours at 1700^OF, the panel was examined to determine the extent of damage at the exposed area. The loss of molybdenum did not appear to be very great, and there were no visible oxide vapors being emitted.

An example of self-healing observed outside our laboratory has been described in a report from one of the industrial aircraft development laboratories. In the course of some tests of coated molybdenum, a corner of a panel was deliberately broken off to simulate possible service damage. The panel of 0.5% titanium-molybdenum alloy had been coated with 0.010 in. Al-Cr-Si alloy and exposed to oxidation for four hours at 2400^OF. The broken specimen was exposed to the highly oxidizing flame of an oxy-acetylene torch for 15 minutes in the temperature range $2425-2580^O$F. No weight change was observed, and visual examination of the specimen after the test revealed that the edge had apparently healed.

An attempt was made to duplicate the latter results in tests at the Climax laboratory. A panel of 0.5% titanium-molybdenum alloy, which had been coated with the Al-Cr-Si coating approximately 0.010 in. thick, and which had been exposed to oxidation for 500 hours at 1800^OF, was selected for the test. A corner of the panel was sawed off, the panel was held in a vise, and the end of the panel containing the exposed corner was heated with an oxy-acetylene torch for 15 minutes in the temperature range $2450-2550^O$F. When the heating flame was removed, only a small amount of smoking was observed during the cooling period.

WADC TR 54-492 Pt 3   61

The specimen was examined metallographically. It was apparent that a protect-ive coating had formed over the exposed edge of the specimen, reducing the area of exposed molybdenum. The microstructure at the healed end of the exposed specimen is shown in Figure 29, which is a composite of a sequence of photomicro-graphs illustrating the change in the structure of the coating at the healed end. It is apparent that the thin layer adjacent to the molybdenum, characteristic of alu-minum-bonded coatings, has formed over the cut end of the specimen also. The eutectic structure near and on the healed end is different from the normal coating structure, and may offer some clue to the mode of formation of the healing layer.

Description of the Testing Program

To define conditions under which self-healing is evident in molybdenum coat-ed with the aluminum-chromium-silicon composition, two types of tests were con-ducted. In one series of tests, coated panels were prepared, and the coating was ground from one edge to provide a controlled defect. In another series of tests, a small defect was created in each one of a group of coated panels by impacting at 1800^OF with a pellet from an air rifle (using the standard ballistic-impact test procedure). Coated specimens with and without defects were oxidation tested for consecutive short periods of time at temperatures in the range 1800-2600°F. Details of the program are given in the following paragraphs.

Exposed-Edge Tests. An aluminum-chromium-silicon coating approximately 0.010 in. thick was applied to a series of 12 panels of unalloyed molybdenum 2 in. by 2 in. by 0.055 in. The panels were diffusion treated two hours at 2000°F in purified hydrogen. Six of the panels were exposed 500 hours at 1800°F to a stream of moving air (standard oxidation test procedure). One edge of each of three as-diffusion-treated specimens, and of three oxidation-tested specimens, was surface ground to remove the coating. All specimens were weighed and ex-posed to oxidation at 1800°, 2100° and 2400°F.

In tests at each temperature, specimens were removed from the furnace, cooled to room temperature, weighed, and returned to the furnace after 15 min-utes, 30 minutes, and after consecutive one-hour exposures. Tests were con-tinued until a 10% loss of weight was measured, or until 50 hours' testing time had elapsed.

Impact-Defect Tests. An Al-Cr-Si coating approximately 0.010 in. thick was applied to a series of six specimens of unalloyed molybdenum, 1 in. by 1-7/8 in. by 0.094 in. The specimens were diffusion treated two hours at 2000°F in purified hydrogen. Four specimens were retained for testing in the as-diffusion treated condition; two were exposed to the oxidation test for 500 hours at 1800°F. One impact defect was created in each of two "as-diffusion-treated" specimens, and in each of the two "exposed" specimens, using the ballistic-impact procedure at 1800°F. The impacted specimens were weighed and then heated for consecutive ten-minute intervals in oxidation test furnaces at 1800° and 2600°F. The two specimens without defects were also weighed and heated in the same manner at 2600°F. After each ten-minute exposure, the specimens were cooled to room temperature and reweighed. Testing was continued for a total testing time of 160 minutes.

WADC TR 54-492 Pt 3   62

Test Results

The results of the exposed-edge tests and impact-defect tests are presented in terms of percent change in weight versus time at the test temperature (Figures 30 and 31). The appearance of the specimens containing impact defects is illustrated in Figure 32.

In tests at 1800°F (Figure 30), the specimens from which the edge was ground after the 1800°F exposure (500 hours) experienced a steady loss in weight upon continued exposure. The specimens from which the edge was ground after diffusion treatment exhibited an increase in weight for a short period of exposure, then gradually lost weight. The specimens containing an impact defect exhibited only a slight loss in weight during exposure after the defect was created.

In tests at 2100°F (Figure 30), the rate of change in weight with exposure time was higher than in tests at 1800°F, but a slight increase in weight was evident during the first few minutes' testing of the as-diffusion-treated specimen.

In tests at 2400°F (Figure 31), the specimens without defect exhibited a significant increase in weight during short exposure, the increase continuing for the as-diffusion-treated specimen, but dropping off for the specimen which had been previously tested 500 hours at 1800°F. Although both specimens containing defects lost weight at a relatively high rate, the "shelf" in the curve for the as-diffusion-treated specimen may be due to the same phenomenon as the weight increase exhibited at lower test temperatures.

In tests at 2600°F (Figure 31), it was interesting to note that all specimens exhibited slight increases in weight. In later stages of testing, specimens without defects began to lose weight before specimens containing defects. After 2-1/2 hours' exposure to oxidizing conditions at 2600°F, the specimens containing defects had shown no weight loss. A macrophotograph of the impact-defect area of one specimen after 30 minutes' exposure at 2600°F is shown in Figure 33. It is apparent that the molybdenum did not oxidize away from the defect area.

Summary

Results of earlier observations (with the aluminum-chromium-silicon coating) and of the foregoing tests appear to support the claim that under certain conditions the coating exhibits "self-healing." The evidence leads this writer to postulate that, rather than "self-healing," the coating is "self-fluxing." Such a mechanism would operate in the following way--when the melting point of a constituent (presumably a eutectic) in the coating is exceeded in the presence of a small area of exposed molybdenum, the molten constituent of the coating wets the area, thus preventing further oxidation. The self-fluxing mechanism appears to be most effective in the presence of smaller defects.
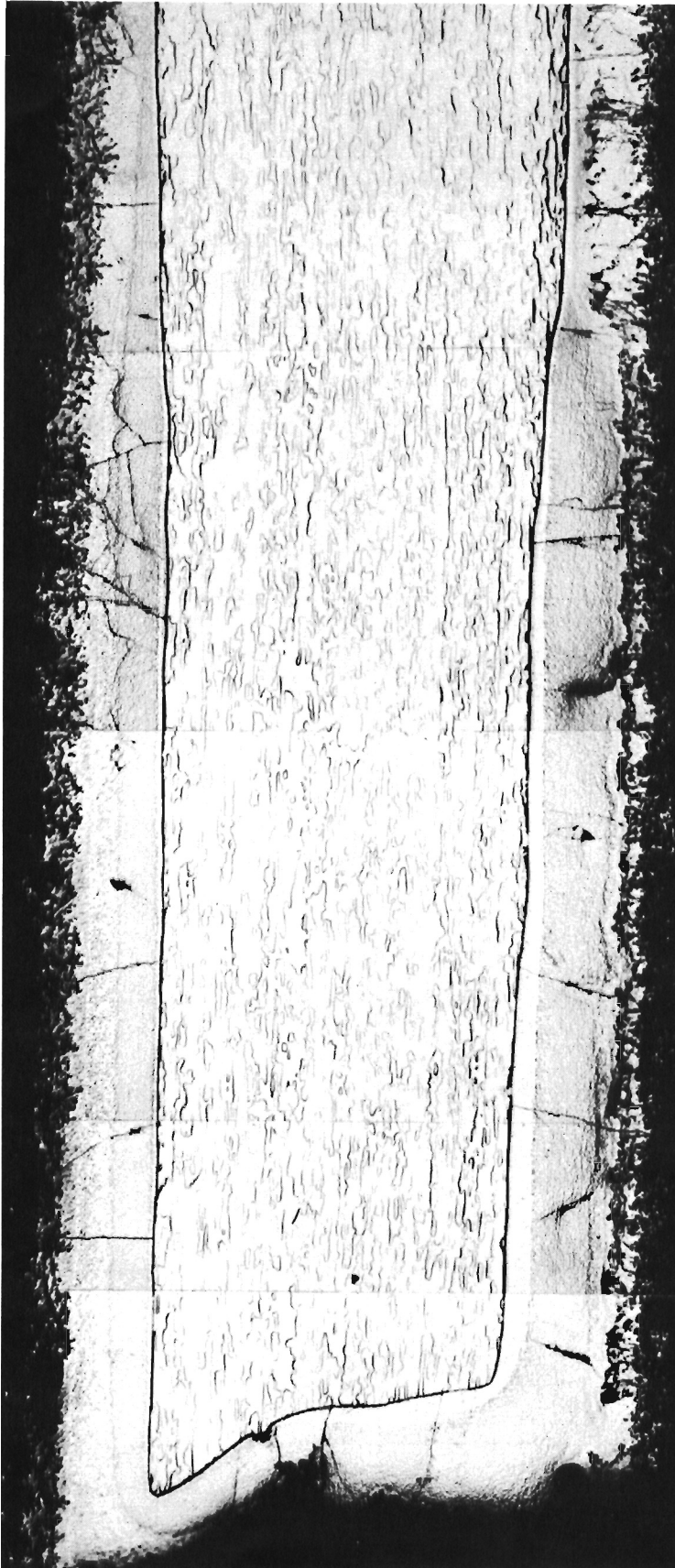
APPROX X45

Polish–Etch–Buff

FIGURE 29 (P1629)

Al-Cr-Si COATING ON 0.5% Ti-Mo ALLOY. DIFFUSION TREATED 2 HOURS AT 2000°F IN DRY ARGON. OXIDATION TESTED 500 HOURS AT 1800°F. CORNER REMOVED FROM SPECIMEN BY SAWING. EXPOSED CORNER HEATED FOR 15 MINUTES IN THE TEMPERATURE RANGE 2450-2550°F USING AN OXY-ACETYLENE TORCH. COMPOSITE MICROGRAPH SHOWING FORMATION OF COATING OVER EXPOSED EDGE OF PANEL.
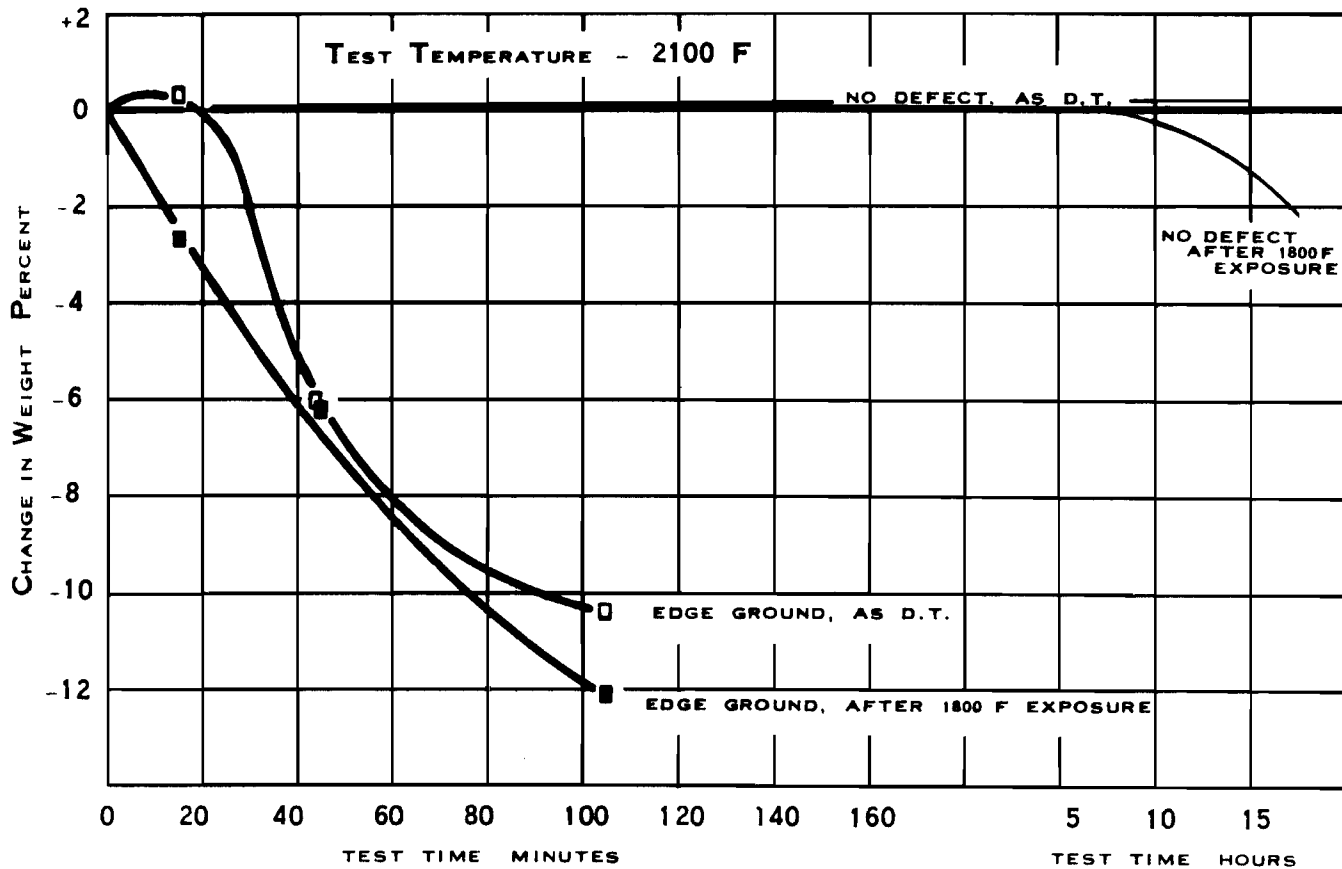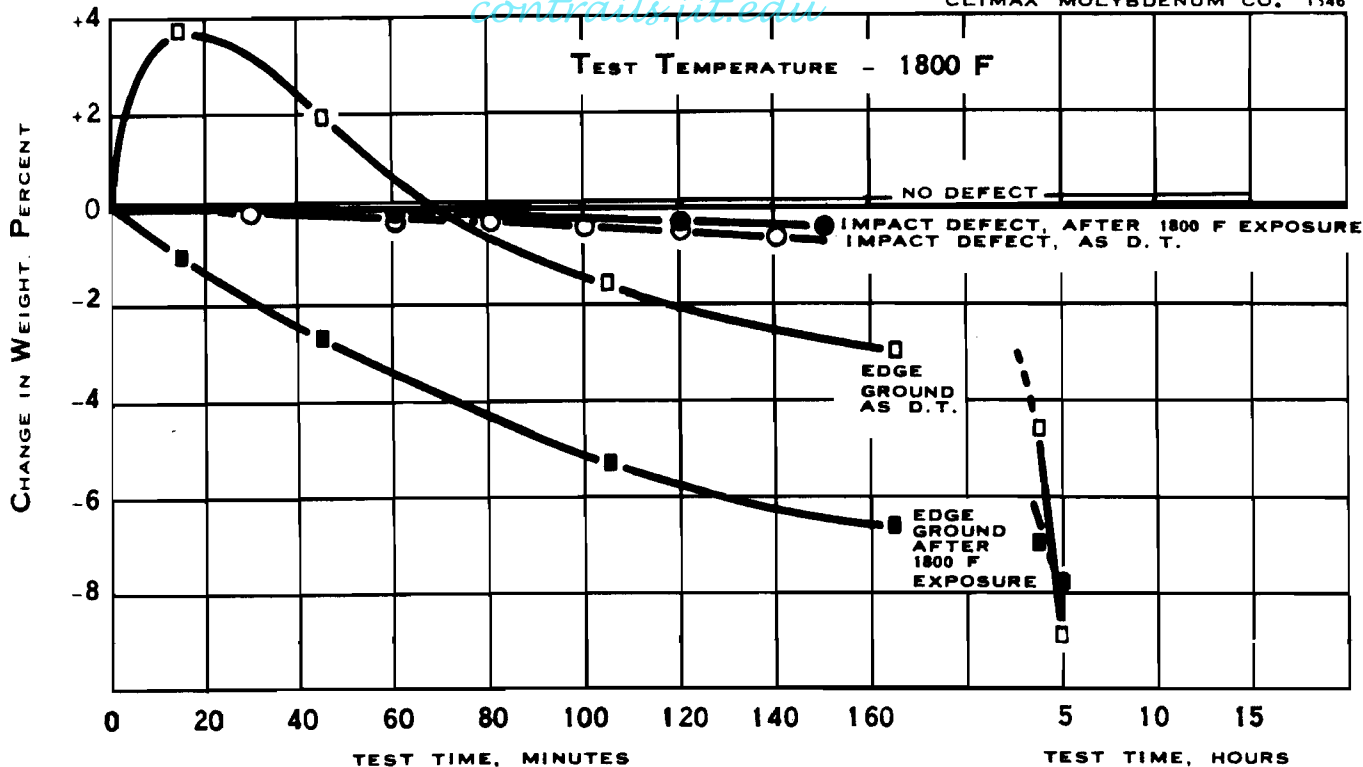
CLIMAX MOLYBDENUM CO. 1146

FIGURE 30 — WEIGHT CHANGES IN COATED MOLYBDENUM
CONTAINING CONTROLLED DEFECTS

(AL-CR-SI COATING, OXIDATION TESTED AT 1800 AND 2100 F)

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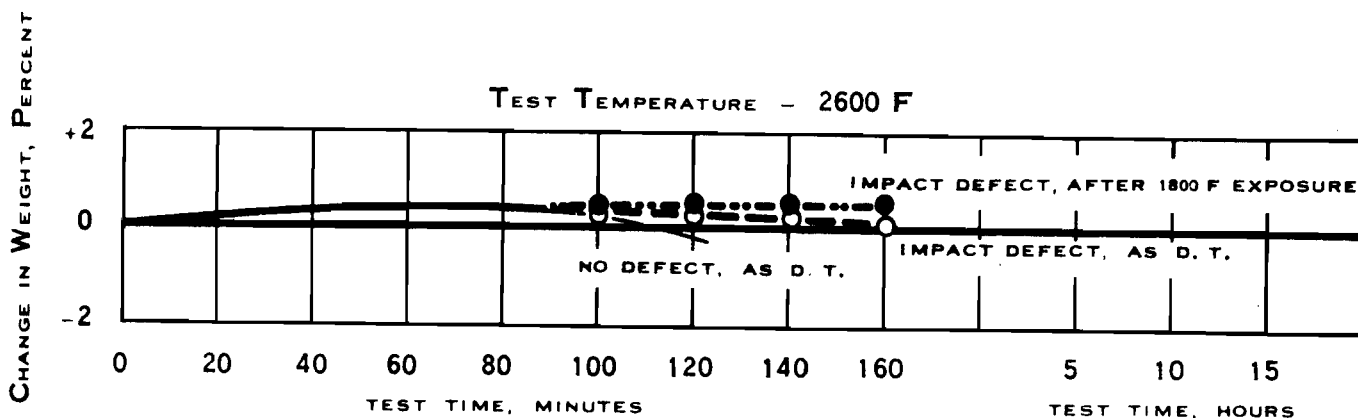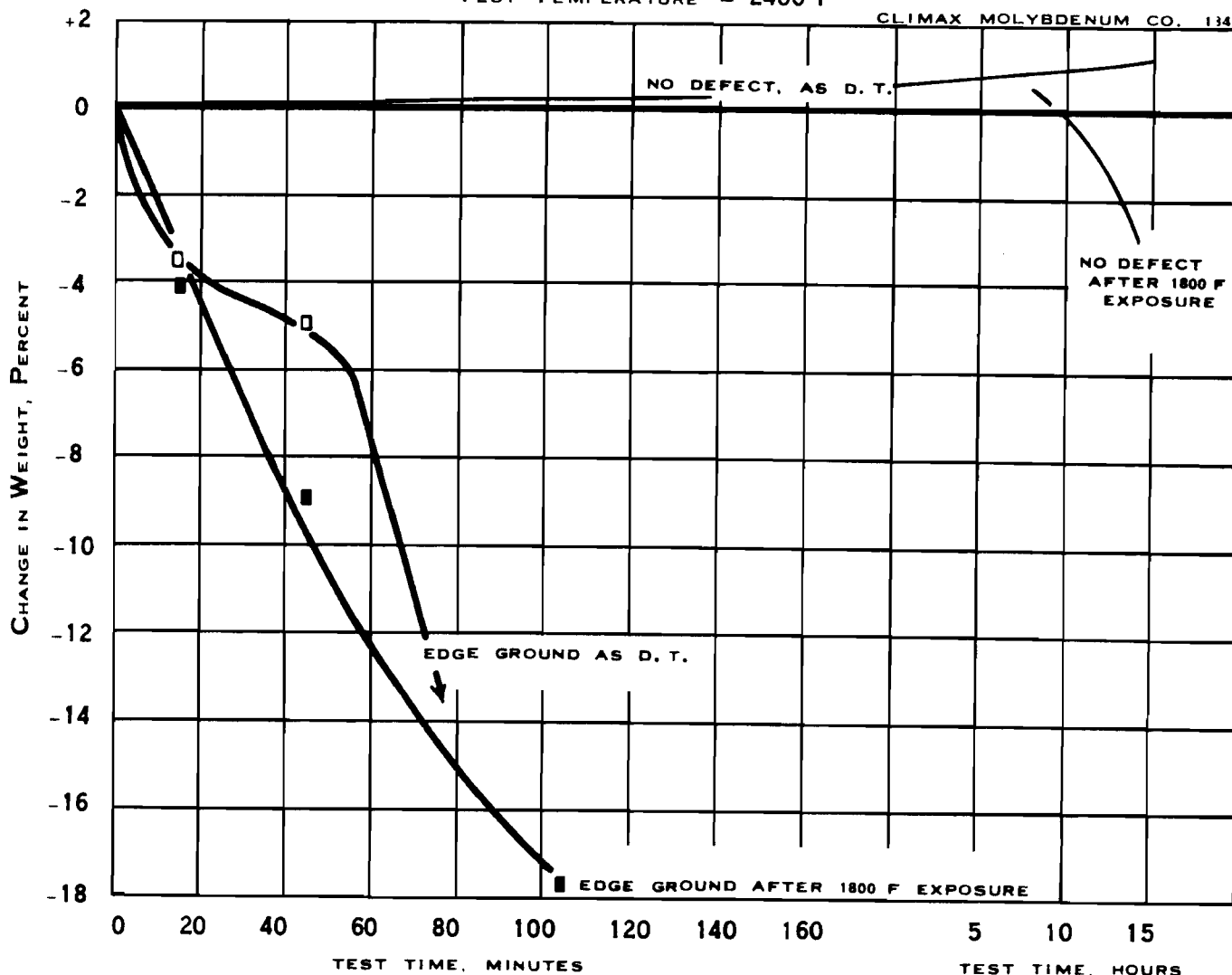
contrails.iit.edu

FIGURE 31 — WEIGHT CHANGES IN COATED MOLYBDENUM
CONTAINING CONTROLLED DEFECTS

(Al-Cr-Si Coating, Oxidation Tested at 2400 and 2600 F)
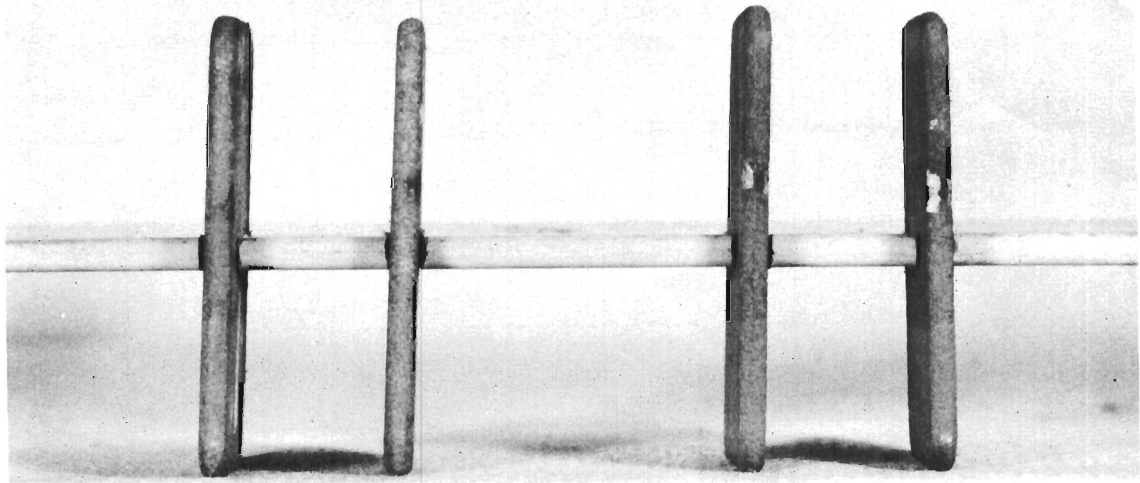
WADC TR 54-492 Pt 3   66

(P1507)   X1

<u>D331</u>　　<u>D332</u>　　　　　　<u>D333</u>　　<u>D334</u>
Oxidation tested　　　　　　Impacted after dif-
500 hr at 1800° F,　　　　fusion treatment
then impacted

FIGURE 32 -   PHOTOGRAPH OF BALLISTIC-IMPACT SPECIMENS BEFORE
OXIDATION TEST. UNALLOYED MOLYBDENUM, COATED
WITH Al-Cr-Si, DIFFUSION TREATED TWO HOURS AT
2000°F IN PURIFIED HYDROGEN
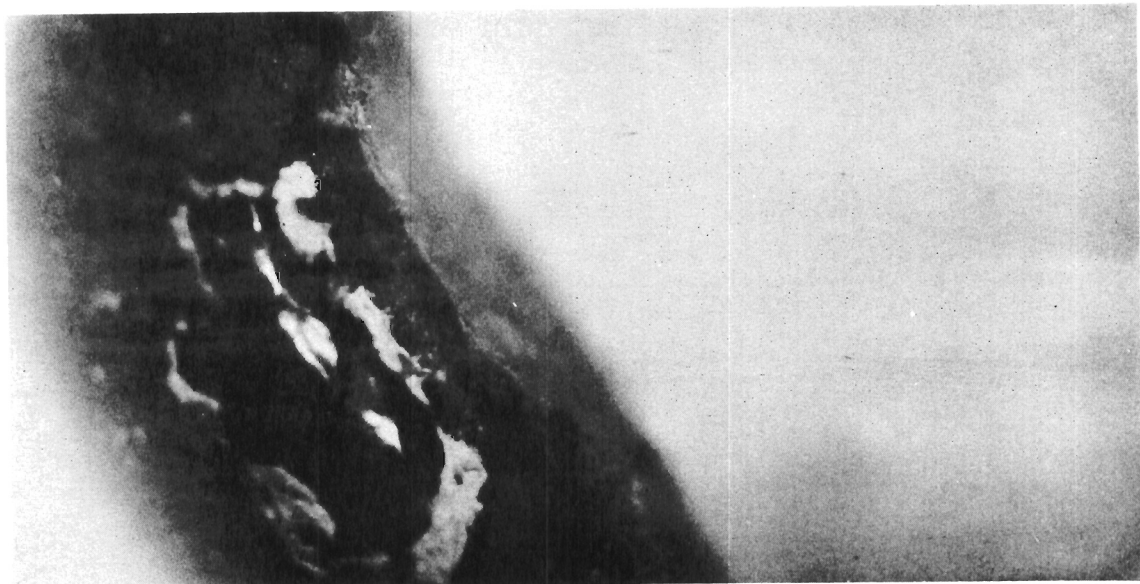
FIGURE 33 (35-15)   APPROX X45

SPECIMEN D332. AFTER 30 MINUTES' EXPOSURE TO OXIDATION
AT 2600°F AFTER IMPACTING. SHOWING NEGLIGIBLE OXIDATION
OF THE MOLYBDENUM EXPOSED BY THE IMPACT DEFECT.

SECTION 9

THE NATURE OF PROMISING COATINGS

During the course of the research on oxidation-resistant coatings for molybdenum, considerable effort has been expended to determine the mechanism by which the promising coatings protect molybdenum from oxidation under the several conditions of exposure. Visual examination has provided some of the evidence, but macroscopic and, especially, microscopic examination have yielded many clues. In this final section of the report, the available test results, metallographic examinations, and x-ray diffraction evidence will be reviewed in an attempt to define the nature of each of the following promising coatings:

1. Aluminum-bonded coatings, exemplified by the single layer Al-Cr-Si composition

2. Nickel-base coatings, exemplified by the Ni-Cr-B and Ni-Si-B compositions

3. Chromium and chromium-nickel coatings, exemplified by the Cr-Ni electrodeposits.

Studies of the Aluminum-Chromium-Silicon Coating

The aluminum-chromium-silicon coating is typical of a series of aluminum-bonded coatings that have shown promise in protecting molybdenum against oxidation at elevated temperatures. Mixtures of aluminum and oxidation-resistant alloy powders can be applied to molybdenum using powder-metal spray-gun techniques, which have been described in earlier reports. As-sprayed, these powders are bonded only mechanically, and require treatment at elevated temperatures to provide an adherent metallurgical bond to the molybdenum. Much of the research and development of coatings over the past few years has been concerned with providing a reproducible metallurgical bond between molybdenum or molybdenum-base alloys and aluminum-bonded coatings. In the course of this research, metallographic studies revealed the presence of an "interfacial zone" as the primary diffusion zone between the molybdenum and the aluminum-bonded coatings. Over a period of several months it became apparent that the presence or absence of this zone (and in some cases, the thickness of this zone) controlled the adherence of the coating. Before discussing the behavior of the aluminum-chromium-silicon coatings in the evaluation tests, the available data on the "interfacial zone", its composition, and variables controlling its formation will be reviewed.

Formation and Growth of the "Interfacial Zone". Early studies under this contract established the fact that adherent Al-Cr-Si coatings on unalloyed molybdenum could be produced by diffusion treatment for two hours at $2000^{\circ}F$ in purified hydrogen. Attempts to lower the diffusion temperature to $1800^{\circ}F$ resulted in failure to produce an adherent coating. The microstructures of the coating-

molybdenum interface after diffusion treating at 1800° and 2000°F are illustrated in Figures 34 and 35. The potassium ferricyanide solution used in the polish-etch-buff procedure for preparing the coated specimens etched the interfacial zone in Figure 35. The zone is not evident in Figure 34.

In the past two years' work under this contract, emphasis has been placed on the development of coatings for the commercial 0.5% titanium-molybdenum alloy, which, by virtue of its higher strength at elevated temperatures and its higher recrystallization temperature, is most promising for application to heat engines. When the Al-Cr-Si coating was applied to this alloy and diffusion treated at 2000°F in purified hydrogen, lack of consistent bonding was evident. This was correlated with the absence of an interfacial zone in the microstructure after diffusion treatment, as illustrated in Figure 36. Extensive studies of diffusion treatment atmospheres and temperatures were conducted under Climax sponsorship to establish a diffusion treatment which would provide consistent adherence of the Al-Cr-Si coating to the 0.5% titanium-molybdenum alloy. Diffusion treatment in dry argon at 2000°F was usually effective in producing a uniform interfacial zone, as illustrated in Figure 37, but occasionally produced a thin, somewhat discontinuous, interfacial zone, as illustrated in Figure 38. It has recently been established that diffusion treatment of Al-Cr-Si coatings on 0.5% Ti-Mo alloy in tank argon at 2200°F consistently produces a uniformly wide interfacial zone without excessive loss of coating thickness, and without recrystallization of the alloy; the microstructure of the bond is shown in Figure 39.

Because of the apparent correlation between a uniform interfacial zone and consistent adherence of the Al-Cr-Si coating, an attempt was made to "grow" the zone (on 0.5% Ti-Mo alloy) sufficiently so that it could be isolated for analysis of its structure and composition. The results of this work, conducted under Climax sponsorship, may be summarized as follows:

1. A wide interfacial zone (approximately 0.005 in.) was achieved during continuous exposure at 2400°F for 236 hours.

2. The interfacial zone was isolated by removal of the outer zones of the coating by mechanical polishing procedures. The underlying molybdenum was removed by grinding and electrolytic polishing.

3. Spectrographic analysis, accurate to within 5-10% of the amount reported, was made of this zone. The results follow:

> 87.0% molybdenum
> 8.8% aluminum
> 1.9% chromium
> 1.3% titanium
> 0.7% silicon

4. Vacuum fusion analyses of two sections of 0.5% titanium-molybdenum alloy, with and without a layer of interfacial zone adhering to the alloy, yielded the following results:

	Parts per Million, By Weight		
	Oxygen	Hydrogen	Nitrogen
Interfacial zone plus base	82,103	2,2	(<10,<10)
Base alone	6,10	<1	(11, 13)

Calculations indicate the interfacial zone contains 0.043% oxygen.

5. X-ray diffraction analyses of the crystal structure of the interfacial zone did not result in positive identification. However, it was apparent that the zone was composed almost entirely of the cubic-phase Mo_3Al, distorted by the presence of chromium, titanium and silicon in the lattice.

In the discussion in the following paragraphs, it will become apparent that this interfacial zone, although not oxidation resistant itself, provides a mechanism for preventing oxidation of the underlying molybdenum.

Behavior of the Al-Cr-Si Coating in Oxidation Tests. The oxidation test, as conducted in this laboratory, provides moderate thermal cycling of the test speci-men; i.e., cooling in air once a day to room temperature. Metallographic studies of the Al-Cr-Si coating have shown that after diffusion treatment, the coating con-tains cracks which extend into the interfacial zone. Despite the presence of these cracks, the coating has exhibited outstanding oxidation resistance. This apparent anomaly can be explained to a reasonable degree by observation of the micro-structure of a failed oxidation-test specimen, as shown in Figures 40 and 41. The specimen (0.5% titanium-molybdenum alloy coated with the Al-Cr-Si composition and diffusion treated for two hours at 2000°F in dried argon) sustained 500 hours' exposure to air at 1800°F and 627 hours' exposure to air at 2000°F before failure. Failure occurred at the edge of the specimen. Evidence in the photomicrographs makes it possible to postulate the following failure mechanism:

1. Cracks appeared in the coating after diffusion treatment, were enlarged, and were supplemented by new and branching cracks during thermal cycling in the oxidation test.

2. Exposure in the oxidation test caused growth of the interfacial zone, as shown in Figure 40 as the 0.0025 in. thick layer adja-cent to the molybdenum.

3. When the specimen cooled from the oxidation-test temperature, thermal contraction of the coating opened the cracks, allowing oxidation on the surfaces of the cracks.

4. Preferential oxidation of the interfacial zone occurred, due to
    the high molybdenum content of the zone. This is apparent from
    the widening of the cracks in this zone.

5. There is substantial evidence that the oxidation of the inter-
    facial zone must be complete before the underlying molybdenum
    is attacked. This is apparent in Figure 41, in which the base
    molybdenum has been oxidized only at the extreme edge of the
    specimen where the interfacial zone is no longer in evidence.
    The "oxidation front" is observed near the center of Figure 41,
    at which point the base molybdenum is just beginning to oxidize
    under a layer of completely oxidized interfacial zone, adjacent
    to a layer of partially oxidized interfacial zone.

6. The complete absence of oxidation of underlying base metal in
    the presence of severely (but not completely) oxidized coating,
    is an outstanding attribute of the aluminum-chromium-silicon
    coating.

Behavior of the Al-Cr-Si Coating in Thermal Shock Tests. The aluminum-
chromium-silicon coating has exhibited better resistance to thermal shock in the
thermal cycling apparatus than any other coating investigated. To explore in
detail the mode of failure of the Al-Cr-Si coating in this test, it was decided to
examine the macrostructure and microstructure of Al-Cr-Si coated 0.5% Ti-Mo
alloy after diffusion treatment and after 50, 100, 200, and 400 thermal cycles from
1800°F. For this series of tests, the specimens were diffusion treated in dry argon
at 2000°F. The microstructure at the coating-molybdenum interface after diffusion
treatment is shown in Figure 42; the interfacial zone is thin and somewhat discon-
tinuous. To investigate a larger area of the interface, a technique was employed
in which the coating was subjected to repeated blows from a small hammer, result-
ing in the coating being chipped from the molybdenum. Examination of the molyb-
denum surface at low magnification revealed markings which correlated with trans-
verse cracks in the coating, as illustrated in Figure 43.

After 50 thermal cycles, the surface of the molybdenum under the coating ex-
hibited a pattern comprising a series of circles, as illustrated in Figure 44. Cor-
relation of the microstructure of the cross section through the specimen (illustrated
in Figures 45 and 46, in which many cracks in the coating can be seen) made it evi-
dent that the dark circular pattern in Figure 44 represented areas of molybdenum
dioxide or areas of oxidized interfacial zone. The circles may be interpreted as the
effect of oxidizing preferentially at the intersection of cracks in the interfacial zone.

After 200 thermal cycles, oxidation of the interfacial zone had increased, as
evidenced by the amount of dark area appearing on the surface of the molybdenum
under the coating, as illustrated in Figure 47. After 390 thermal cycles, the oxi-
dation has progressed considerably, and there is evidence of attack on the base
molybdenum in the macrograph, Figure 48. The microstructure of a cross section
through the specimen, illustrated in Figure 49, substantiates this observation.

WADC TR 54-492 Pt 3   71

It was considered probable that the evident discontinuities in the interfacial zone of this series of specimens (illustrated in Figure 42) may have contributed to premature attack on the underlying molybdenum in the tests described above. For this reason, another series of thermal shock specimens was examined. The specimens were similar in base composition and coating composition to the previous series, but had been diffusion treated at 2200^OF in tank argon. Some of the specimens in this series sustained 1,200-1,300 thermal cycles from 1800^OF before failure, but premature edge failures occurred in other specimens after shorter exposures. The microstructure of the unheated section of a thermal shock specimen was examined; the microstructure is illustrated in Figure 50. The wide interfacial zone produced by the 2200^OF diffusion treatment is evident in the photomicrograph.

One end of one thermal shock specimen exhibited an edge failure after 429 cycles from 1800^OF. The specimen was examined macroscopically after the coating was chipped from the tested surface. After 429 cycles, the oxidation pattern on the surface illustrated in Figure 51 compares favorably with the oxidation pattern exhibited by another specimen, E321 in Figure 44. This specimen, diffusion treated in dry argon at 2000^OF, had sustained only 50 thermal cycles at the time of examination.

Another thermal shock specimen, from the series diffusion treated at 2200^OF, sustained 1,361 thermal cycles before failure. The coating was chipped from the tested surface of this specimen, and the surface was examined macroscopically. The oxidation on the surface after 1,361 cycles, illustrated in Figure 52, is no more severe than the oxidation on the surface of specimen E323, Figure 48; the latter specimen, diffusion treated at 2000^OF, had sustained only 390 thermal cycles from 1800^OF at the time of examination. Metallographic examination of the cross section of the specimen which sustained 1,361 thermal cycles (Figure 53) provided evidence that oxidation of the wide interfacial zone preceded and delayed oxidation of the underlying base molybdenum.

The results cited above provide dramatic evidence that a substantial interfacial zone increases the effectiveness of the Al-Cr-Si coating in preventing oxidation of the base molybdenum.

Behavior of the Al-Cr-Si Coating in the Ballistic-Impact Test. The aluminum-chromium-silicon coating has shown consistent inability to deform without spalling under the impact of a steel pellet fired at high muzzle velocities in the ballistic-impact test at 1800^OF, while several other coatings have shown considerable ductility in this test. Although the test conditions may be severe, the test does serve to measure an attribute of coatings to which some consideration may be given for certain heat engine applications. For this reason the behavior of the Al-Cr-Si coating in this test should be studied.

In tests reported previously, specimens of unalloyed molybdenum, coated with the Al-Cr-Si coating and subjected to the standard ballistic-impact test on the edge of the specimen at 1800^OF (muzzle velocity of steel pellet: 330 feet per second),

exhibited oxidation immediately upon subsequent exposure at 1800°F. At a lower impact energy (135 feet per second muzzle velocity) the coating deformed and did not spall off, and the specimen did not emit oxide vapors before 120 hours' exposure to subsequent oxidation tests.

To explore the possibility that the Al-Cr-Si coating might exhibit greater tolerance for the impact test at higher test temperatures (presumably the coating might be more plastic at higher temperatures and thus resist spalling), a series of twelve impact test specimens (1 in. by 1-7/8 in. by 0.094 in.) were prepared from 0.5% Ti-Mo alloy sheet. An aluminum-chromium-silicon coating 0.010 in. thick was applied to the specimens, and the specimens were diffusion treated two hours at 2200°F in tank argon. A few of the specimens were subjected to an exploratory series of tests in which they were subjected to ballistic impact from pellets fired at three muzzle velocities while heated at 1800°, 2000°, 2200°, and 2400°F. It was possible to estimate the level of impact tolerable at each test temperature by observing the specimens in subsequent oxidation tests at the temperatures to which they were heated for impacting. Check tests were made on specimens subjected to four impacts at one test temperature. The results are given in the following table:

TABLE 10

| Test Temp, °F | Life in Oxidation Test after Impacting, hr | | |
| | Impact Test Muzzle Velocity | | |
	115 ft/sec	215 ft/sec	310 ft/sec
1800	48	0	0
2000	48	6	0
2200		6	0
2400		6	0

The results of the tests indicated that higher testing temperatures increased the resistance of the Al-Cr-Si coating to spalling in the ballistic-impact test, but the results did not approach the tolerance for ballistic impact exhibited by other coatings in tests at 1800°F.

The inability of the Al-Cr-Si coating to resist spalling at higher impact energy levels is attributed to the hardness of the coating. Once spalling has occurred, the base molybdenum or the interfacial zone is exposed to ready oxidation from the atmosphere. As shown in the previous section, some "self-healing," especially at higher test temperatures, occurs in the spalled area, which reduces the rate of oxidation at the defect, but does not prevent oxidation.

Behavior of the Al-Cr-Si Coating in Erosion Tests. As reported in Section 1, the as-diffusion-treated Al-Cr-Si coating withstood exposure to erosion by aluminum oxide grit for 25-30 minutes at 1800°F. After exposure to oxidation for 200 hours at 2000°F, the Al-Cr-Si coating withstood exposure to erosion for 40-45 minutes. Macroscopic and microscopic examination of eroded specimens reveal that in the test the coating is gradually worn away under the action of the hot grit,

finally exposing the base molybdenum. It was noted in the tests with specimens subjected to 200 hours' oxidation exposure at 2000°F prior to the erosion test at 1800°F, that the wide interfacial zone which developed in the specimen resisted the erosive action of the hot grit, adding 50% to the life of the coating in the erosion test. Apparently the interfacial zone, although hard, is not as friable as the outer layers of the Al-Cr-Si coating.

Studies of the Nickel-Base Coatings

The Ni-Cr-B coatings (Colmonoy No. 5 and No. 6) and the Ni-Si-B coating (Coast Metals 50, modified) have been extensively studied under this contract. Although they are different in composition, the behavior of these coatings in evaluation tests is quite similar. For this reason they will be discussed together in this section of the report. The similarity of behavior of nickel-base coatings can be extended further to include nickel-clad molybdenum, which has been subjected to evaluation tests under this contract, although it was tested less extensively than the sprayed-metal compositions.

Behavior of Nickel-Base Coatings in Oxidation Test.
In contrast to the aluminum-bonded coatings, which develop minute cracks during elevated temperature exposure, the nickel-base coatings exhibit much less tendency to crack. The ductility of the nickel-base coatings apparently delays or minimizes rupture of the coating in the moderate thermal cycling of the oxidation test.

Ultimate failure of the nickel-base coatings apparently does occur through cracks, however. Microexamination of a specimen of 0.5% Ti-Mo alloy, coated with Coast Metals alloy and oxidation tested 500 hours at 1800°F, revealed cracking in the coating on one face of the specimen, as illustrated in Figure 54. Examination of the molybdenum-coating interface at high magnification revealed intergranular oxidation of the molybdenum, as illustrated in Figure 55. From the disintegration to powder that occurs upon ultimate failure of oxidation test specimens of nickel-coated molybdenum, it is possible to postulate the following failure mechanism:

1. Cracks eventually form in the nickel-base coating as a result of thermal stresses in the oxidation test.

2. Oxidation of the coating and the underlying molybdenum proceeds by diffusion of oxygen along these cracks.

3. Oxygen, molybdenum and nickel combine to form nickel molybdate, which forms and remains in place at the high temperatures and does not volatilize.

4. Upon cooling from the test temperature, the nickel molybdate undergoes a phase change which results in powdering of the molybdate.

WADC TR 54-492 Pt 3   74

5.   Apparently the powdering of the molybdate creates more paths
     for oxygen to enter the coating, accelerating the molybdate
     formation and creating a gross defect when the specimen is
     subsequently cooled.

Another characteristic of nickel-base coatings is the recrystallization of the
molybdenum adjacent to the coating. The recrystallization which occurs as a re-
sult of the presence of the coating is most obvious in specimens of alloyed molyb-
denum, in which exposure to the test temperature would not normally result in re-
crystallization. The recrystallized zones observed in Figure 54 are typical of
those observed with nickel-base alloy coatings on 0.5% titanium-molybdenum alloy.
Some recrystallization occurs during di ffusion treatment at 2000°F; subsequent
exposure at 1800°F increased the thickness of the recrystallized zone. The re-
crystallization is attributed to the diffusion of nickel into the molybdenum. Studies
of molybdenum-base alloys have shown that nickel lowers the recrystallization
temperature of molybdenum; hence, exposure of nickel-coated molybdenum to
temperatures below the recrystallization temperature of the 0.5% titanium-
molybdenum alloy sheet (but above the recrystallization temperature of the dif-
fusion layers containing nickel) will result in recrystallized zones in the molyb-
denum adjacent to the coating. In many applications for metallic molybdenum, the
presence of recrystallized zones may not be important. In highly stressed com-
ponents, however, the reduced load-carrying ability of recrystallized molybdenum-
base alloy, as compared to that of the strain-hardened material, should be recog-
nized, and the stress-carrying cross section designed accordingly.

Another limitation of the use of nickel-base alloys as molybdenum coating
components is the relatively low melting range - even after alloying with the
base molybdenum. This has been discussed in detail in Section 6 of this report.

Behavior of Nickel-Base Alloys in Thermal Shock Tests. In tests at 1800°F
in the thermal cycling apparatus, nickel-clad unalloyed molybdenum withstood a
minimum of 310 cycles (excluding failures at edges); the Ni-Cr-B coating, 185
cycles; and the Ni-Si-B coating, 108 cycles. Although differences were observed
between the several nickel-base coatings in their resistance to thermal shock,
all exhibited sufficient resistance to consider the coatings promising (although
the specimens distorted in test), and all were less resistant than the Al-Cr-Si
coating. In more recent tests with specimens of 0.5% Ti-Mo alloy coated with
Coast Metals 50 and Colmonoy alloy No. 5, the specimens showed no distortion
in the test, but exhibited minimum life in the test of 135 and 67 cycles, respec-
tively.

Metallographic examination of 0.5% Ti-Mo alloy specimens, coated with Col-
monoy No. 5 and modified Coast Metals 50 alloys and subjected to thermal cycling
from 1800°F for periods short of the average life of the specimen, yielded infor-
mation concerning the mode of failure in the thermal cycling test. One such speci-
men, coated with Colmonoy No. 5 and subjected to 20 thermal cycles from 1800°F,
was sectioned for metallographic examination. Photomicrographs of the structure
at the coating-molybdenum interface are presented in Figure 56. Cracks had

WADC TR 54-492 Pt 3   75

apparently developed in the coating after only 20 thermal cycles. Of primary interest is the manner in which oxidation has occurred along the interface between the coating and the molybdenum. It has been noted in testing such coatings that ultimate failure occurs by peeling of the coating. Oxidation along the interface between two materials having different thermal expansion characteristics would promote a peeling type of failure. Similar metallographic examination of 0.5% Ti-Mo alloy specimens, coated with modified Coast Metals 50 alloy and subjected to 100 thermal cycles from $1800^{O}F$, revealed cracking of the coating, also oxidation between the coating and the molybdenum, and between the coating and the high molybdenum diffusion zone (Figure 57).

     Behavior of Nickel-Base Coatings in Ballistic-Impact Tests. Both the Ni-Cr-B alloy sprayed coating (Colmonoy No. 5) and the Ni-Si-B alloy sprayed coating (Coast Metals 50) have exhibited excellent resistance to spalling in the ballistic-impact test. Apparently these coatings have sufficiently ductility to absorb the impact of the steel pellet with local deformation that does not rupture the coating.

     Behavior of Nickel-Base Coatings in Erosion Tests. The nickel-base coatings have shown good resistance to erosion by a stream of aluminum oxide grit at $1800^{O}F$. The Ni-Si-B coating resisted erosion to a slightly greater degree than the Ni-Cr-B coating. The good erosion resistance is attributed to the apparent plasticity of the coating at the test temperature.

Studies of Electrodeposited Chromium and Chromium-Nickel Composites

     As has been stated in Section 3 of this report, chromium holds promise as a coating for molybdenum by virtue of its low thermal expansion coefficient and low diffusivity in molybdenum. Electrodeposited chromium, when used alone as an oxidation-resistant coating for molybdenum, tends to crack under thermal cycling conditions, even when deposited as so-called "low-contraction" or "stress-free" chromium. Oxidation at the base of these cracks produces pit-type failures in the base molybdenum, such as those shown in a previous report.*

     One solution to oxidation through cracks in the chromium has been found in the case of the Cr-Ni composite electroplates, exemplified by the National Bureau of Standards coating described in Section 3 of this report. In this coating, a ductile nickel electrodeposit provides a sealing layer over the chromium. Details of the coating, and its behavior in evaluation tests have been described in the earlier discussion, and will not be repeated here. In the specimens studied under this contract, nickel constitutes a partially adherent sheath over an adherent electrodeposit of chromium. The nickel sheath separates from the chromium by blistering, and ultimate rupture of the nickel allows oxygen to enter through cracks in the chromium into the underlying molybdenum, and results in the formation of pits in the molybdenum.

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*WADC TR 54-492, Part 2, page 25

Specimens of 0.5% titanium-molybdenum alloy, electroplated with the chromium-nickel composite, exhibited recrystallization of the molybdenum after diffusion treatment or extended exposure at elevated test temperatures. This behavior parallels observations of nickel-base coatings, and is attributed to the diffusion of chromium or nickel into the base metal, lowering the recrystallization temperature of the base metal.

Summary of the Nature of Promising Coatings

It is possible to summarize the behavior and nature of the general types of coatings studied under this contract in the following statements:

1. Al-bonded coatings. These coatings are characterized by excellent bonding to base molybdenum through the formation of a Mo_3Al-type layer which delays oxidation of underlying molybdenum. In evaluation tests at $1800^O F$, the coatings exhibit good resistance to oxidation and thermal shock; moderate resistance to erosion; and poor resistance to ballistic impact. Oxidation tests at higher temperatures indicate the coatings to be useful at temperatures up to $2600^O F$.

2. Ni-base coatings. These ductile coatings serve well until cracks occur, allowing oxidation through the cracks, resulting in the formation of nickel molybdate, which in turn accelerates failure under thermal cycling conditions. In evaluation tests at $1800^O F$, the coatings exhibit good resistance to oxidation and ballistic impact; and moderate resistance to erosion and thermal shock. Oxidation tests at higher temperatures indicate the coatings to be useful at temperatures up to $2200^O F$.

3. Cr and Cr-Ni electrodeposited coatings. Cracking of chromium promotes pit-type attack on underlying molybdenum. The presence of a nickel overlayer delays this attack. In tests at $1800^O F$, these coatings exhibit good resistance to ballistic impact and erosion; erratic behavior in the oxidation test; and poor resistance to thermal shock.

It is apparent that no one coating provides optimum protection under all evaluation test conditions. It is probable that individual uses for molybdenum require coatings which emphasize one attribute in preference to others.

It appears to the staff of this laboratory that the question is no longer "Is there a coating which will protect molybdenum against elevated-temperature oxidation?" but "Which coating will most satisfactorily protect molybdenum against elevated-temperature oxidation?" The final answer to such a question will be found in component testing. Laboratory evaluation tests can serve to measure attributes of coatings, and aid in the selection of the coating most suitable for the intended service conditions. It is hoped that this report, including Parts 1 and 2 published at earlier dates, will reduce component testing time and accelerate the use of molybdenum in heat engine applications by providing a guide to the selection of coatings.

WADC TR 54-492 Pt 3   77
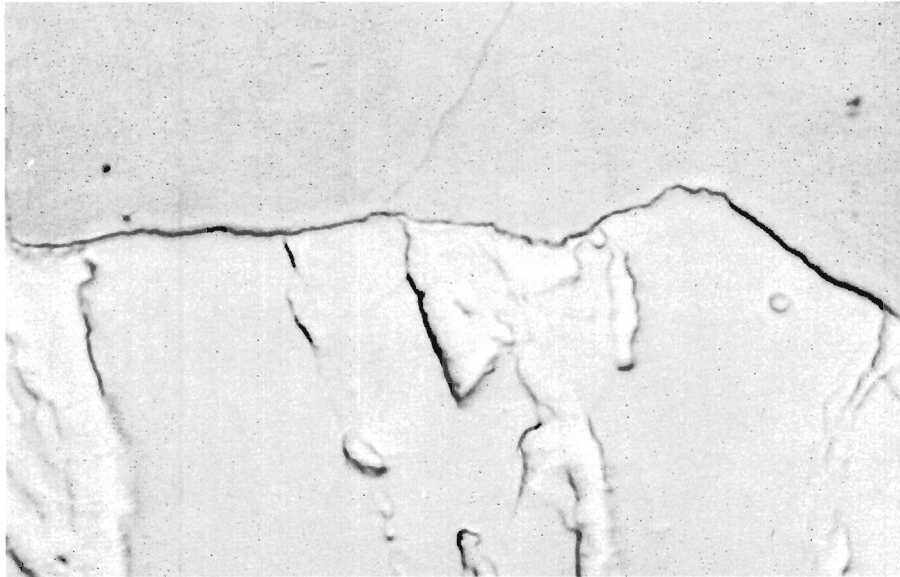
FIGURE 34 (M4244)   Polish-Etch-Buff   X2000

Specimen C93. Al-Cr-Si on unalloyed molybdenum.
Diffusion treated two hours at 1800^OF in purified
hydrogen. Note absence of interfacial zone.
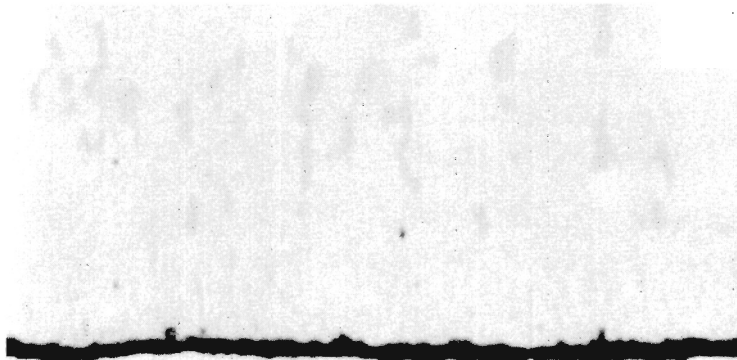
FIGURE 35 (M4314) Polish-Etch-Buff X2000

Specimen C394. Al-Cr-Si on unalloyed molybdenum.
Diffusion treated two hours at 2000^OF in purified
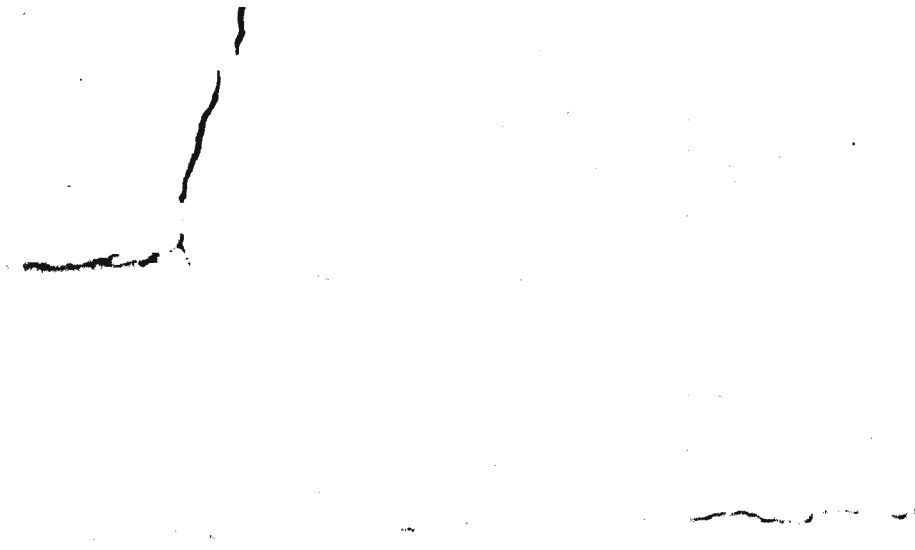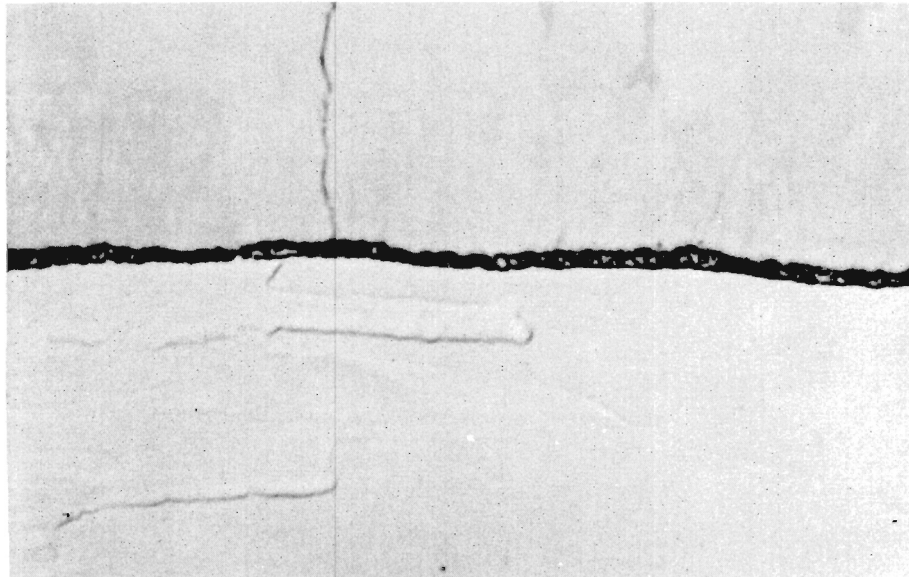hydrogen. Note interfacial zone.

FIGURE 36 (M4161)   Polish-Etch-Buff   X2000

Specimen C291. Al-Cr-Si on 0.5% Ti-Mo alloy. Diffusion
treated two hours at 2000°F in purified hydrogen. Note
absence of interfacial zone.

FIGURE 37 (M5157)   Polish-Etch-Buff   X2000

Specimen D296. Al-Cr-Si on 0.5% Ti-Mo alloy. Diffusion
treated two hours at 2000°F in dried argon. Note more
continuous interfacial zone.
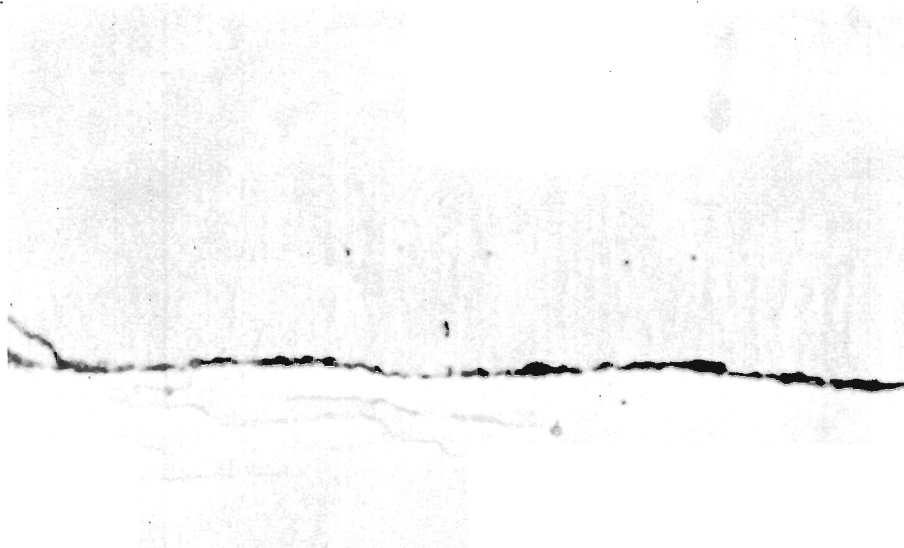
FIGURE 38 (M6257)   Polish-Etch-Buff   X2000

Specimen E321. Al-Cr-Si on 0.5% Ti-Mo alloy. Diffusion treated two hours at 2000°F in dried argon. Thin, some-what discontinuous interfacial zone.
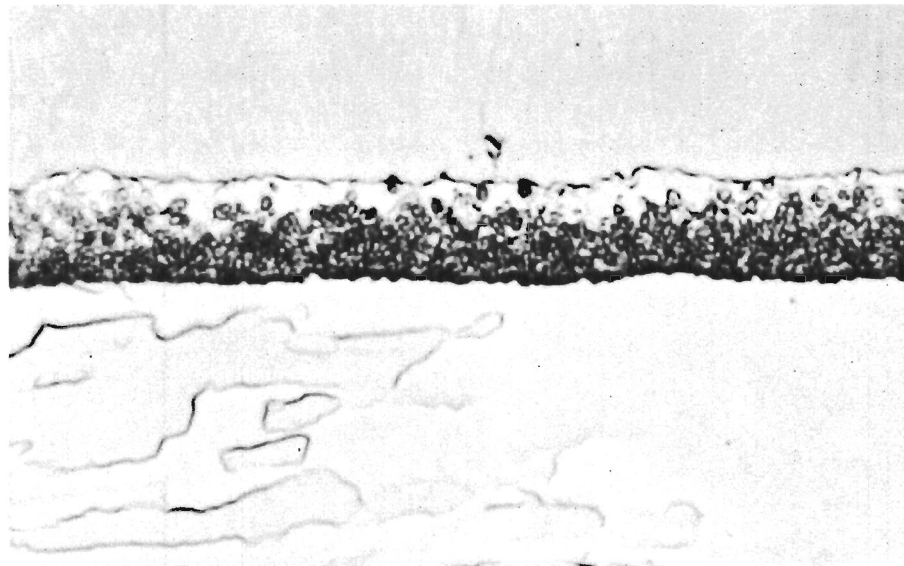
FIGURE 39 (M6436)   Polish-Etch-Buff   X2000

Specimen E396-B. Al-Cr-Si on 0.5% Ti-Mo alloy. Diffusion treated two hours at 2200°F in tank argon. Note wide interfacial zone.

WADC TR 54-492 Pt 3   80
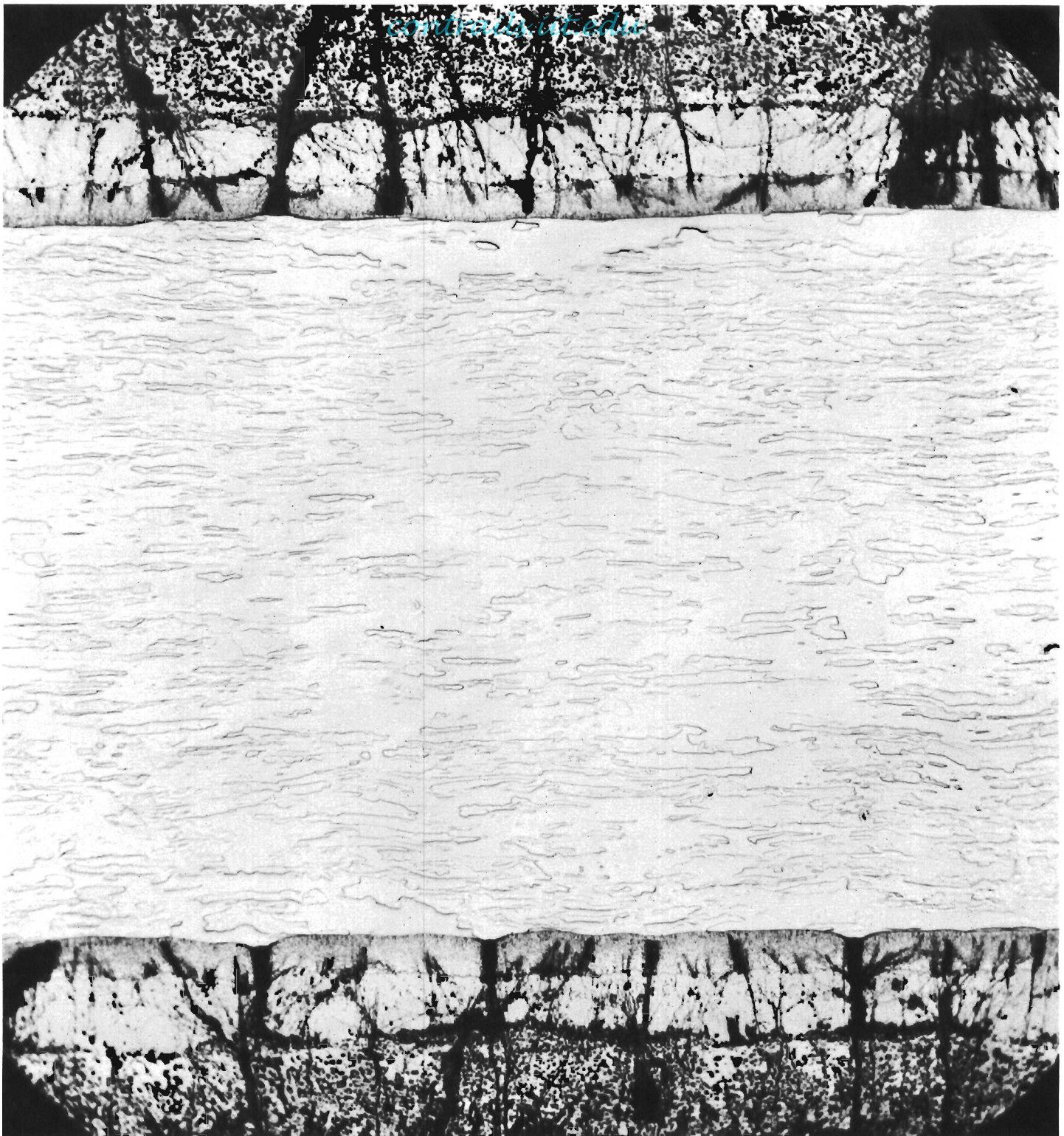
FIGURE 40 (M5265)   Polish-Etch-Buff   X100

SPECIMEN D289. Al-Cr-Si ON 0.5% Ti-Mo ALLOY. DIFFUSION TREATED TWO HOURS AT 2000°F IN DRIED ARGON. MICROSTRUCTURE OF CROSS SECTION AFTER EXPOSURE TO OXIDATION FOR 500 HOURS AT 1800°F AND 627 HOURS AT 2000°F IN FLOWING AIR.

WADC TR 54-492 Pt 3   81

X75

Polish-Etch-Buff

FIGURE 41 (M5266, M5267) SPECIMEN D289. MICROSTRUCTURE OF CROSS SECTION AT FAILED EDGE OF TEST PANEL, SHOWING PROGRESS OF OXIDATION.
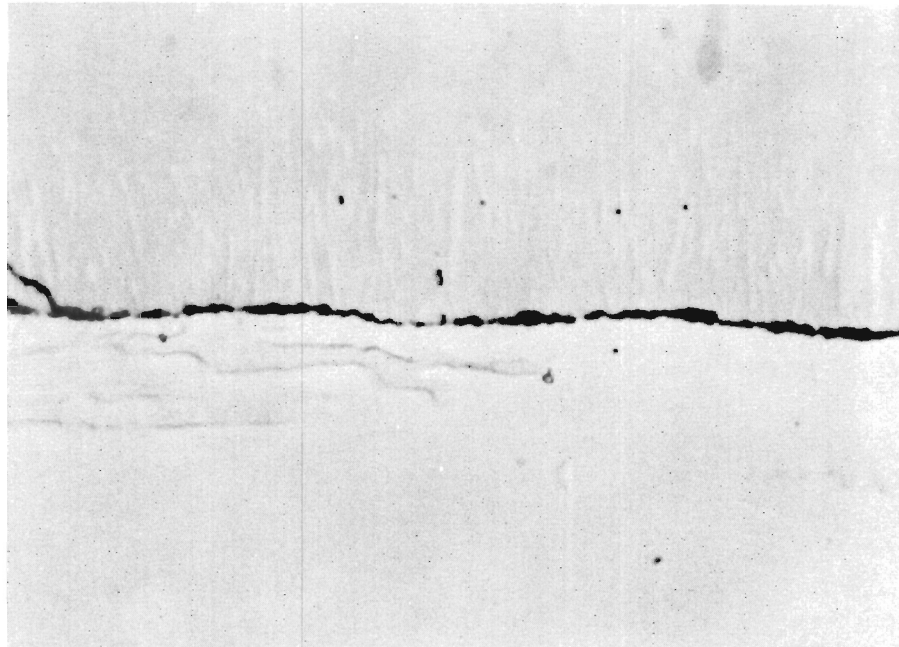
FIGURE 42 (M6257)   Polish-Etch-Buff   X2000

Microstructure at interface
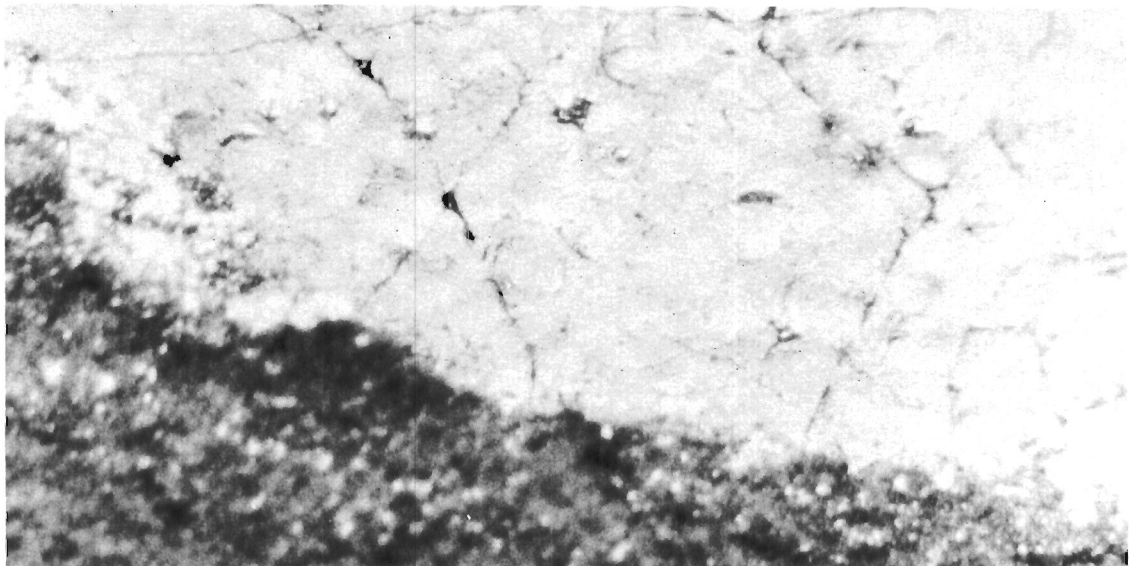
FIGURE 43 (35-10)   APPROX X45

Macrostructure of Mo surface at coating interface
after chipping coating off

SPECIMEN E321. Al-Cr-Si ON 0.5% Ti-Mo ALLOY. DIFFUSION
TREATED TWO HOURS AT 2000°F IN DRY ARGON.

WADC TR 54-492 Pt 3   83
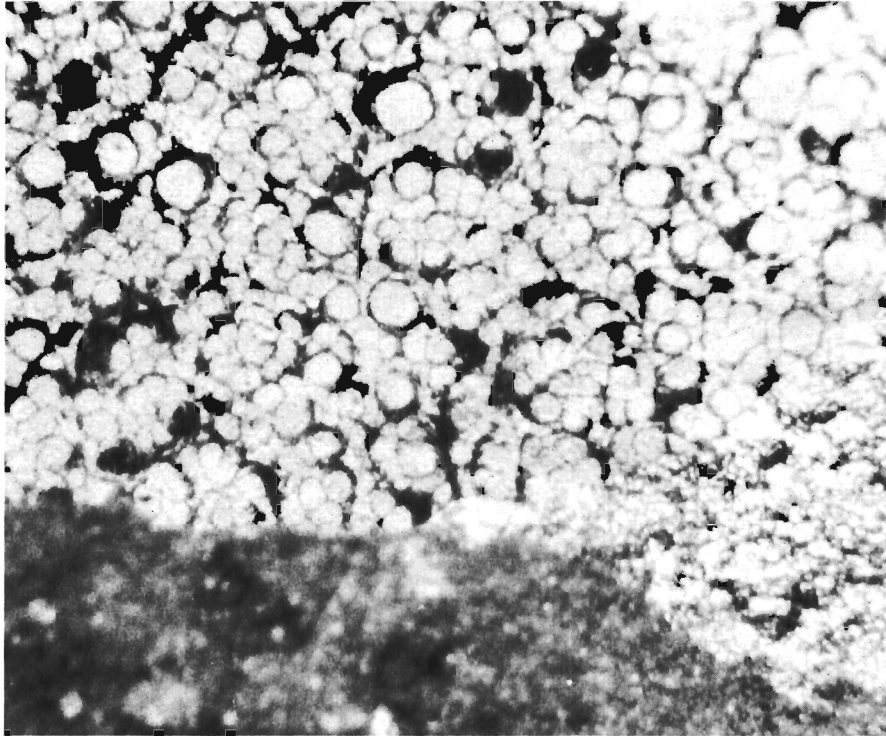
FIGURE 44 (35-11)   APPROX X45

Specimen E321. Macrostructure of Mo surface at coating
interface after chipping coating off.   After 50 cycles
from 1800°F in thermal cycling apparatus.   Note dark
molybdenum oxide in circular pattern.

WADC TR 54-492 Pt 3   84
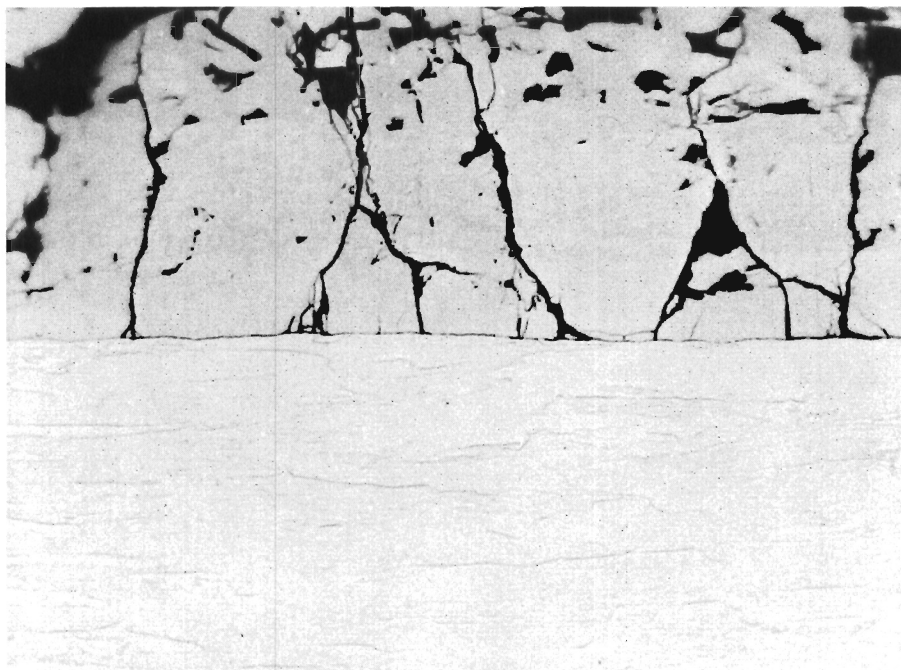
(M6256)   Polish-Etch-Buff   X100
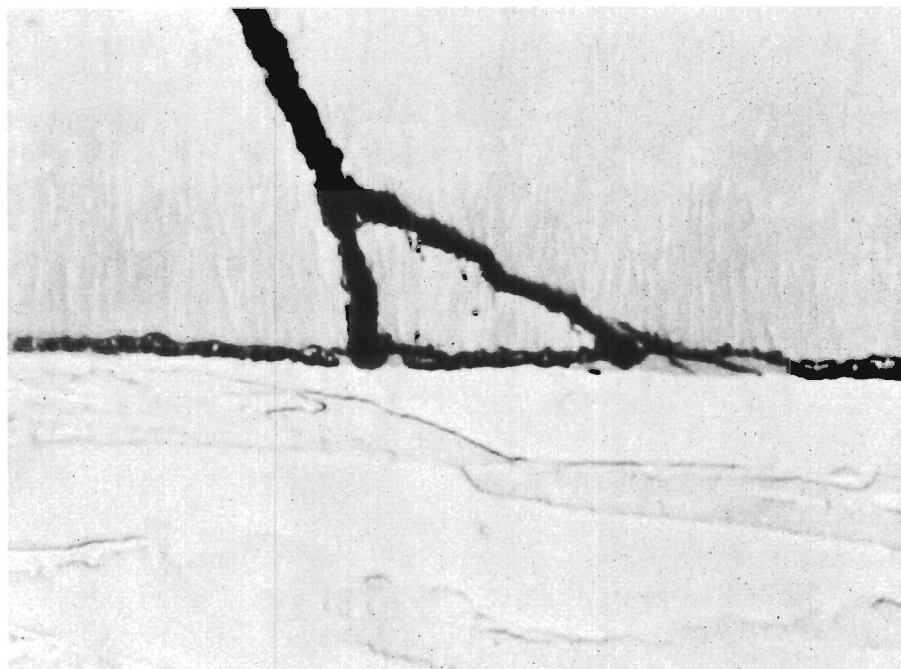
(M6258)   Polish-Etch-Buff   X2000

FIGURE 45 -   SPECIMEN E321.   Al-Cr-Si ON 0.5% Ti-Mo ALLOY.
              AFTER 50 CYCLES FROM 1800°F IN THERMAL CYCLING
              APPARATUS.   NOTE OXIDATION OF INTERFACIAL ZONE.
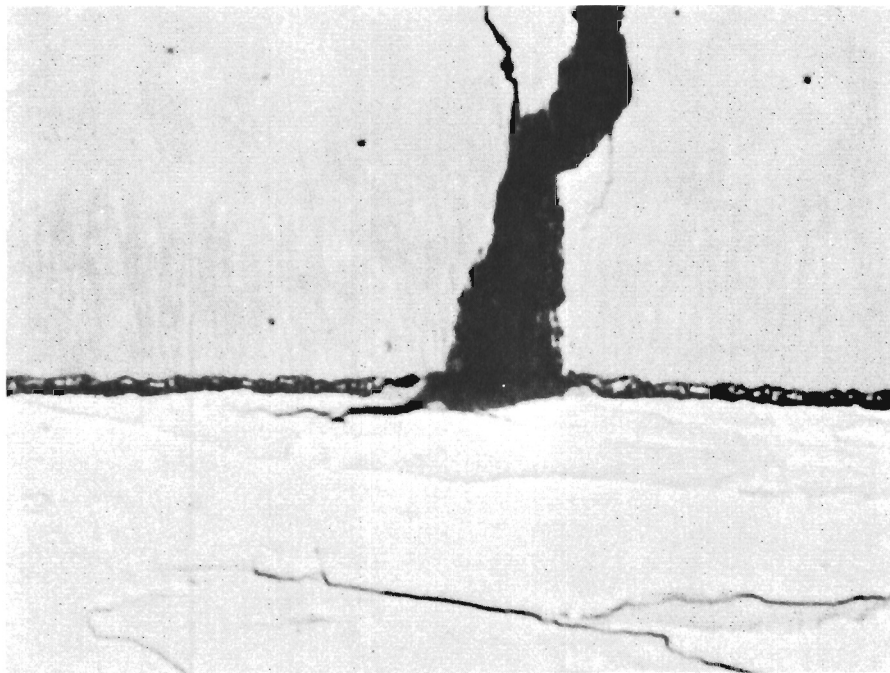
(M6259)   Polish-Etch-Buff   X2000
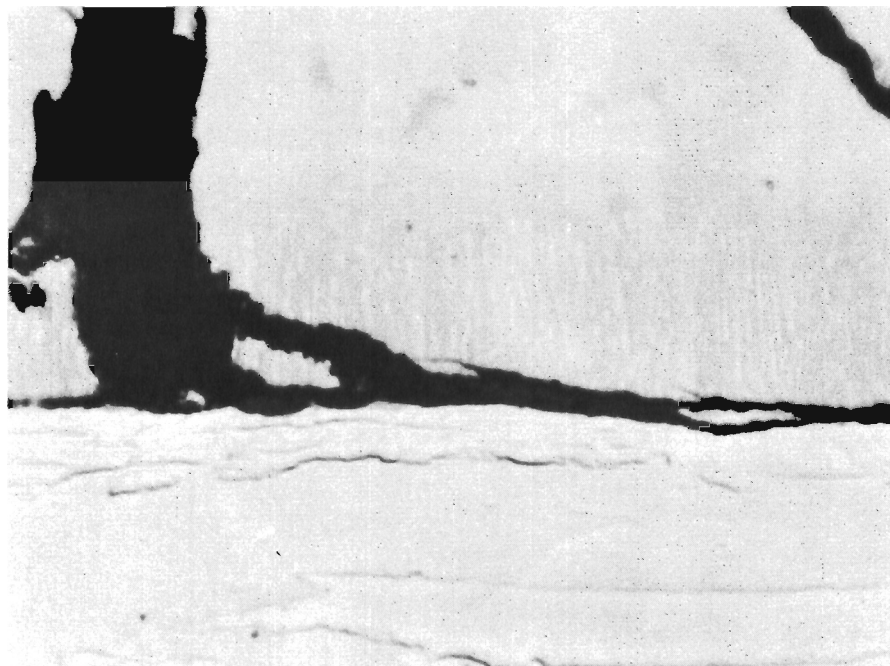
(M6260)   Polish-Etch-Buff   X2000

FIGURE 46 -   SPECIMEN E321. Al-Cr-Si ON 0.5% Ti-Mo ALLOY.
               AFTER 50 CYCLES FROM 1800°F IN THERMAL CYCLING
               APPARATUS. ADDITIONAL EVIDENCE OF OXIDATION
               AND CRACKING ALONG INTERFACIAL ZONE.
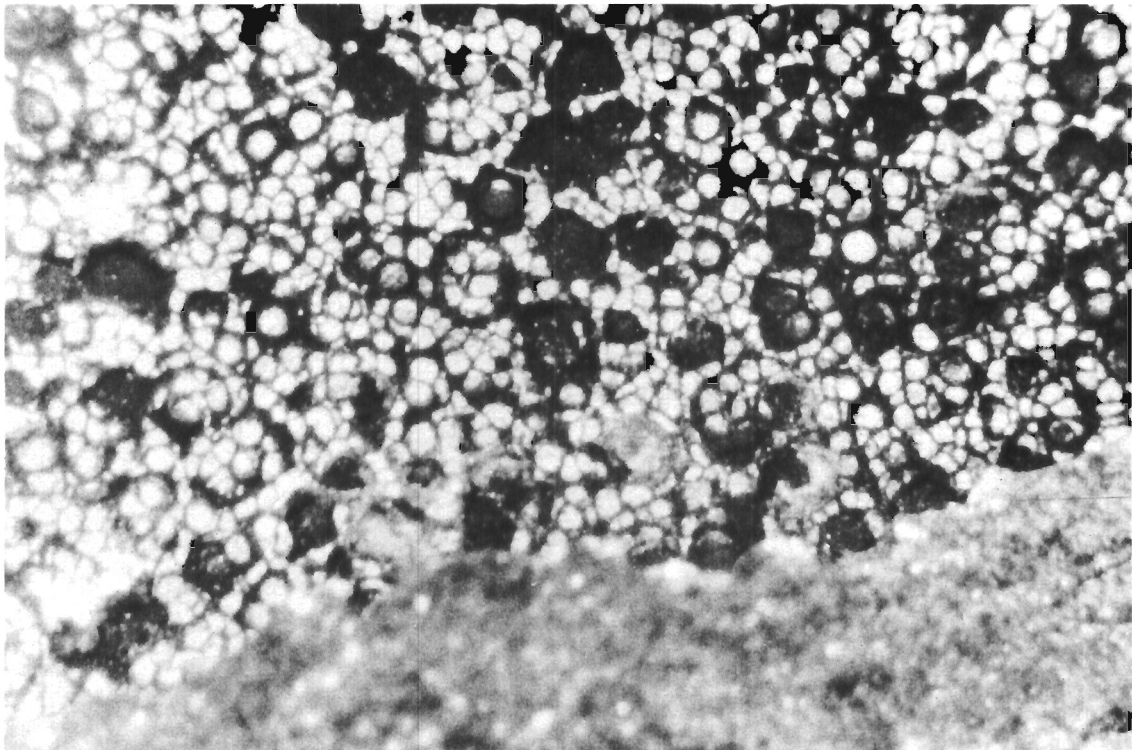
FIGURE 47 (35-13)   **APPROX X45**

Specimen E322. Al-Cr-Si on 0.5% Ti-Mo alloy. After 200 cycles from 1800°F in thermal cycling apparatus. Appearance of molybdenum surface at interface.
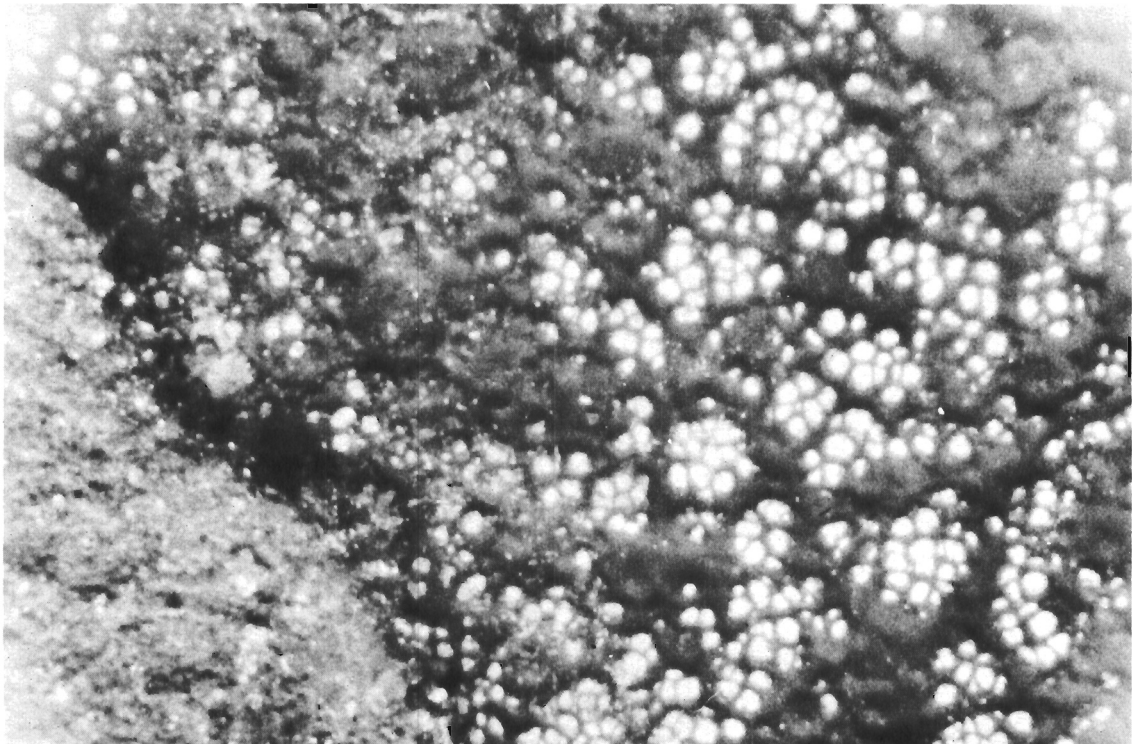
FIGURE 48 (35-14)   **APPROX X45**

Specimen E323. Al-Cr-Si on 0.5% Ti-Mo alloy. After 390 cycles from 1800°F in thermal cycling apparatus. Appearance of molybdenum surface at interface.

(M6262)   Polish–Etch–Buff   X100

(M6263)   Polish–Etch–Buff   X100
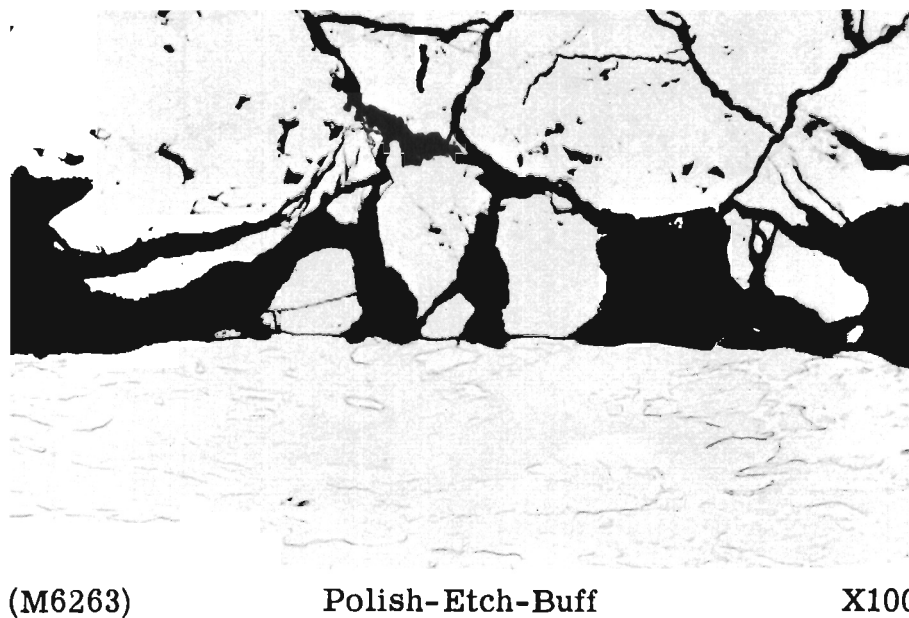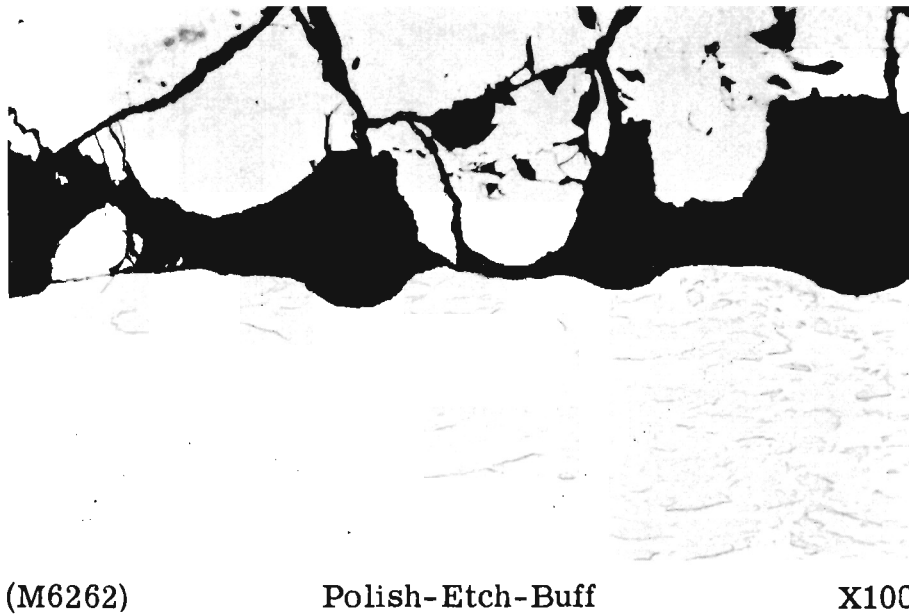
FIGURE 49 –   SPECIMEN E323.   MICROSTRUCTURE AT INTERFACE SHOWING ATTACK ON THE BASE MOLYBDENUM AFTER 390 CYCLES FROM 1800° F IN THERMAL CYCLING APPARATUS.

WADC TR 54-492 Pt 3   88
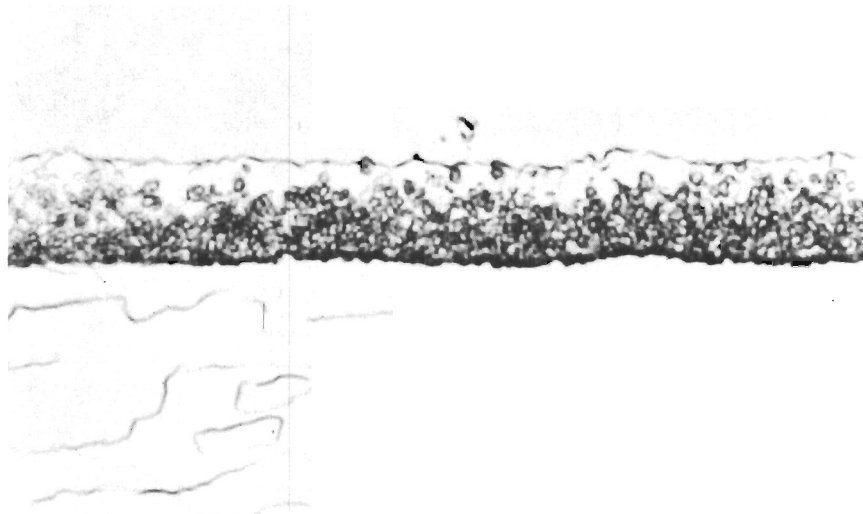
FIGURE 50 (M6436)　　Polish-Etch-Buff　　　X2000

Specimen E396-B.　Al-Cr-Si on 0.5% Ti-Mo alloy.
Diffusion treated two hours at 2200°F in tank
argon.　Note wide interfacial zone.
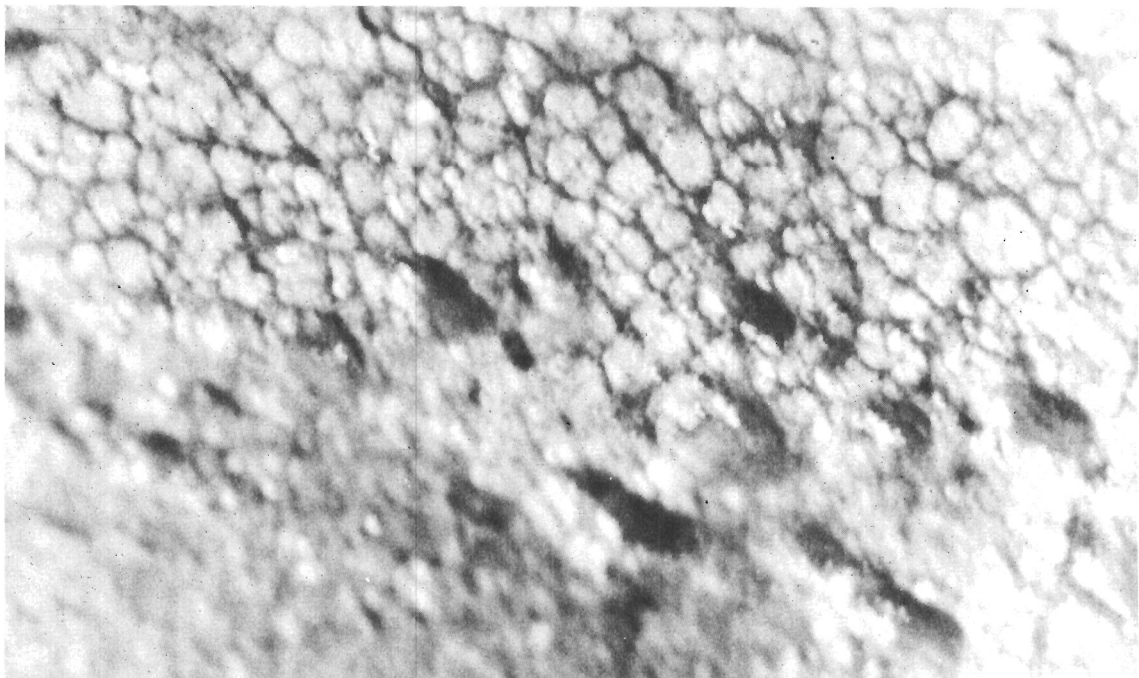
FIGURE 51 (35-24)　　　　　　　　　　　APPROX X45

Specimen E396.　Al-Cr-Si on 0.5% Ti-Mo alloy.　Diffusion
treated two hours at 2200°F in tank argon.　After 429 cycles
from 1800°F in thermal cycling apparatus.　Appearance of
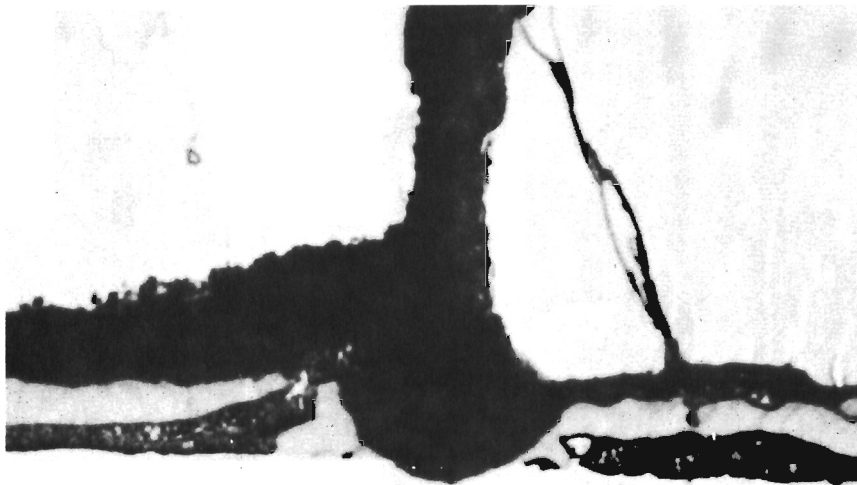molybdenum surface at interface.
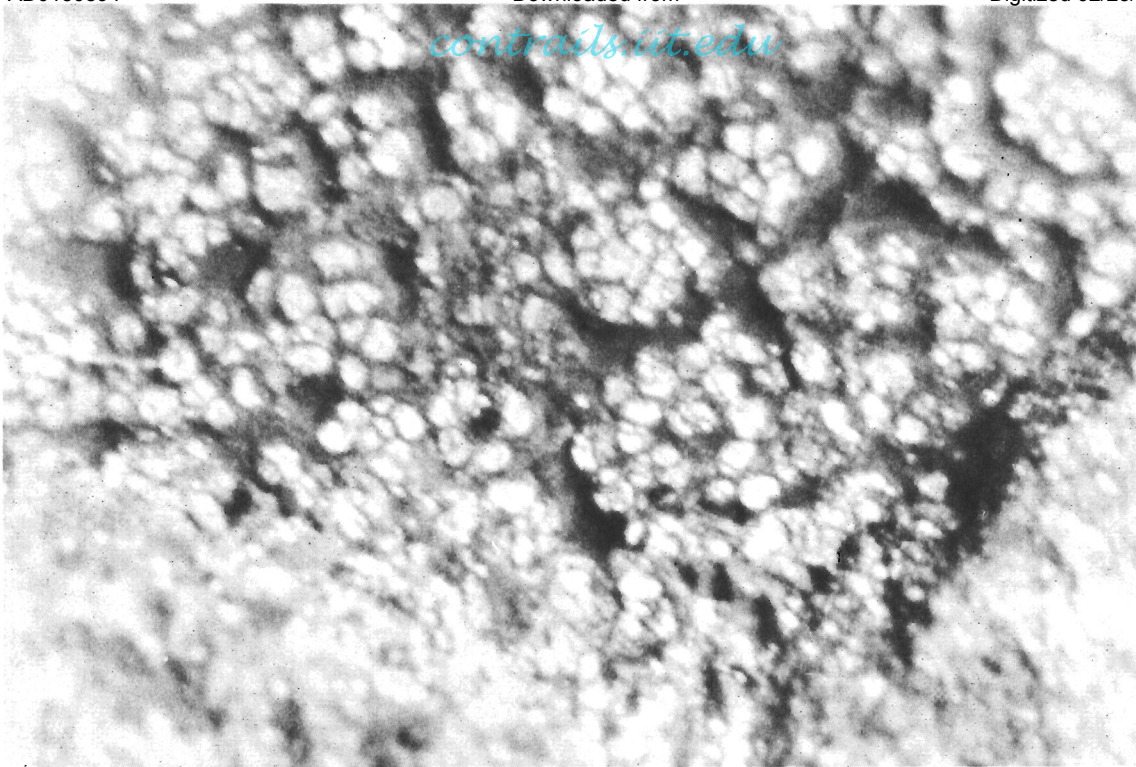
FIGURE 52 (35-23)   APPROX X45

Specimen E394.   Al-Cr-Si on 0.5% Ti-Mo alloy.   Diffusion
treated two hours at 2200°F in tank argon.   After 1,361
thermal cycles from 1800°F in thermal cycling apparatus.
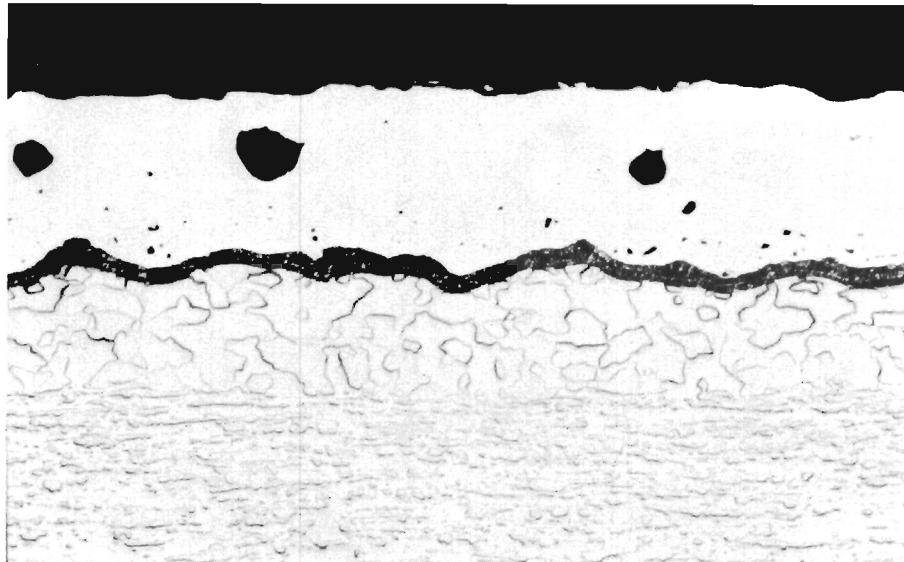Appearance of molybdenum surface at interface.
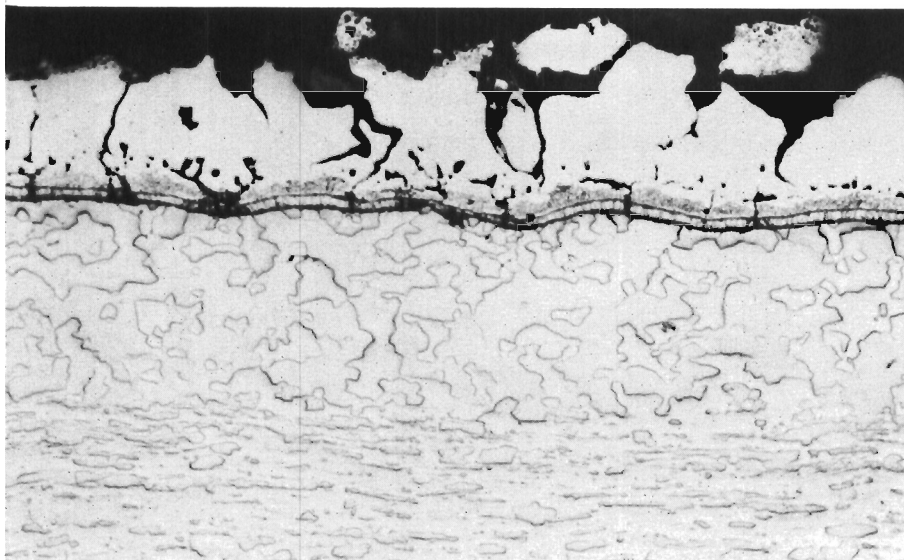

FIGURE 53 (M6944)   Polish-Etch-Buff   X2000

Specimen E394.   Microstructure at interface, showing
oxidation of wide interfacial zone before oxidation
of base molybdenum.

(M4848)   Polish-Etch-Buff   X100

(M4847)   Polish-Etch-Buff   X100

FIGURE 54 - SPECIMEN C422. COAST METALS MODIFIED 50 ALLOY
           ON 0.5% Ti-Mo ALLOY. DIFFUSION TREATED TWO HOURS
           AT 2000°F IN PURIFIED HYDROGEN. OXIDATION TESTED
           500 HOURS AT 1800°F. TWO PHOTOMICROGRAPHS REPRE-
           SENTATIVE OF STRUCTURES OBSERVED ON OPPOSITE
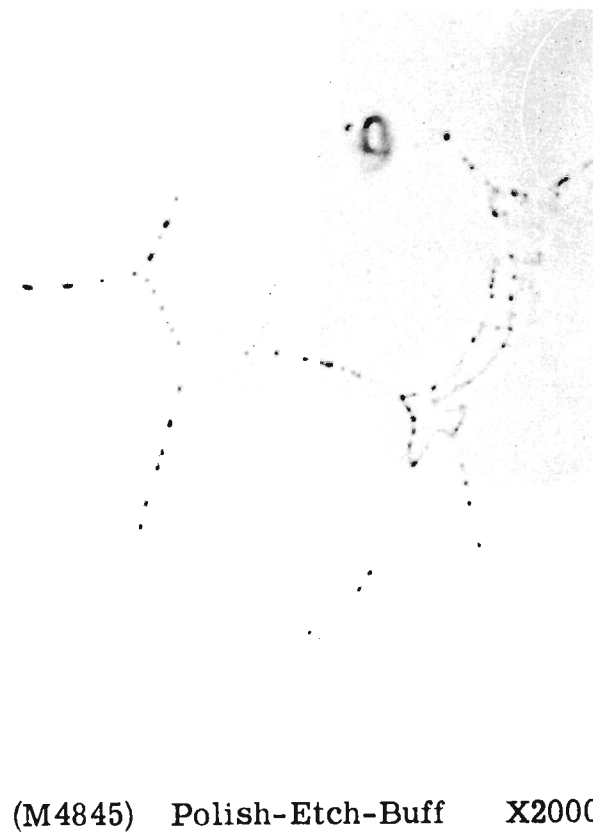   SIDES OF THE SPECIMEN.

WADC TR 54-492 Pt 3   91

Coating

Molybdenum

(M4846)   Polish-Etch-Buff   X2000

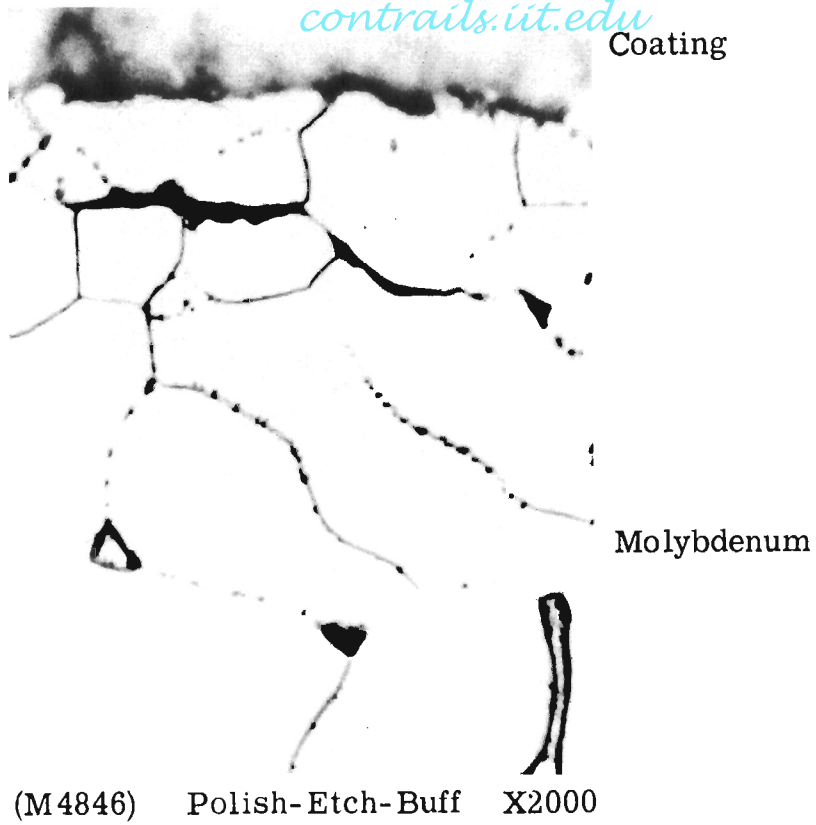(M4845)   Polish-Etch-Buff   X2000

FIGURE 55 -   SPECIMEN C422.   SHOWING OXIDATION AT MOLYBDENUM
              GRAIN BOUNDARIES IN RECRYSTALLIZED LAYER BENEATH
              THE COATING.

WADC TR 54-492 Pt 3   92

(M6945)   Polish-Etch-Buff   X100
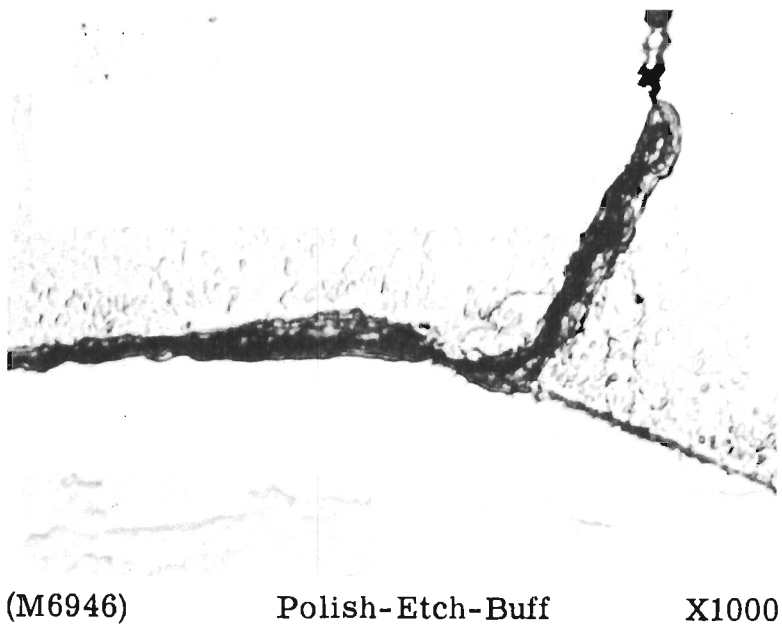

(M6946)   Polish-Etch-Buff   X1000
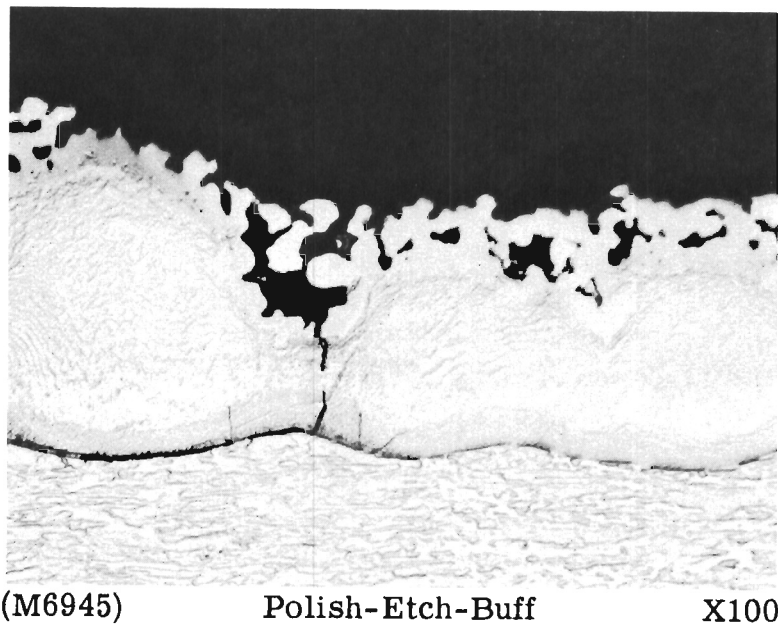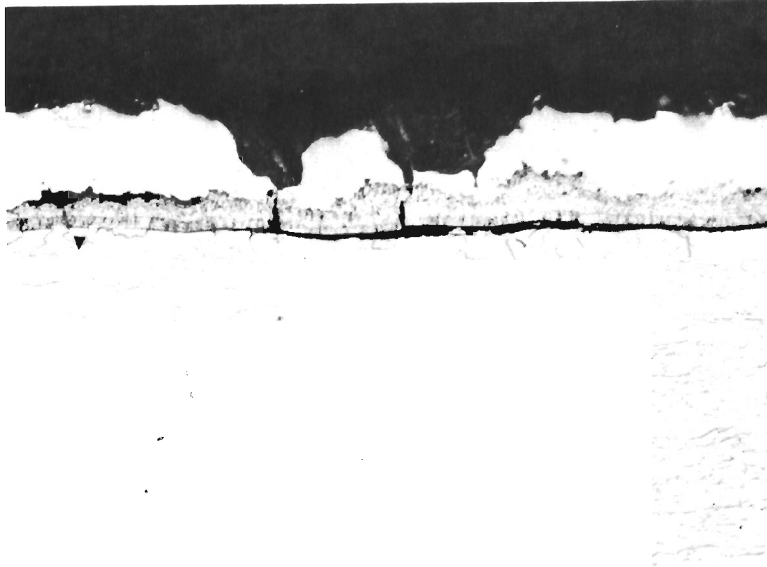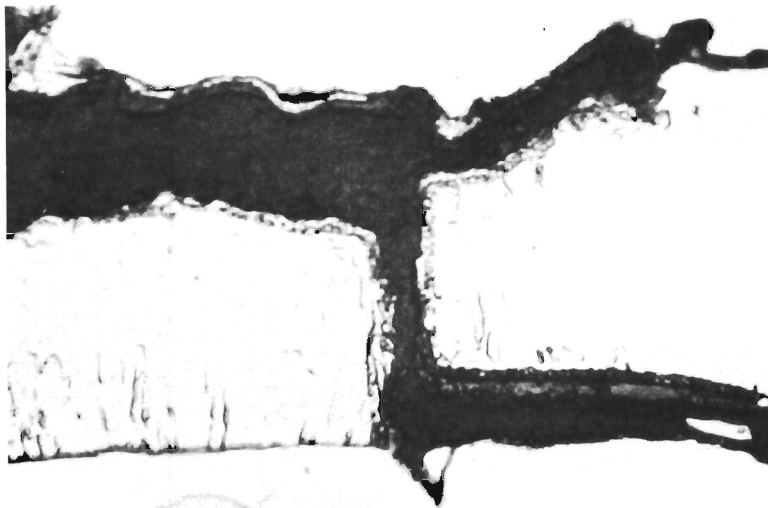
FIGURE 56 -   SPECIMEN E324.   COLMONOY NO. 5 ON 0.5% Ti-Mo ALLOY.
               DIFFUSION TREATED TWO HOURS AT 2000°F IN DRY ARGON.
               SUBJECTED TO 20 THERMAL CYCLES FROM 1800°F. NOTE
               OXIDATION AT INTERFACE ADJACENT TO CRACK ON COATING.

WADC TR 54-492 Pt 3   93

(M6947)   Polish-Etch-Buff   X100

(M6948)   Polish-Etch-Buff   X1000

FIGURE 57 - SPECIMEN E328. COAST METALS MODIFIED 50 ON 0.5% Ti-Mo ALLOY. DIFFUSION TREATED TWO HOURS AT 2000°F IN DRY ARGON. SUBJECTED TO 100 THERMAL CYCLES FROM 1800° F. NOTE OXIDATION AT MOLYBDENUM-COATING INTERFACE AND AT INTERFACE BETWEEN DIFFUSION ZONE AND UNAFFECTED COATING.

WADC TR 54-492 Pt 3   94