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OXIDATION-RESISTANT COATINGS FOR MOLYBDENUM

J. R. BLANCHARD

CLIMAX MOLYBDENUM COMPANY OF MICHIGAN

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WRIGHT AIR DEVELOPMENT CENTER

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AERONAUTICAL RESEARCH LABORATORY
CONTRACT No. AF 33(616)-2488
PROJECT No. 7351

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Carpenter Litho & Prtg. Co., Springfield, O.
200 - 29 September 1955

FOREWORD

This report serves as a summary of experimental work performed during a four-year period and is issued in lieu of the Second Quarterly Progress Report under USAF Contract No. AF 33(616)-2488, Task 70646, Corrosion and Heat Resisting Alloys, Project 7351, Metallic Materials. The initial 3-1/2 years of experimental work was done under USAF Contract No. AF 33(038)-16197. Both contracts were administered under the direction of the Aeronautical Research Laboratory, Directorate of Research, Wright Air Development Center. At various times during the project Lt. George Johnson, Capt. John Mosher, and Lt. John P. Hirth served as Project Engineers.

Work at Climax Molybdenum Company of Michigan was performed by J. R. Blanchard, Project Engineer, under the supervision of H. E. Hostetter and D. V. Doane, Supervisors; A. J. Herzig, President, and G. A. Timmons, Vice President and Director of Research. The metallographic work was performed by W. C. Coons, Project Engineer. The x-ray diffraction studies were made by M. Semchyshen, Technical Advisor.

The ductility tests were conducted at Engineering Research Institute, University of Michigan, Ann Arbor, Michigan, under the supervision of A. I. Rush and J. W. Freeman. The data for the stress-rupture tests were obtained at Wright Air Development Center and reported by W. H. Rector in Technical Note WCRT 54-162.

ABSTRACT

During the period December 1950 - December 1954, the Research Laboratory of the Climax Molybdenum Company investigated sprayed-metal coatings, applied with commercial metallizing equipment, for the protection of molybdenum against oxidation at 1700° and 1800°F. The procedures employed for applying and testing coatings are described. Tests with electroplated chromium coatings are also included.

The results obtained and summarized in this report showed that 12 of the oxidation-resistant alloys investigated had the capacity to protect molybdenum against oxidation for at least 500 hours at 1700° and 1800°F. Two aluminum-chromium-silicon alloy coatings and a Colmonoy No. 5 coating were investigated more thoroughly than other compositions. These coatings had the capacity to protect molybdenum from oxidation while sustaining elongations of 2-5% in 100 or 500 hours at 1800°F. They were capable of withstanding a fair amount of thermal shock and could be ground to a smooth finish.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

Leslie B. Williams

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

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INTRODUCTION

Molybdenum and molybdenum-base alloys are potential structural materials for service at elevated temperatures. At 1600°F molybdenum-base alloys are superior in strength to all "super alloys" commercially available at the present time. At higher temperatures the gap between the "super alloys" and molybdenum-base alloys widens markedly. Operating performance and efficiency of reaction engines can be improved substantially by increasing the temperature of the propelling gases, therefore, there is an ever-present desire of engineers to design such engines for higher and higher temperatures, but they are limited by the engineering materials available for construction. Consideration is already being given to operating gas turbines in which the components will be subjected to temperatures of 1800-2000°F. Research data have demonstrated that molybdenum alloys can develop the strength required of such engine components and the development of the arc-casting process has advanced to a stage where production of the alloys on a commercial basis can be assured. Fabrication of the alloys can be accomplished on available, commercial production machinery. These alloys are now available commercially in the form of semi-finished products such as bars 3 in. in diameter and smaller, also plate and sheet.

The application of molybdenum and molybdenum-base alloys to parts operating at high temperatures has been handicapped by the rapid oxidation of molybdenum at temperatures above 1200°F. The oxide of molybdenum formed at 1200°F and above has a high vapor pressure, therefore, it evaporates rapidly, exposing fresh surfaces to oxidation. Oxidation proceeds continuously until the metal has been consumed. Since most of the anticipated applications of molybdenum involve oxidizing conditions, the molybdenum-base alloy itself must resist oxidation or the alloy must be protected from oxygen.

Attempts to develop oxidation-resistant molybdenum alloys have not been successful because alloys with sufficient nickel, chromium, silicon, etc., to resist oxidation to a commercially acceptable extent are unforgeable and/or they no longer exhibit the high strength at elevated temperatures.

To provide the necessary resistance to oxidation the alternative method has been investigated, i.e., coating the molybdenum-base alloy part with an oxidation-resistant substance. A coating must satisfy the following basic requirements:

(1) The coating itself must be oxidation resistant.

(2) The coating must cover the molybdenum so completely that no oxygen reaches any portion of the original part.

(3) The coating must be firmly bonded to the molybdenum.

(4) The coating must be applied and completely processed without recrystallizing the molybdenum alloy because the high strengths developed by these alloys at elevated temperatures are dependent upon strain-hardening (produced by working below the recrystallization temperature).

(5) The oxidation resistance of the coating must not deteriorate if molybdenum diffuses into the protective layers.

Several metallic compositions which satisfy the above basic requirements for coatings have been studied to determine the best procedures for applying them and to test their capacities to protect molybdenum from oxidation under anticipated service conditions.

Methods of Coating Molybdenum

The various methods of applying a protective coating to molybdenum that have been investigated at the Climax laboratory and elsewhere include the following:

(1) Cladding
(2) Immersion in molten metal bath
(3) Cementation
(4) Deposition from vapor phase
(5) Enameling (ceramic coating)
(6) Electroplating
(7) Metallizing (metal spraying)

Each of the above methods requires special techniques and each has its limitations with respect to the size and shape of the article that can be coated. Some of the methods require excessively high temperatures in forming or in bonding the coating while other methods are restricted to the coating of small and regular shapes. Coating by metallizing has several unique advantages. In coating by metallizing, the size and shape of the article that can be coated is not restricted except that some internal surfaces are inaccessible. The skill required to apply the coating can be developed readily. A wide variety of compositions of coating can be selected so that the bonding treatment will not recrystallize molybdenum-base alloys.

The major portion of the research sponsored by Wright Air Development Center at Climax Molybdenum Company Research Laboratory has been confined to the investigation of metallic coatings applied by the metallizing process During the four years of performance under two contracts, there has been a gradual evolution of methods and techniques for processing and testing the coatings. Many of the data presented in this report were obtained early in the investigation when there was little background or experience, but the evaluations made, and lessons learned, from the preliminary steps were important to the over-all development and formed the bases for improvements which followed; therefore, the early results are presented even though the methods and techniques are now considered obsolete and inadequate.

PART I

EQUIPMENT AND PROCEDURE FOR SPRAY COATING MOLYBDENUM

The Metallizing Process

Coating molybdenum by metallizing is accomplished in three steps. First, the surface of the molybdenum is roughened by grit blasting. Second, all surfaces are sprayed with the coating material; third, the spray-coated article is heat treated to consolidate the coating and to obtain a metallurgical bond of the coating to the molybdenum. The coated molybdenum article is then ready for exposure to air at elevated temperatures. A detailed description of the procedure employed for spray coating molybdenum test specimens is given below.

Preparation of Molybdenum Specimens

The edges and corners of the specimens to be coated are rounded with a file and all surfaces are roughened by grit blasting to facilitate a mechanical bond of the coating to the molybdenum. Either coarse-grade aluminum oxide grit or SAE Grade G-25 iron grit is used in blasting. When the iron grit is used, the iron grit embedded in the specimens is removed by dissolving in concentrated hydrochloric acid, which does not attack molybdenum. Acid-cleaned specimens are washed in hot water, alcohol and ether.

Application of Spray Coat

Two types of spraying guns are employed for applying the sprayed-metal coatings to the molybdenum specimens. A Metco Type 2E gun manufactured by Metallizing Engineering Company, Long Island City, New York, is used for spraying with wire. Wire sizes in the range 15 gage to 1/8-in. diameter can be sprayed with this gun.

A Colmonoy Model B Spraywelder manufactured by Wall-Colmonoy Company, Detroit, Michigan, is used for spraying metallic powders. Metals or mixtures of metals that cannot be obtained readily in the form of wire are applied with this gun. The powders are approximately minus 150-mesh particle size.

Coatings are applied to the molybdenum specimens either as a single layer or as multiple layers. The desired thickness of the single-layer coating is applied with one type of spraying gun and one composition of coating material. On the basis of rate of build-up of coating during spraying and the appearance of coatings after the diffusion treatment, 20% aluminum was employed in mixtures with the majority of alloy powders for single-layer coatings.

The multilayer coating is applied with the two types of spraying guns and two compositions of material for spraying. Satisfactory results have been obtained with three-layer coatings, the first and third layers of which were aluminum Alloy 13 applied with a Metco gun using 1/16-in. diameter wire.

The second layer was a mixture of 33% aluminum powder and 67% of an oxidation-resistant material such as chromium silicide and was applied with a Colmonoy Spraywelder. The original purpose of the three layers was to produce wetting and bonding to molybdenum with the first layer and to provide oxidation resistance and raise the melting point of the coating with the second layer. The third layer was added to protect the somewhat porous second layer from damage until the coating could be bonded and consolidated by heat treatment. The results of the tests with three-layer coatings have been reasonably satisfactory; nevertheless, the single-layer coatings are simpler to apply and appear to be more satisfactory in the tests conducted to date.

Most coatings have been applied in thicknesses totaling approximately 0.010 in. as measured after diffusion treatment. In the tests to which the coatings have been subjected, this thickness was adequate. Later investigations may reveal that a lesser thickness would be sufficient.

Originally, the specimens were spray coated by manual movement of the gun across the specimen. For spraying a 2 in. by 2 in. by 0.050 in. specimen, the panel was rested at about a 60-degree angle on a steel grid. The gun was moved in a horizontal direction back and forth until the 2 in. by 2 in. surface appeared to be covered. The direction of motion of the gun was then changed to a vertical movement. The horizontal and vertical passes were repeated until the desired thickness of coatings was applied. With practice, the movement of the gun could be controlled so that about a 0.001-in.-thick layer could be applied with each horizontal or vertical series of passes.

After one 2 in. by 2 in. face had the required coating thickness, the panel was turned 180 degrees and the other face was coated. The panel was then handled with a pair of tongs for spraying the four edges. For spraying the edges the gun was moved back and forth along the line of the edge.

Usually from three to five panels were placed side by side and sprayed at the same time. All panels were included in the horizontal passes, but only one panel was sprayed with each vertical pass of the gun. The panels were handled individually for coating the edges.

Recently the movement of the spray gun has been mechanized. This was done to insure an application of a uniformly-thick coating and to insure a completely-covered specimen. For spraying 2 in. by 2 in. by 0.050 in. panels the gun is driven in a horizontal direction across five panels. Figure 1 is a photograph of the equipment set to spray the 2 in. by 2 in. surfaces. The panels are held in place on the manifold by a differential pressure as a result of reduced pressure in the manifold created by a vacuum cleaner. At the end of each pass the movement is stopped and the position of the gun is raised or lowered 1/8 in. for the next pass in the reverse direction. The positioning of the gun in the vertical direction for each horizontal pass is accomplished by turning a crank which moves a screw attached to the gun rest. After the surfaces of the panels have been covered with the first series of passes, the panels are rotated 90 degrees on the manifold by turning the sleeve on which each panel rests. The turning motion is restricted to 90 degrees by a stop located in a slot of the sleeve. The sleeve and the slot can be seen in the photograph of Figure 2 which shows the position of the equipment for spraying the edges. The panels are rotated after each series of passes until the 2 in. by 2 in. surface has the required thickness of coating, then the panels are reversed on the sleeves and the opposite sides are coated.

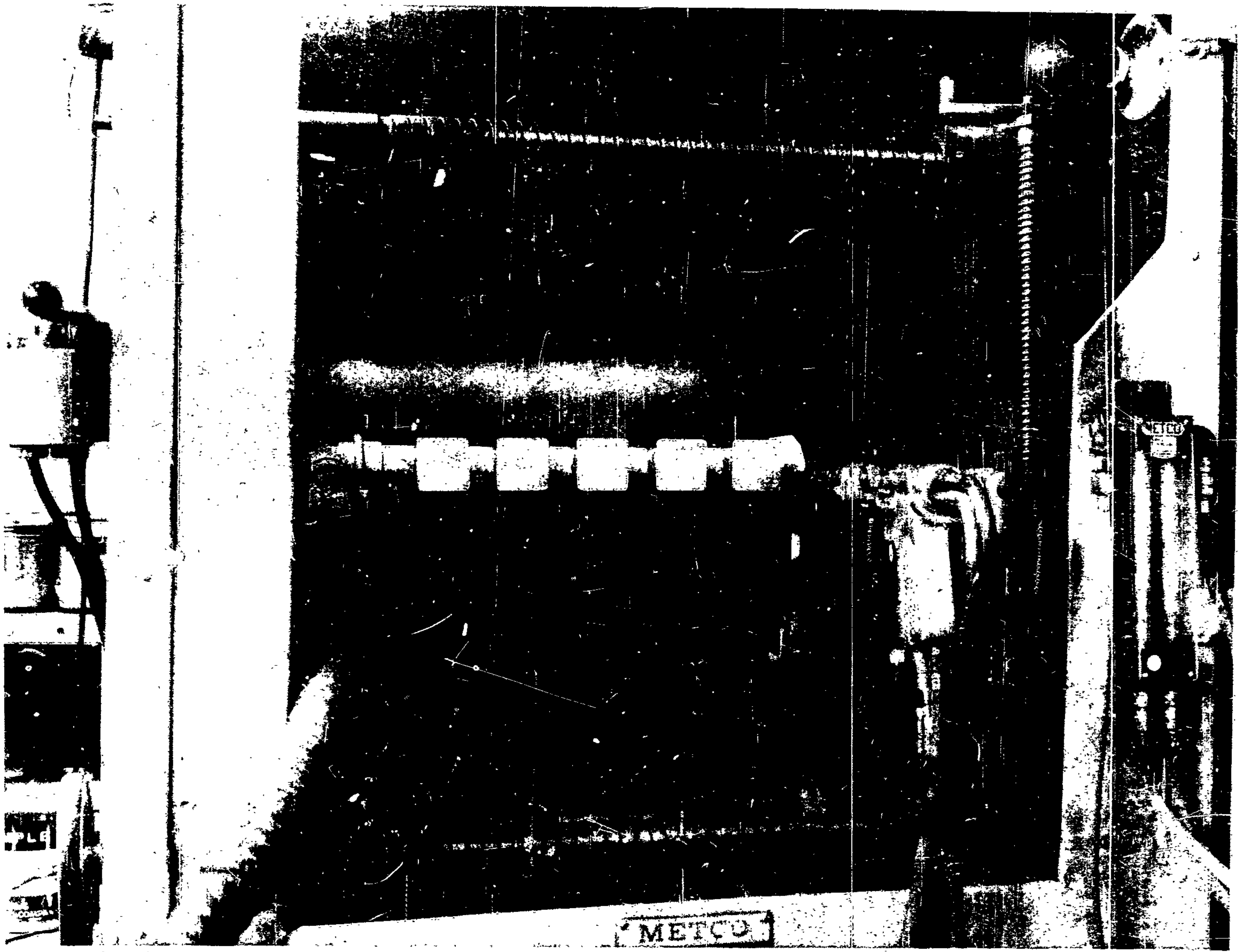


FIG 1 (P1145) - **EQUIPMENT FOR MECHANICAL MOVEMENT OF SPRAY GUN FOR SPRAY COATING MOLYBDENUM PANELS**
Equipment in Position for Spray Coating Panel Faces

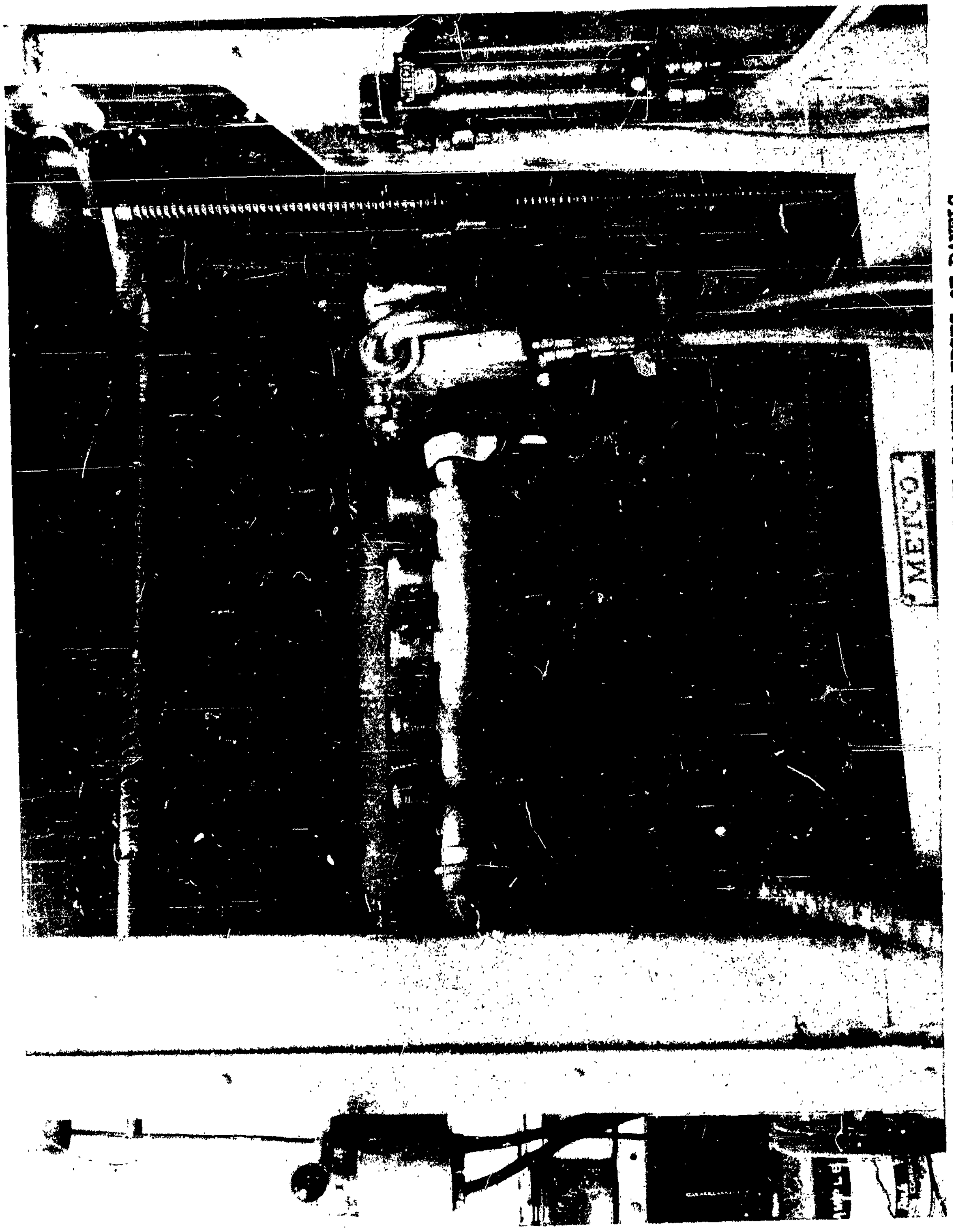


FIG 2 (P1144) - EQUIPMENT IN POSITION FOR SPRAY COATING EDGES OF PANELS

The edges of the panels are coated as follows: two edges, the edge facing the gun and an adjacent edge, are sprayed with the panels in a horizontal plane as shown in Figure 2. By turning the manifold 180 degrees on its longitudinal axis, the panels can be held in a second horizontal plane, below the axis of the manifold, and the remaining two edges of each panel are sprayed. Although the panels are now below the opening of the sleeve, the vacuum cleaner maintains a pressure differential sufficient to support the weight of a panel and to prevent it from moving during the spraying operation.

Another special fixture was designed for coating round bars so that the entire cylindrical surface of a bar can be coated without changing the position of the bar and without overlapping the coating. The device consists of a motorized variable-speed drive to rotate the bar and a tail stock that is adjustable to accommodate bars up to 14 in. long. A center hole 0.052 in. diameter by 1/32 in. deep is drilled in one end of the bar to fit into the floating center of the tail stock. Two holes, 1/4 in. apart and the same size as the center hole, are drilled on the diameter of the other end of the bar. Two phonograph needles, mounted in the end of a steel bar that is attached to the motorized drive, fit into the two holes of the molybdenum bar to rotate the bar for spraying. The spray gun is moved by the mechanical device described above.

After the cylindrical surface is sprayed, the bar is removed from the fixture and the bar ends are sprayed manually.

Diffusion Treatment

The single and multilayer coatings containing a fairly high percentage of aluminum have a liquid phase during the diffusion treatment. The coatings, therefore, have a tendency to adhere to the supporting fixture. To prevent adherence during the diffusion treatment, the sprayed specimens are painted with a slurry consisting of fine aluminum oxide powder and methyl alcohol.

The diffusion treatment to bond the sprayed-metal coating to the molybdenum is accomplished by heating in a purified and dried hydrogen atmosphere for two hours at 2000°F. The furnace employed is heated electrically using molybdenum elements in a "tank" hydrogen atmosphere. The heated zone of the furnace is 4 in. wide by 5 in. high by 24 in. long. Painted panels are stacked in piles on a tray and placed in a retort; other specimens are supported in racks in the retort. As soon as the air has been purged from the retort and replaced with purified hydrogen, the retort is inserted in the heating furnace which is at 2000°F. The retort is removed from the furnace after the specimens have been held at 2000°F for two hours, cooling in still air to about 75°F in 30-40 minutes. The aluminum oxide is brushed from the specimens prior to subsequent tests.

The retort is a Type 304 stainless steel tube 2-3/4 in. i.d. by 54 in. long, welded at one end to a stainless steel plate, to provide a gas-tight joint in the furnace. A 24-in. length of the retort projects out of the furnace. The cold end of the retort is fitted with a rubber O-ring gasket and a steel plate that is bolted into position to make the end gas tight. Purified hydrogen is introduced into the retort near the welded end; the gas passes through a 1/4-in. diameter tube that extends from the cold end to the hot end on the inside and bottom of the retort. The purified hydrogen then flows over the specimens and is discharged to the atmosphere at the end of the retort outside of the furnace.

The temperature during diffusion treatment is measured using a chromel-alumel thermocouple inside a 5/16 in. o.d. Type 304 stainless steel tube projecting inside the retort to the vicinity of the specimens.

The hydrogen used for the atmosphere inside the retort is tank hydrogen that has been purified by passing over a palladium catalyst ("Deoxo" tower) to react remaining oxygen with a portion of the hydrogen and through an activated alumina drying tower ("Lectrodryer") to remove moisture. The dew point of the purified hydrogen is below -40°F.

The time and temperature of the diffusion treatment have not been investigated thoroughly; however, it has been found in oxidation tests at 1800°F with a single-layer aluminum-chromium-silicon coating that a two-hour diffusion treatment at 2000°F produced much more satisfactory results than did a two-hour diffusion treatment at 1800°F.

PART II

LABORATORY TEST PROCEDURES APPLIED TO COATED MOLYBDENUM SAMPLES

Tests to Evaluate Coatings

As a first requirement, a coating must protect the molybdenum from oxidation at elevated temperatures for a minimum period of time. At the Climax Laboratory, the requirement is 500 hours at 1800°F. The conditions imposed upon a coating during service will vary depending on the application; however, a prospective coating must, in many cases, have the capacity to withstand thermal shock and thermal cycling and some plastic deformation. Other desirable characteristics include the ability to resist impact of small objects and to resist erosion and corrosion by hot combustion gases. A smooth coating surface or one that is machinable to a smooth surface is also advantageous.

For this project, tests have been established for evaluating coatings with regard to the following requisites:

(1) resistance to oxidation at 1700°-2000°F
(2) capacity to sustain thermal shock
(3) capacity to withstand thermal cycling
(4) ability to sustain plastic deformation
(5) ability to be finished to a smooth surface.

Oxidation Test

The first test to which a prospective coating is subjected is an oxidation test in moving air at 1800°F. The specimen is usually a 2-in. by 2-in. by 0.050-in. molybdenum panel completely covered with the coating to be tested. This specimen was selected partly because it presented the problem of protecting thin edges which would, in many cases, be involved in the coating of actual parts.

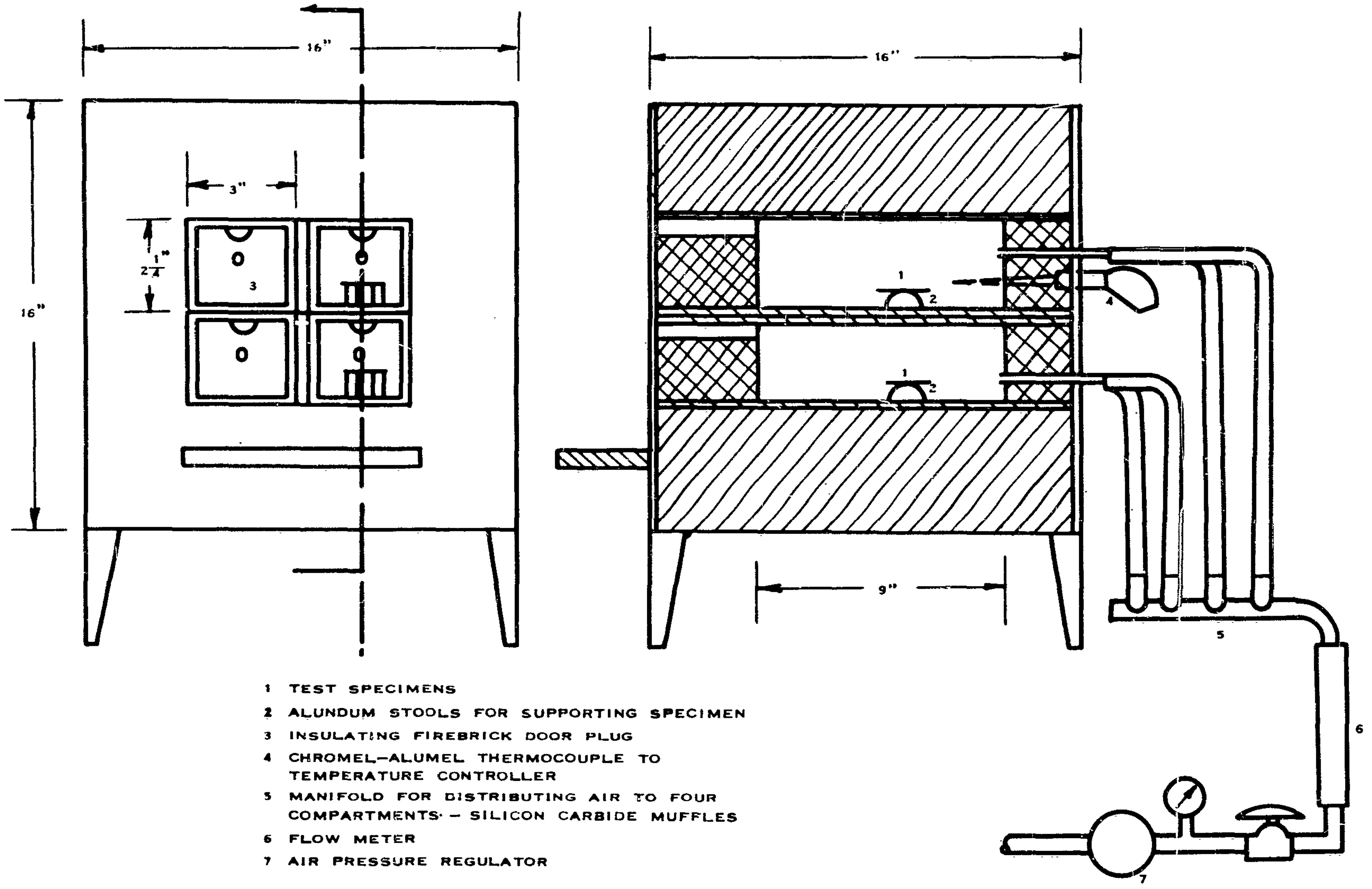
The specimen is placed in a separate compartment in an electrically-heated muffle furnace. Tests in this laboratory and at other research laboratories have indicated that molybdic oxide may react with certain metals or metallic oxides to accelerate oxidation. A failure of one type of coating in a furnace would permit the generation of MoO_3 which might react with another coated specimen and cause a premature failure, resulting in a false evaluation. Testing in separate compartments assures accurate evaluations since the only atmosphere responsible for failure is unadulterated air.

The specimen is supported horizontally on the cylindrical surfaces of two alundum half-cylinders with one-inch radii and 3/8-inch widths. Contact of the coating with each pedestal is limited to an area 3/8-in. by only a few thousandths of an inch; such support permits practically all of the surface of each coating to be exposed to moving air.

Each furnace is divided into four compartments. Air is introduced at the rear of each compartment and is regulated to flow over the specimen at a velocity of about 25 feet per minute. A sketch of the furnace showing the components is presented in Figure 3. Photographs of the front and rear of a battery of six furnaces are shown in Figures 4 and 5. Each muffle has a separate insulating fire-brick plug which contains a slot for the exit of the flowing air. The plug fits snugly in the muffle and is removed when specimens are inserted or withdrawn.

During the initial eight hours of the oxidation test, the specimen is observed closely for evidence of coating failure which is manifested by the emanation of visible vapors of molybdic oxide from the specimen. If no evidence of failure is exhibited, the specimen is removed from the furnace, cooled in still air to 75°F and examined visually for flaws or spots of potential failure. If the coating appears to be in good condition, the specimen is placed in the furnace for 16 hours and then re-examined after cooling to 75°F. Thereafter the specimen is removed from the furnace every 24 hours for inspection at 75°F. Specimens that have endured for 50-100 hours at 1800°F are not removed for inspection on Saturdays and Sundays. Each week, therefore, a specimen is inspected at 75°F five times at 24-hour intervals and one time at a 72-hour interval.

If a specimen does not fail during a 500-hour exposure at 1800°F, the test is concluded. Recently, the procedure has been extended so that the testing of specimens is continued at 2000°F after the 500-hour test at 1800°F has been concluded.



1 TEST SPECIMENS
2 ALUNDUM STOOLS FOR SUPPORTING SPECIMEN
3 INSULATING FIREBRICK DOOR PLUG
4 CHROMEL–ALUMEL THERMOCOUPLE TO TEMPERATURE CONTROLLER
5 MANIFOLD FOR DISTRIBUTING AIR TO FOUR COMPARTMENTS – SILICON CARBIDE MUFFLES
6 FLOW METER
7 AIR PRESSURE REGULATOR

FIGURE 3 — OXIDATION TEST FURNACE WITH FOUR SEPARATE COMPARTMENTS

HOSKINS ELECTRIC MUFFLE FURNACE TYPE FH–204
(689)

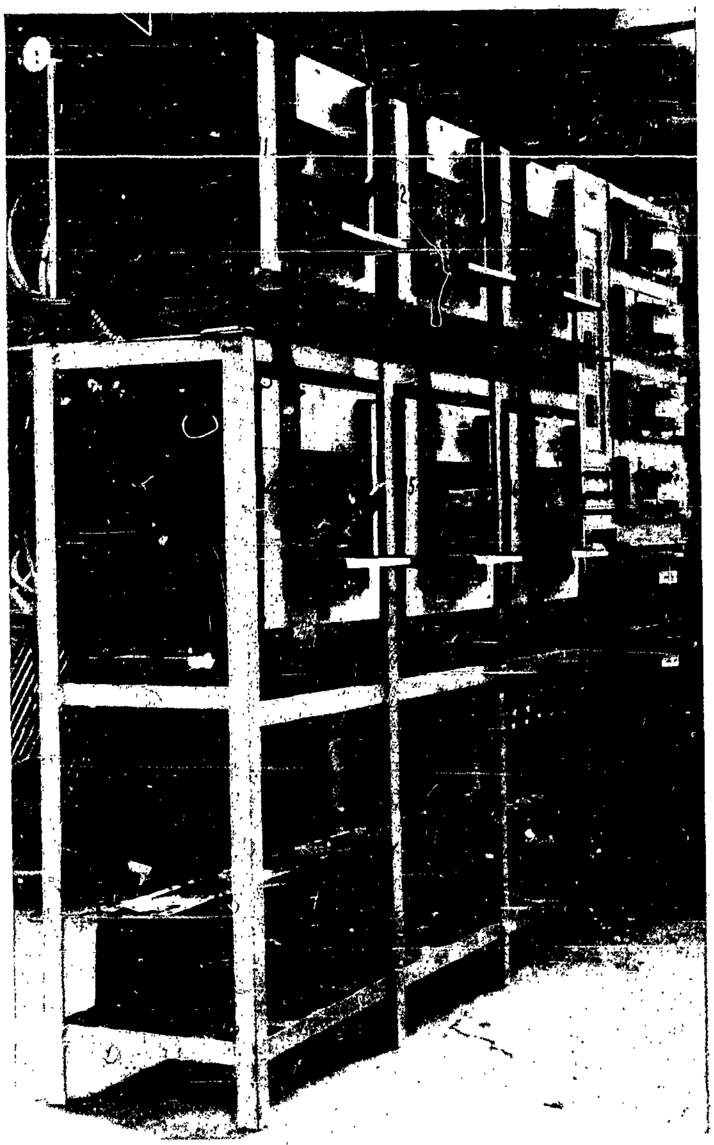


FIG 4 (P1142) - FRONT VIEW OF SIX FURNACES FOR CONDUCTING OXIDATION TESTS IN AIR AT 1800°F

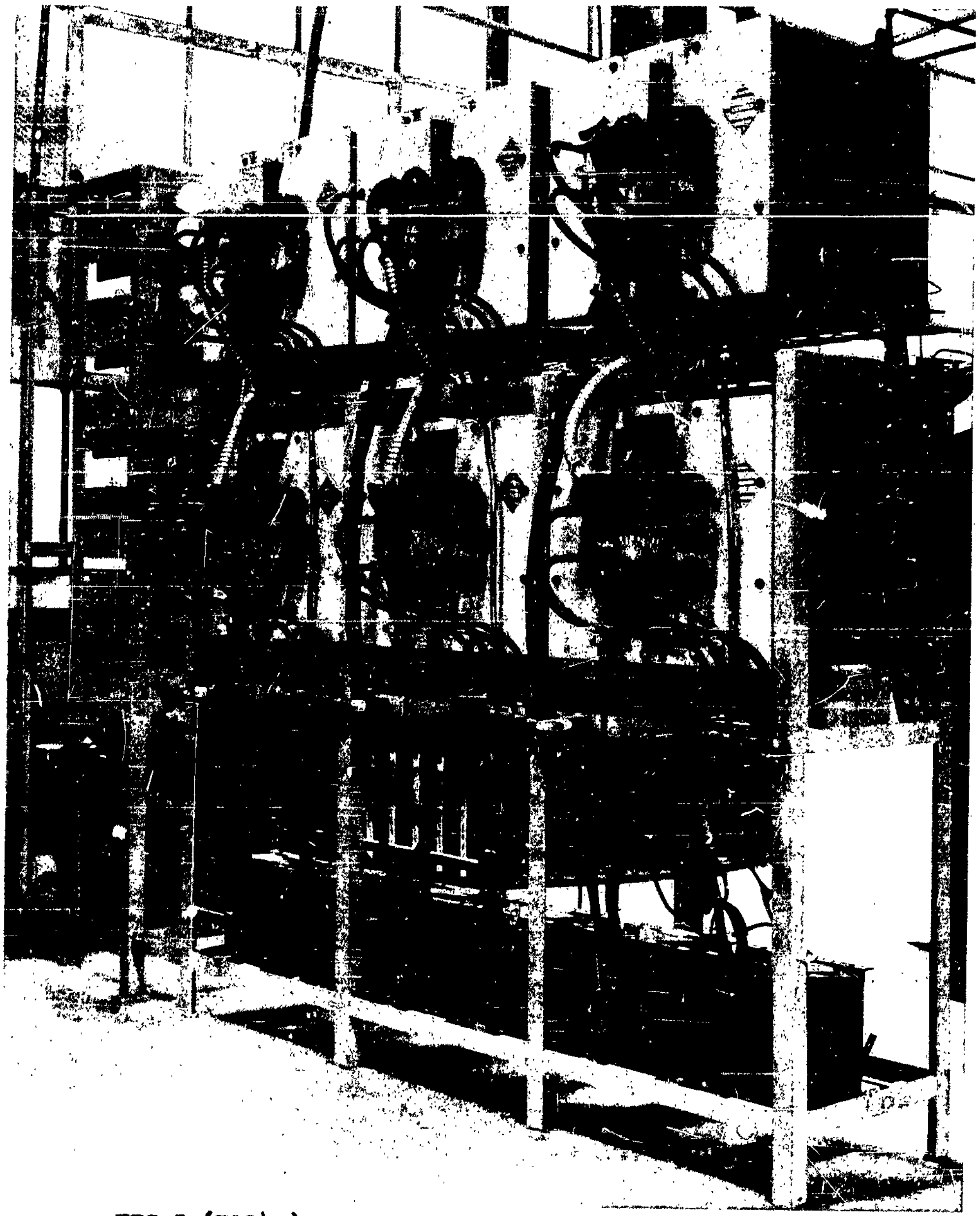


FIG 5 (P1143) - REAR VIEW OF OXIDATION TEST FURNACES

Three specimens of a prospective coating composition are usually oxidation tested to determine whether the coating has merit. If one of the three specimens survives the 500-hour oxidation test at 1800°F and if the spraying qualities of the material and appearance of the coating are satisfactory, the composition then may be evaluated further by subjecting a group of ten or more specimens to oxidation at 1800°F to determine the reproducibility of results.

Oxidation Test with Mechanically-Finished Coatings

For some applications, it is highly desirable for a coating to have a smooth surface. In other cases, a coated article must be held within definite size limits for proper fit, weight, or dynamic balance. The as-coated surfaces of sprayed-metal coatings usually cannot meet these requirements; they must be mechanically finished. The shape of the test specimen for determining the feasibility of mechanically finishing a sprayed-metal coating was selected on the basis of ease of handling while producing the smooth surface. The specimen is a bar approximately 5/8 in. diameter by 4 in. long. The spray-coated bar after receiving a diffusion treatment is centered in a collet in a lathe. The coating is ground to the required thickness and surface finish with a tool post grinder. The following are data relative to the grinding operation applied to two coatings tested to date:

(1) Grinding Wheel (Dry Grinding)
    Norton Company Silicon Carbide No. 39C100H7V
    4-1/2 in. diameter
    Speed - 4600 rpm

(2) Lathe
    Speed - 100 rpm
    Feed - 0.002 in. per revolution on radius - roughing
    0.0005 in. per revolution on radius - finishing

If the surface finish of the ground coating is satisfactory, the specimen is subjected to an oxidation test at 1800°F, using the equipment and procedures described previously.

Thermal-Shock Test

Some thermal shock results from the daily inspection of the specimens in the regular oxidation test. Removal from the furnace at 1800°F, cooling to 75°F in still air and reheating to 1800°F constitute a degree of thermal shock for the coating of the 2 in. by 2 in. by 0.050 in. panels. A more drastic thermal shock than this was desired. Two different special thermal shock tests were devised. The first test consisted of water quenching the specimen from the oxidation test furnace and then reheating to the testing temperature in the furnace. This cycle was repeated continuously until the specimen had been quenched 20 times and reheated 20 times. In 10 of the quenchings, only one-half of the specimen was immersed in water. If the coating had not failed during the 20 quenching cycles, the specimen was left in the furnace at the oxidation testing temperature for 24 hours. If no failure occurred during this period, the specimen was subjected to another series of 20 water quenches and 20 reheatings. The daily series of quenchings were continued until the coating failed. The test was conducted usually with specimens that had already endured for 500 hours in the regular oxidation test.

Thermal Cycling Test

Although the thermal shock tests were severe in cooling, the reheating rate was not so severe. A special thermal-cycling apparatus was constructed to incorporate drastic heating and cooling. The apparatus comprises a device for heating three coated specimens 4 in. by 1 in. by 0.050 in. simultaneously in separate gas flames to 1800°F, removing the specimens from the flame, and cooling them to about 80°F in an air blast. A section approximately one inch square at one end of each specimen is heated in the flame produced by a one-inch-diameter blast tip burning natural gas with compressed air. The cycling is performed automatically with an air-operated motor and time-delay relays. Every 10 cycles the specimens are allowed to cool in still air so that failures might be detected.

A sketch of the apparatus is shown in Figure 6. Figure 7 is a photograph showing the components of the apparatus. A view of the apparatus looking down on the specimens at the cooling station is shown in Figure 8.

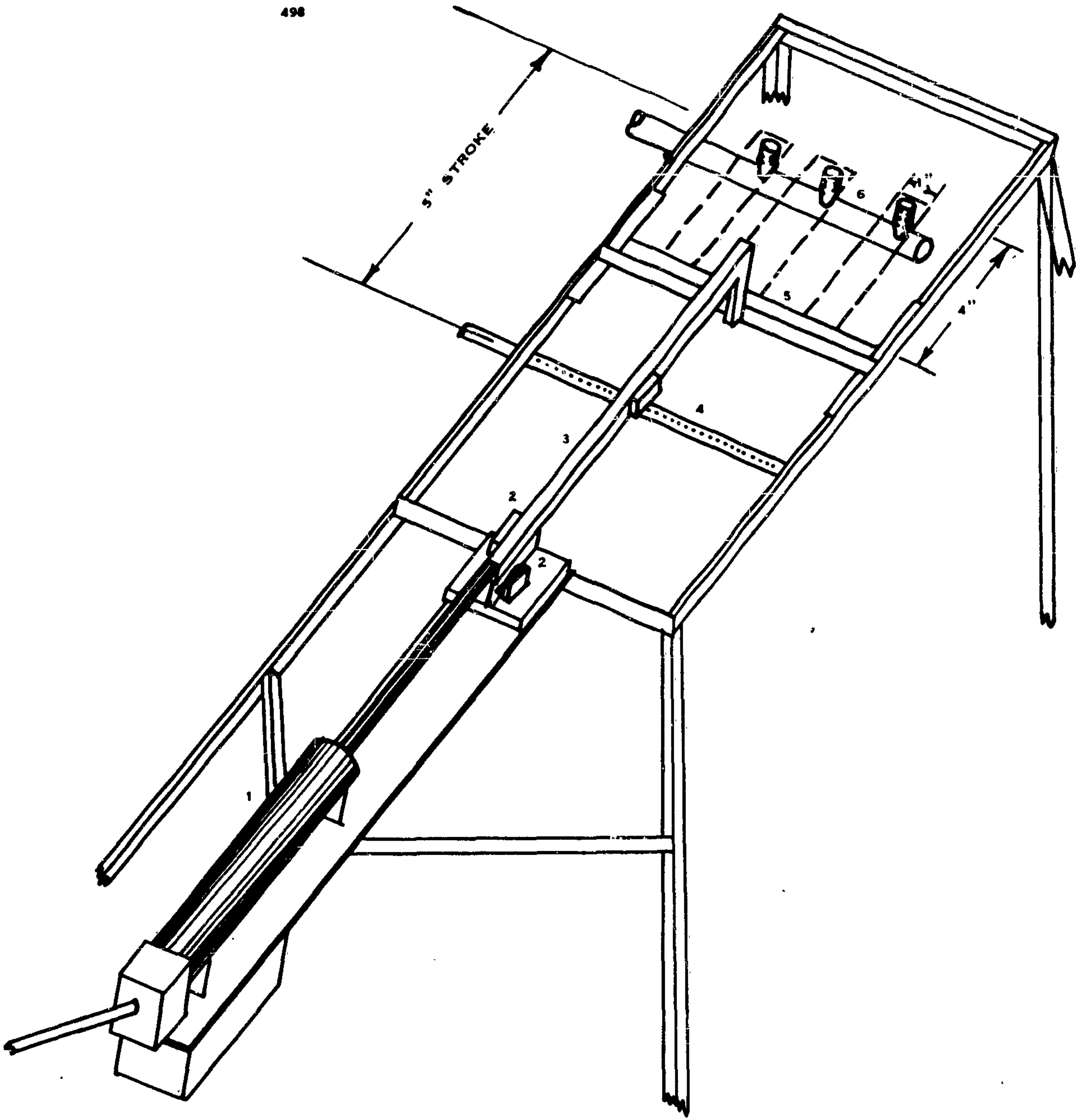
To establish a suitable thermal cycle, a special panel was prepared for temperature measurements. A small hole was drilled at the geometric center of the heated section of a coated panel, and the bead of the chromel-alumel thermocouple was peened into the hole. With specimen mounted in the apparatus, the flame and time-delay relays were adjusted to give the following cycle:

(1) Heating from 80°F to 1800°F - 30 seconds
(2) Holding at 1800°F to 1830°F - 15 seconds
(3) Cooling from 1830°F to 80°F - 45 seconds

This cycle is presented graphically in Figure 9. The temperature measurements obtained with the chromel-alumel thermocouple were correlated with those obtained with an optical pyrometer sighted on the specimen; the optical pyrometer is used in the standard test procedure.

Ductility Tests

To evaluate the capacity of promising coatings to sustain a small amount of plastic deformation at elevated temperatures while continuing to protect molybdenum from oxidizing, coated specimens were tested under load at elevated temperatures. It was not the purpose of the test to measure the maximum deformation that the coating could withstand, but to determine whether the coating could sustain a deformation of the same order of magnitude that could be tolerated in the commercial design of an article such as a turbine bucket. The maximum allowable design deformation in a turbine bucket is



1. AIR MOTOR WITH PISTON OF 5" STROKE
2. LIMIT MICROSWITCHES
3. TRANSITE PISTON EXTENSION
4. VENTED AIR-COOLING MANIFOLD
5. SLED MOUNTING FOR THREE TEST SPECIMENS
6. GAS-AIR MANIFOLD WITH THREE BURNERS
   PRESSURE REGULATION 30-35 PSI

FIGURE 6 — THERMAL CYCLING APPARATUS

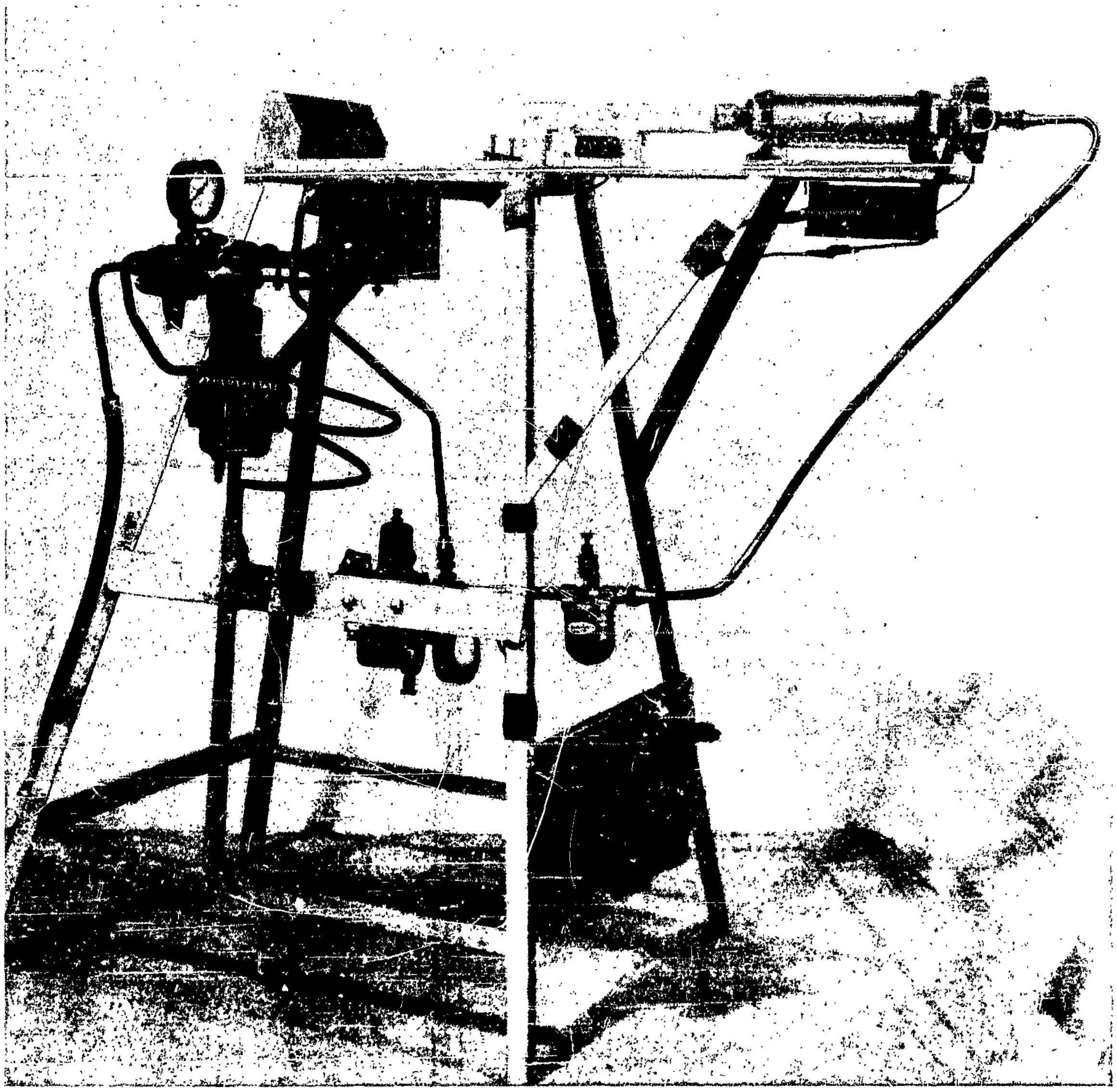


FIG 7 (P1067) - FRONT VIEW OF THERMAL CYCLING APPARATUS

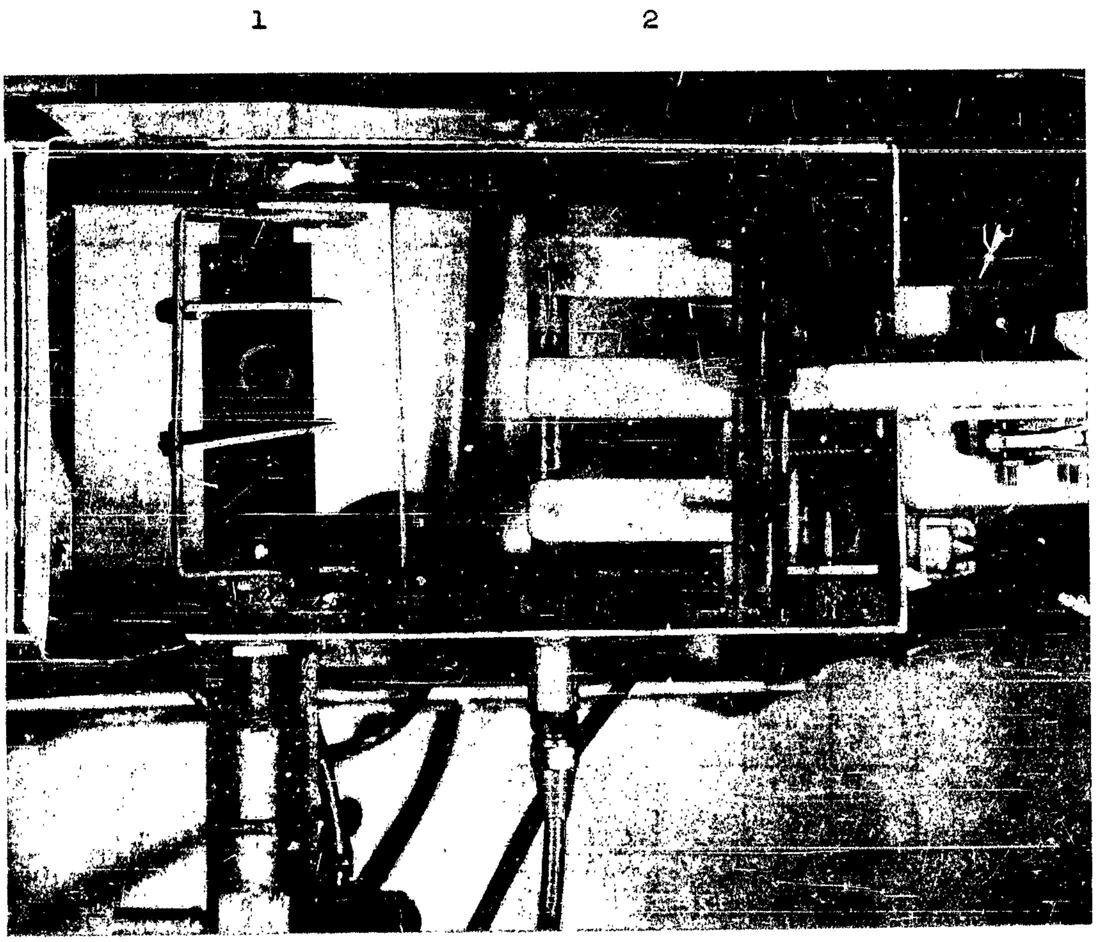


FIG 8 (P1068) - TOP VIEW OF THERMAL CYCLING APPARATUS SHOWING (1) THE GAS BURNERS AND (2) THE SPECIMENS SUSPENDED OVER THE AIR COOLING MANIFOLD

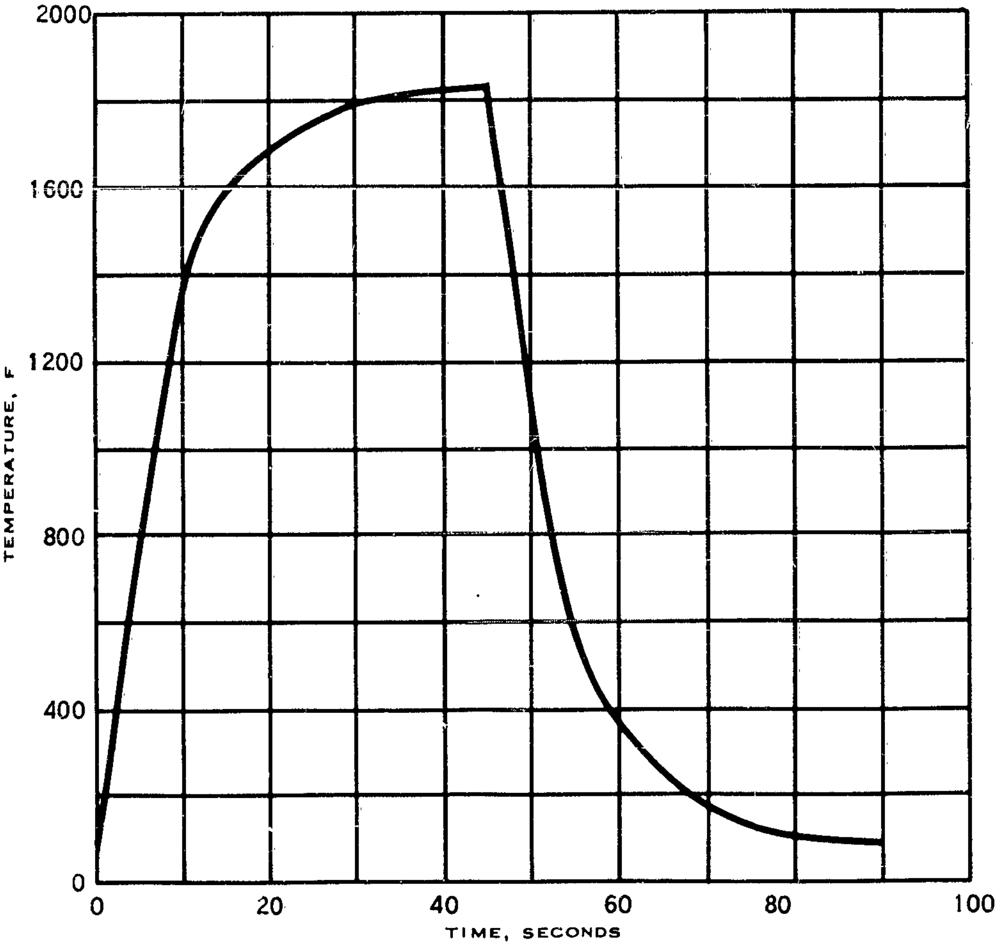


FIGURE 9 — HEATING AND COOLING CURVE OF SPECIMEN IN CYCLIC THERMAL SHOCK TEST

SPRAY COATED MOLYBDENUM SPECIMEN
4 IN. BY 1 IN. BY 0.055 IN.

TIME FOR ONE COMPLETE CYCLE WAS 90 SECONDS seldom greater than 1%. Owing to the possibility of localized over-stressing, elongations of 2% may occur under certain circumstances; therefore, a capacity to sustain a minimum of 2% elongation was required of a coating.

Two methods of testing the ductility of coated molybdenum have been employed. With both methods a sheet-type creep-rupture specimen shown in the sketch of Figure 10 was employed. The specimen was coated to within two inches of each end. Stress was applied through pins in holes in the uncoated ends; these ends extended out of the heating furnace sufficiently to be unoxidized during testing. In one test the specimen was loaded in a tensile testing machine and the gage section stressed in air at 1800°F sufficiently during a two- to three-hour period to produce a 2% elongation. The specimen was removed from the test and then the gage section was subjected to a standard oxidation test at 1800°F in the unstressed condition. The specimen was removed daily from the furnace for visual inspection. This test was continued for a 100-hour period at 1800°F.

The other test consisted of applying a stress to the specimen in a creep-rupture testing machine so that at the end of continuous stressing for 100 hours in air at 1800°F, an elongation in the range 2-5% would be effected. This test was also conducted at 1800°F to produce a similar elongation in a 500-hour stressing interval.

The actual percent elongation was calculated after the test by measuring the distance between pencil marks placed on the 2.25-in. gage section before the test.

Gradient-Temperature Oxidation Test

In the ductility test, the temperatures of the coatings ranged from 1800°F at the gage section to about 500°F near the grip ends of the shank section. This gradient provided an additional opportunity to evaluate the ability of the coating to protect molybdenum at temperatures lower than 1800°F.

There is no positive assurance that a coating which protects molybdenum at 1800°F will also protect it at all lower temperatures. It is essential, however, owing to temperature gradients in service applications and to the possibility of slow rates of heating to the maximum temperature, that a successful coating protect the underlying metal at all intermediate temperatures. The ductility test, just described, provided an opportunity to test the capacities of coatings to protect molybdenum at all temperatures up to 1800°F. After each test the specimens were carefully examined from one end to the other to detect any flaws which could have developed in the regions of lower temperatures. The absence of flaws was accepted as a manifestation of the effectiveness of the coating at the lower temperatures.

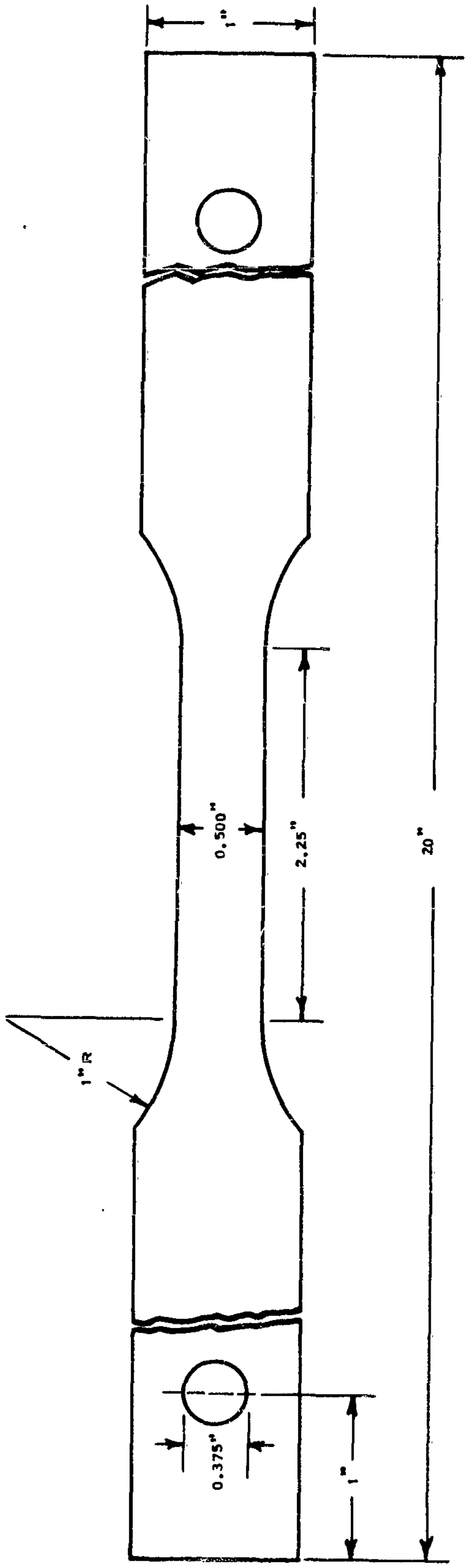


FIGURE 10 — CREEP-RUPTURE SHEET SPECIMEN FOR DUCTILITY TESTS

PART III

INVESTIGATION OF SPRAYED-METAL COATINGS

Chemical Composition of Promising Sprayed-Metal Coatings

Many different coating compositions have been sprayed on molybdenum panels to determine their capacities to protect molybdenum from oxidation at elevated temperatures. The selection of a particular composition for testing was based on the probability that the coating:

(1) would be oxidation resistant at 1800°F.

(2) would form a metallurgical bond to molybdenum upon heating in a purified hydrogen atmosphere at 2000°F.

(3) could be applied with a metallizing gun to build up readily any desired coating thickness on molybdenum.

In screening tests to evaluate a prospective coating composition, usually three 2 in. by 2 in. by 0.050 in. panels of molybdenum have been spray coated and subjected to the oxidation test at 1700° or 1800°F. If at least one of the three panels endured for 500 hours of oxidation testing, the coating composition was considered "promising." The failure of one or two of the three panels prior to 500 hours of testing was attributed to coating technique rather than to coating composition. The alloys classed as "promising" are listed in Table 1.

With the exception of the Colmonoy alloys, aluminum was used in a powder mixture with the alloys of Table 1 because of the high-melting points of these alloys. Aluminum served as a binder for the alloy so that a thick deposit could be built up. Aluminum also formed an excellent metallurgical bond to molybdenum upon diffusion treating in purified hydrogen at 2000°F. It was unnecessary to add aluminum to the Colmonoy alloys because they had low melting temperature ranges and formed metallurgical bonds to molybdenum at 2000°F.

The amounts of aluminum used in the mixture with one of the alloys varied between 10 and 50%; all percentages within this range offered satisfactory oxidation protection. When 10% or less of aluminum was used, the rate of coating build-up during spraying was not so great as when larger percentages of aluminum were used. When the mixture contained 50% aluminum, the surface of the coating after the diffusion treatment was not so smooth as when lesser amounts were employed.

TABLE 1

CHEMICAL COMPOSITIONS OF ALLOY POWDERS[1] USED IN COATINGS

	Percent								Source of Powder[2]
	Si	Cr	Al	Ni	Mo	B	Fe	Others	
Cr-Si Alloy	40.55	55.96	0.44				1.40		A
Cr-Mo-Si Alloy	32.97	31.30			31.29		0.71		A
Mo-Ni-Si Alloy	32.17		1.53	30.57	37.0		0.22		A
Fe-Si Alloy	50/78						bal.		B
Aluminum Alloy 13 (wire)	11/13		bal.						C
Aluminum Alloy 43 (wire)	5/7		bal.						D
Ni-Si Alloy	30			60			7	3 Ca	E
Colmonoy No. 5 Alloy	4.01	12.07		79.16		2.36	4.13	0.46 C	F
Colmonoy No. 6 Alloy	4.33	15.29		72.19		2.77	4.41	1.02 C	F
Fe-Cr-Si Alloy	40/42	39/42					bal.	.05 C max.	G
Si-Fe-Cu-Mg Alloy	40.04						bal.	15.85 Cu 10.73 Mg	G
Si + Al (powder mixture)	10/90		90/10						

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[1] minus 150 mesh particle size

[2] A - Climax Molybdenum Company
B - Electro Metallurgical Company
C - Bohn Aluminum Company
D - Metallizing Engineering Company
E - Steel Sales Corporation
F - Wall Colmonoy Company
G - Vanadium Corporation of America

Extended Testing of Three Sprayed Metal Compositions

Three coating compositions which were exceptionally promising on the basis of the oxidation test at 1800°F and on the basis of appearance after the diffusion treatment were selected for a more comprehensive testing program to determine their capacities to satisfy the other coating requirements.

(1) Single-layer coating: 0.010 in. 20% Al + 80% Cr-Si

(2) Three-layer coating:
Layer 1 - 0.003 in. Aluminum Alloy 13
Layer 2 - 0.005 in. 33% Al + 67% Cr-Si Alloy
Layer 3 - Same as Layer 1

(3) Single-layer coating: 0.010 in. Colmonoy No. 5 and/or Colmonoy No. 6

The three coatings were subjected to ductility, thermal-cycling, gradient-temperature-oxidation and reproducibility-oxidation tests. The single-layer aluminum-chromium-silicon alloy and Colmonoy No. 5 coatings were also subjected to stress-rupture tests.1/ Specimens were prepared by grit blasting with aluminum-oxide grit; manual spraying was employed.

Diffusion-treated and oxidation-tested specimens were subjected to metallographic, x-ray diffraction, and chemical studies, to determine the nature of the three coatings, to study the diffusion mechanism, and to study the mode of failure.

Ductility Tests

For the ductility tests, a 0.75% vanadium-molybdenum alloy was used as the base material. The test comprised stressing the specimens for 100 or 500 hours at 1800°F in air to produce an elongation in the range 2-5%. The results are shown in Table 2; the three coatings had the capacities to withstand the prescribed elongations while protecting the molybdenum against oxidation. Similar results were obtained with the Colmonoy No. 6 alloy coating.

Visual inspection of the ductility test specimens revealed no coating failures along the length of the specimen. The test, therefore, also showed that the three coatings were protective in the temperature range existing along the length of the test specimen. The temperature varied from 1800°F at the gage section to about 500°F at the section adjacent to the uncoated ends.

Stress-Rupture Tests

Stress-rupture tests were conducted in air at 1800° and 2000°F with coated unalloyed molybdenum sheet specimens similar in dimensions to the ductility-test specimen of Figure 10; the single-layer aluminum-chromium-silicon and the Colmonoy No. 5 alloy coatings were employed. The data obtained are given in Table 3 and Figure 11. Table 3B shows that the stresses required for rupture in 1, 10, 50 and 100 hours at 1800°F with both coatings in air were comparable to the stresses required to rupture uncoated molybdenum

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1/ Stress-rupture tests were conducted at WADC

TABLE 2

RESULTS OF DUCTILITY TESTS WITH COATED 0.75% VANADIUM-MOLYBDENUM ALLOY SHEET AT 1800°F IN AIR[1]

Coating Composition (0.010-in. thick except as noted)	No. of Specimens	Temp, °F	Stress, psi	Time of Test, hr	Elong. % in 2.25 in.
Colmonoy No. 5 Alloy	3	1800	23,000/25,000	55/129	3.5/5.0
	2	1800	17,000	498/502	2.0/2.2
Colmonoy No. 6 Alloy	3	1800	23,500/24,500	27/136	7.0/7.5
	2	1800	16,500/17,000	509/511	1.7/2.2
10/20% Al + 90/80% Cr-Si Alloy	5	1800	24,500/27,000	93/162	2.1/3.25
	2	1800	18,000/18,500	500/508	2.2/3.0
Three-Layer Al-Cr-Si Coating Layers 1 and 3: 0.003 in. Alloy 13 Layer 2: 0.005 in. 20/33% Al + 80/67% Cr-Si Alloy	3	1800	23,500/30,000	72/168	2.5/4.8
	2	1800	17,000	498/502	1.7/2.2

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[1] Specimens were not ruptured. No coating failure was exhibited along the entire length of any specimen.

TABLE 3

STRESS-RUPTURE PROPERTIES OF COATED UNALLOYED ARC-CAST MOLYBDENUM AT 1800° AND 2000°F

A - STRESS-RUPTURE VALUES FROM INDIVIDUAL TESTS

Coating Composition (0.010-in.-thick layer)	Stress, psi	Rupture Time, hr	Elong. % in 2 in.	Test Temp., °F
Al-Cr-Si (20% Al + 80% Cr-Si)	20,000	0.3	15	1800
	17,500	0.7	8	"
	15,000	39.6	27	"
	13,000	88.2	24	"
	13,000	140.1	24	"
	13,000	98.7	20	"
	10,000	389.4	24	"
	10,000	27.0	25	2000
	8,000	87.7	14	"
	6,500	163.3	9	"
Colmonoy No. 5	20,000	1.7	35	1800
	17,000	10.8	35	"
	16,000	19.8	27	"
	13,000	100.1	26	"
	13,000	1.5	20	"
	13,000	59.5	-	"
	10,000	189.9	30	"
	10,000	23.7	34	2000
	8,500	288.4	9	1800
	8,500	665.4	24	"
	8,000	30.2	8	2000
	6,500	180.5	13	"

B - COMPARISON OF STRESS-RUPTURE VALUES OF COATED AND UNCOATED UNALLOYED MOLYBDENUM AT 1800°F

Material	Stress for Rupture, psi			
	1 hr	10 hr	50 hr	100 hr
Al-Cr-Si coated specimen in air 1/	17,900	15,300	13,900	13,000
Colmonoy No. 5 coated specimen in air 1/	22,000	16,700	14,000	12,500
Unalloyed Molybdenum in vacuum 2/	18,000	15,000	13,000	12,000

1/ Values from curve of Figure 11

2/ Arc-cast molybdenum-base alloys, Fourth Annual Report NR 039-002, by Climax Molybdenum Company of Michigan, 1953, by M. Semchyshen and R. Q. Barr

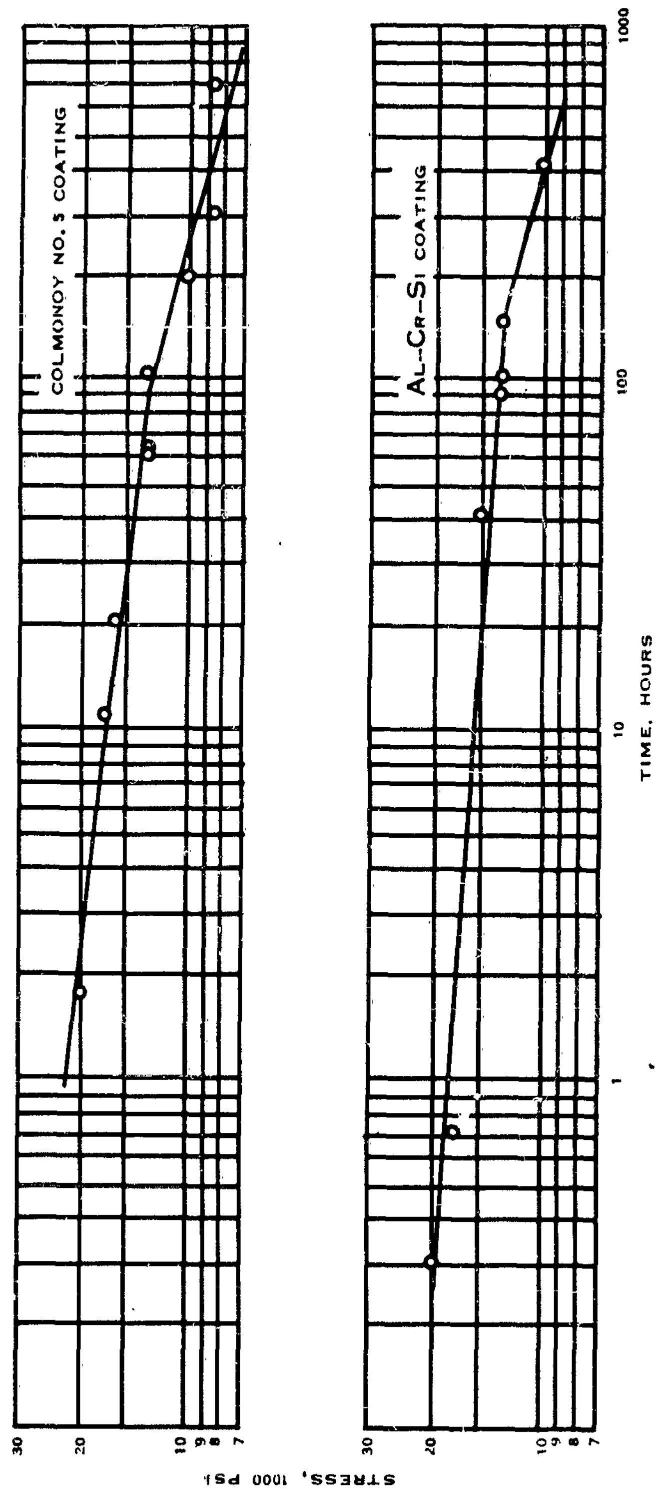


FIGURE 11 — STRESS RUPTURE PROPERTIES OF COATED MOLYBDENUM SHEET AT 1800° F

bars in vacuum at 1800°F. These data indicate that both coatings were adequately ductile and protective and had no deleterious effect upon the properties of the molybdenum. Tests conducted at 2000°F indicated that the coatings may be satisfactory at that temperature.

Data in Table 3 for the individual stress-rupture tests show that both coatings endured for over 300 hours under sufficient stress at 1800°F to produce a 24% elongation upon rupture without prior coating failure.

Thermal-Cycling Tests

The three coatings were tested in triplicate using the thermal-cycling apparatus described in Part II. The data of Table 4 present a comparison of their resistances to thermal cycling; the greatest resistance was exhibited by the single-layer aluminum-chromium-silicon coating which withstood from 509 to 571 heating and cooling cycles before failure. The Colmonoy No. 5 coating withstood from 133 to 225 cycles and the three-layer aluminum-chromium-silicon coating failed in 36-44 cycles. A considerable amount of distortion was produced by thermal cycling the Colmonoy specimens; whereas, the other two coatings were relatively undistorted. The coatings did not spall or peel, but were cracked sufficiently to allow the substrate molybdenum to oxidize at the base of the cracks at a very low rate.

Thermal-Shock Tests

An additional test imposed on the three-layer aluminum-chromium-silicon coating was the water-quenching thermal-shock test described in detail in Part II. This test consisted of water quenching a coated panel after it had endured for 500 hours without failure in air at 1700°F; a panel was quenched from 1700°F into water twenty times each day until failure. Eleven three-layer aluminum-chromium-silicon coated panels were tested (see Table 4). One panel endured as many as twenty daily series of quenches (400 separate quenchings) after the initial 500-hour regular oxidation test at 1700°F. The total exposure at 1700°F for this panel amounted to 1100 hours. After several series of the daily quenchings, the panels usually became quite distorted. Failures always occurred at cracks in the coating at the edges of the panels. The coatings on none of the panels spalled during testing.

Reproducibility of Oxidation Test Results

In order to determine the reproducibility of results in oxidation tests at 1800°F with a large group of specimens, twenty panels of molybdenum were coated with each of the three coatings being evaluated. The panels were blasted with coarse-grade aluminum-oxide grit and sprayed manually as described in Part I. The procedure and equipment for the oxidation test are described in Part II.

TABLE 4

RESULTS OF THERMAL SHOCK TESTS

A - TESTS WITH THERMAL CYCLING APPARATUS[1/]

Coating Composition	Number of Cycles before Failure No. 1	No. 2	No. 3
Al-Cr-Si			
Three-layer	36	44	40
One-layer	571	569	509
Colmonoy No. 5	218	225	133

B - WATER-QUENCHING TESTS WITH THREE-LAYER Al-Cr-Si COATING[1/]

Sample No.	Life of Coating: Regular Oxidation Test	Thermal Shock Test	Total Life	No. of Series of Quenches before Failure
1	511 hr	74 hr	585 hr	4
2	511	336	847	10
3	500	48	548	2
4	500	288	788	8
5	500	308	808	9
6	520	456	976	15
7	504	480	984	15
8	560	48	608	3
9	500	600	1100	20
10	500	216	716	8
11	504	96	600	3

[1/] Temperature range during test
Test A 80°-1830°F
Test B 80°-1700°F

The results of the oxidation tests at 1800°F, given in Figure 12, show that more than 50% of the panels failed in less than 500 hours of testing, exhibiting very poor reproducibility of results. The cause of the numerous failures that occurred before the end of the 500-hour period was attributed to variables in the spray coating process. These were investigated; the results of the investigation are reported in the next section.

Metallographic, X-ray Diffraction and Chemical Observation

Specimens coated with the three coating compositions which were extensively tested were also subjected to detailed examinations of microstructure and chemical composition in an attempt to define the phases present in the coatings and the changes in the nature of the coatings as a result of oxidation tests.

Metallographic examination of coated molybdenum specimens indicated that a considerable amount of molybdenum had diffused into the coating as a result of heating two hours at 2000°F. The amount of diffusion appeared to increase with time of exposure at 1700° or 1800°F in the oxidation test. Early work with two three-layer coatings, one composed of aluminum and silicon and the other composed of aluminum-iron-silicon, revealed by chemical analysis that after a diffusion treatment of two hours at 2000°F a concentration of about 36% molybdenum was present at a distance of 0.006-0.008 in. from the molybdenum-coating interface. A similar amount of molybdenum was found at the same distance from the interface of another specimen that had been diffusion treated 1/2 hour at 1700°F and subsequently tested in air for 682 hours at 1700°F. X-ray diffraction analysis gave complex diffraction patterns. Molybdenum disilicide was tentatively identified as one major constituent. Other phases were present but could not be identified.

In order to illustrate the progress of diffusion occurring in a single-layer aluminum-chromium-silicon coating during the regular 1800°F oxidation test, panels were examined after 0, 25, 50, 100, 200 and 500 hours' exposure at 1800°F. Representative structures near the coating-molybdenum interface are shown in Figures 13-15. The diffusion of molybdenum into the coating was extensive and progressed with time forming complex phases that have been difficult to identify. X-ray and chemical methods of identification of these phases are discussed later in connection with the three-layer aluminum-chromium-silicon coating.

The irregularity of the interface at the base of the crack in Figure 14B was caused by the presence of a small molybdenum carbide which interfered with the interdiffusion of the coating and molybdenum. This effect is illustrated more clearly with another specimen in Figure 16.

Coating cracks were purposely included in each of the photomicrographs of Figures 13-15 to show that within the 500-hour period of testing at 1800°F the molybdenum was not oxidized at the base of the cracks. Evidently the coating expands sufficiently upon heating to 1800°F that the cracks are closed, and thus air is prevented from gaining access to the molybdenum at 1800°F.

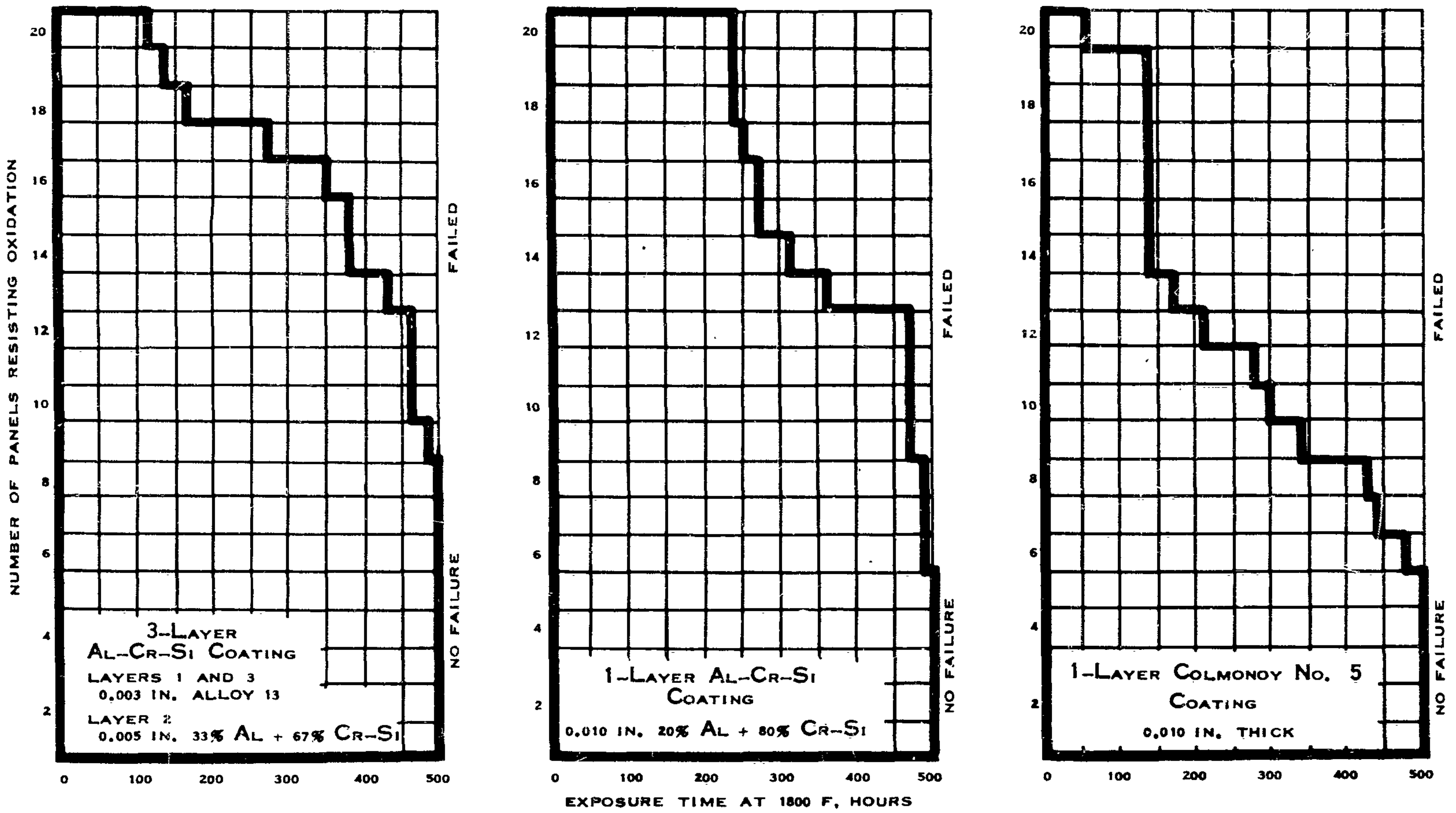
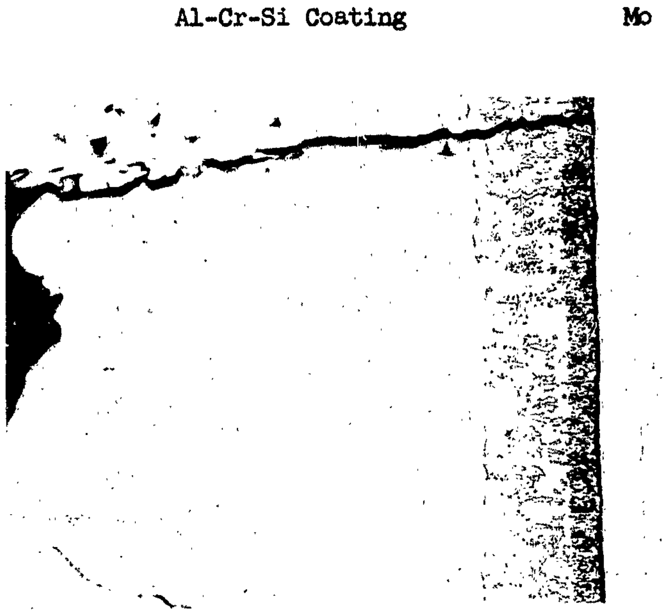


FIGURE 12 — FAILURE DISTRIBUTION CURVES FOR OXIDATION TESTS WITH THREE COATING COMPOSITIONS

PANELS WERE GRIT-BLASTED WITH ALUMINA AND MANUALLY SPRAYED



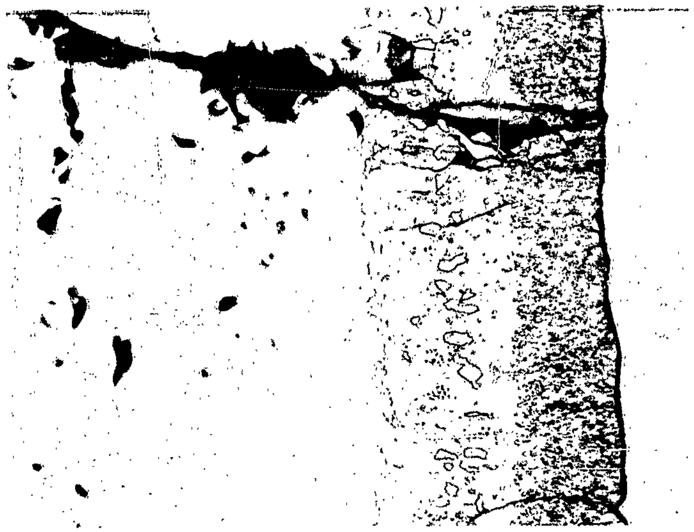
M4308 Etchant: NaOH + $K_3Fe(CN)_6$ 500X

A. Diffusion Treated Two Hours in Purified Hydrogen at 2000°F

M4309 Etchant: NaOH + $K_3Fe(CN)_6$ 500X

B. Oxidation Tested 25 Hours in Air at 1800°F

FIG 13 - MICROSTRUCTURES OF Al-Cr-Si COATINGS ON MOLYBDENUM AFTER DIFFUSION TREATING AND AFTER OXIDATION TESTING IN AIR FOR 25 HOURS AT 1800°F



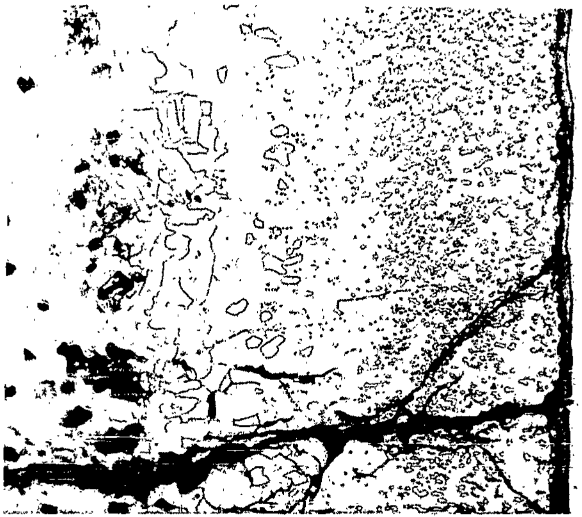
M4310 Etchant: NaOH + $K_3Fe(CN)_6$ 500X

A. Oxidation Tested 50 Hours in Air at 1800°F

M4311 Etchant: NaOH + $K_3Fe(CN)_6$ 500X

B. Oxidation Tested 100 Hours in Air at 1800°F

FIG 14 - MICROSTRUCTURES OF Al-Cr-Si COATINGS ON MOLYBDENUM AFTER OXIDATION TESTING IN AIR FOR 50 AND 100 HOURS AT 1800°F



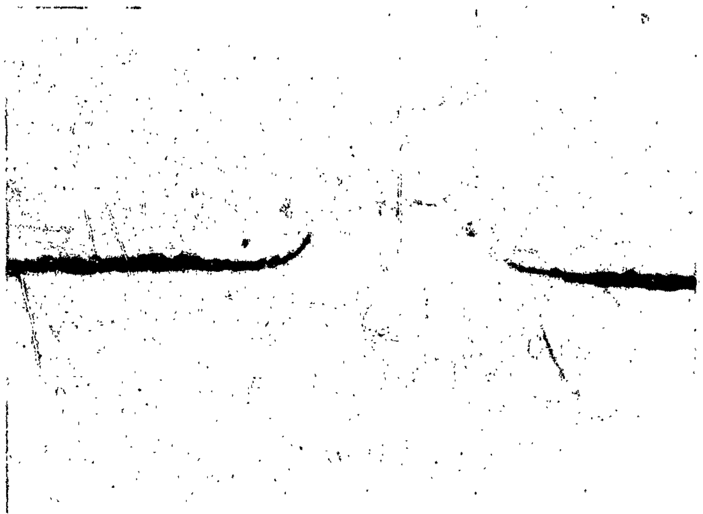
M4318 Etchant: NaOH + $K_3Fe(CN)_6$ 500X

A. Oxidation Tested 200 Hours in Air at 1800°F

M4457 Etchant: NaOH + $K_3Fe(CN)_6$ 500X

B. Oxidation Tested 500 Hours in Air at 1800°F

FIG 15 - MICROSTRUCTURES OF Al-Cr-Si COATINGS ON MOLYBDENUM AFTER OXIDATION TESTING IN AIR FOR 200 AND 500 HOURS AT 1800°F



M4163 Polish-etch-buff 2000X

FIG 16 - MICROSTRUCTURE OF Al-Cr-Si COATING ON MOLYBDENUM DIFFUSION TREATED TWO HOURS IN PURIFIED HYDROGEN AT 2000°F, SHOWING MOLYBDENUM CARBIDE INTERFERENCE WITH INTERDIFFUSION OF COATING AND MOLYBDENUM

An investigation to identify the constituents in the coatings was performed with a three-layer aluminum-chromium-silicon coating. Two specimens were studied. One specimen was examined in the as-diffusion-treated condition (two hours at 2000°F). The other specimen had been subjected to an oxidation test in air at 1700°F for 500 hours after the diffusion treatment. After the loosely adherent coating particles had been rubbed off with coarse grade emery paper, about 0.001-0.002 in. of the outer surface of the coating was removed with a cemented carbide file. The oxygen contents of filings were determined by vacuum-fusion analysis, with the following results:

(1)	As-diffusion-treated sample	1.3% oxygen
(2)	After oxidation test	3.2% oxygen

The results showed that the coating was essentially metallic. The microstructures of the coated specimens after the filings were removed are shown in Figures 17 and 18 to illustrate the structure present immediately adjacent to the layer that was analyzed.

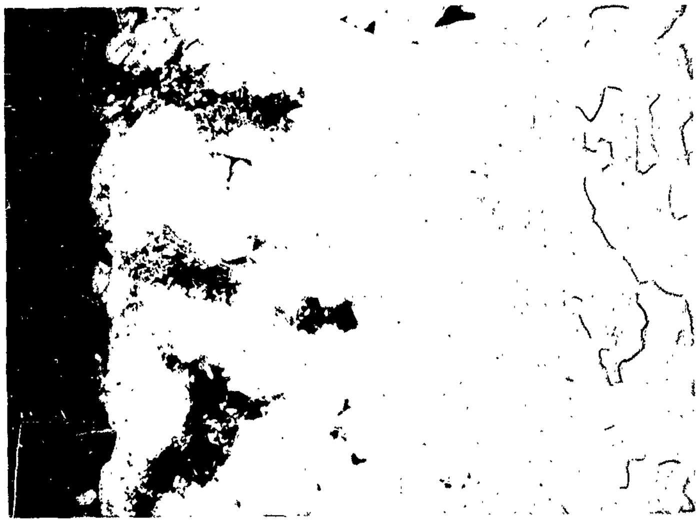
Because of the complexity of the alloy system and, in view of the difficulty experienced with the interpretations of the X-ray diffraction patterns of other samples, a set of reference standards was prepared to assist in the interpretation of the X-ray diffraction patterns obtained from the filings of the two specimens. For this work, separate patterns were obtained for the aluminum Alloy 13 and for the mixture of 33% aluminum plus 67% chromium-silicon alloy. In addition, each of the two materials was sprayed on a separate molybdenum panel and treated two hours in hydrogen at 2000°F to produce diffusion of molybdenum. Diffraction patterns were obtained from filings from the two experimental panels. Using these data, the phases identified in the surface layers of the aluminum-chromium-silicon coating before the oxidation test (as-diffusion-treated) were as follows:

(1) Al-Mo-Si compounds
(2) CrSi plus $CrSi_2$
(3) Alpha Al

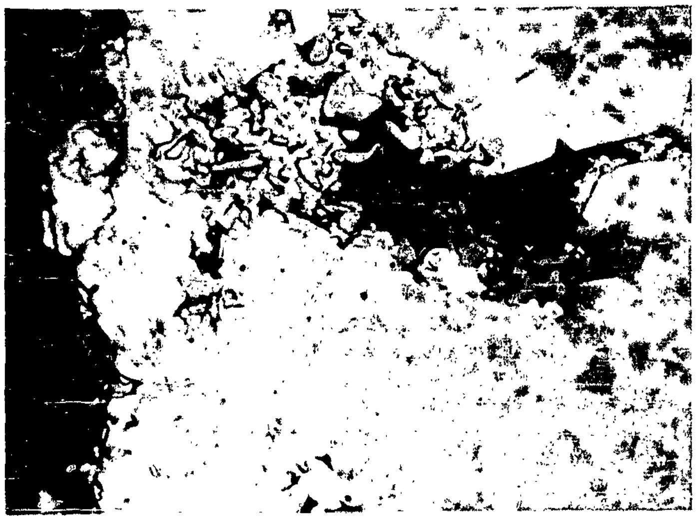
The constitution of the surface layers of the aluminum-chromium-silicon coating after the diffusion treatment and after exposure to air for 500 hours at 1700°F was interpreted to be a mixture of the following phases in order of decreasing prominence:

(1) Cr-Si compounds
(2) Al-Mo-Si compounds
(3) SiO_2

The results of the chemical, X-ray and metallographic analyses showed that the coating remained substantially metallic during the 500-hour exposure to air at 1700°F.



M3327 Polish-etch-buff 250X



M3328 Polish-etch-buff 1000X

FIG 17 - THREE-LAYER Al-Cr-Si COATING DIFFUSION TREATED FOR TWO HOURS IN PURIFIED HYDROGEN AT 2000°F
Structure of coating showing location of filed surface with respect to molybdenum substrate

M3329 Polish-etch-buff 250X

M3330 Polish-etch-buff 1000X

FIG 18 - THREE-LAYER Al-Cr-Si COATING DIFFUSION TREATED FOR TWO HOURS IN PURIFIED HYDROGEN AT 2000°F AND HEATED IN AIR FOR 500 HOURS AT 1800°F
Structure of coating showing location of filed surface with respect to molybdenum substrate

Effects of Coatings on the Molybdenum Alloy

It was observed that the stress required to produce an elongation in the range 2-5% in 100 hours at 1800°F with coated 0.75% vanadium alloy was less for the specimens coated with the Colmonoy alloys than for the specimens coated with aluminum-chromium-silicon composition (see Table 2). Metallographic examination of specimens, before and after testing, revealed a phenomenon which may explain this observation. The Colmonoy-coated specimens exhibited complete recrystallization of the 0.75% vanadium-molybdenum alloy in a narrow zone adjacent to the coating. This is shown in Figures 19 and 20 with specimens as-diffusion treated, and after testing under stress for 27 and 136 hours, respectively, at 1800°F. The photomicrographs show that, as-diffusion treated, the specimen had a narrow recrystallized zone, and that the width of the recrystallized zone increased with increase in exposure time at 1800°F.

The structure of a ductility test specimen having a three-layer aluminum-chromium-silicon coating is shown in Figure 20B. There was no evidence of localized recrystallization of the base material adjacent to the coating after 168 hours of testing under stress at 1800°F.

The lower resistance to plastic deformation at 1800°F, exhibited by the Colmonoy-coated specimens when compared with the aluminum-chromium-silicon specimens, is ascribed to the presence of the zone of complete recrystallization in the base material adjacent to the Colmonoy coating. Since the base material and the heat treatment of the specimens shown in Figures 20A and 20B were the same, the cause of the complete recrystallization in the base material adjacent to the Colmonoy coating must be attributed to the composition of the coating. Diffusion of elements from the coating into the base material would be expected to raise the recrystallization temperature, but the diffusion of vanadium, carbon and/or oxygen from the base material into the coating would be expected to lower the recrystallization temperature of the vanadium-molybdenum alloy. It is tentatively concluded, therefore, that the Colmonoy composition favors diffusion of one of the components of the 0.75% vanadium-molybdenum alloy into the coating.

Investigation of Spray-Coating Variables

Mechanical Spraying

The specimens employed for tests described in the preceding sections were prepared by blasting with coarse-grade aluminum-oxide grit to roughen the surface of the molybdenum for mechanical bonding of the sprayed coating. The coatings were applied by manual movement of the spray gun. After spraying, the specimens were diffusion treated in purified hydrogen for two hours at 2000°F to obtain a metallurgical bond. Two of the three steps in the coating process were modified in an effort to improve the coating; namely, (1) the method of spraying with the metallizing gun and (2) the grit-blasting technique.

M3179 Etchant: NaOH + $K_3Fe(CN)_6$ 250X

A. Diffusion Treated Two Hours in Purified Hydrogen at 2000°F

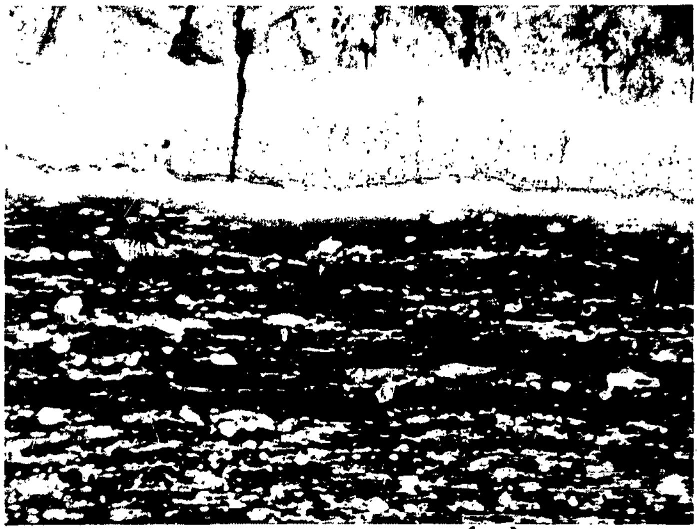
M3180 Etchant: NaOH + $K_3Fe(CN)_6$ 250X

B. Stressed for 27 Hours in Air at 1800°F

FIG 19 - MICROSTRUCTURES AT GAGE SECTIONS OF COATED DUCTILITY TEST SPECIMENS AS DIFFUSION TREATED AND AFTER STRESSING FOR 27 HOURS IN AIR AT 1800°F

M3160 Etchant: NaOH + $K_3Fe(CN)_6$ 250X

A. Stressed for 136 Hours in Air at
1800°F. Colmonoy No. 6 Coating



M3172 Etchant: NaOH + $K_3Fe(CN)_6$ 250X

B. Stressed for 168 Hours in Air at
1800°F. Al-Cr-Si Coating

FIG 20 - MICROSTRUCTURES AT GAGE SECTIONS OF COATED DUCTILITY TEST SPECIMENS AFTER STRESSING FOR 100+ HOURS IN AIR AT 1800°F, showing effect of coating composition on recrystallization of 0.75% vanadium-molybdenum alloy

It seemed logical that the reproducibility of results would be improved if the coating was applied by mechanical movement of the spray gun instead of by manual movement. A coating mechanically applied could be expected to be more uniform in thickness than a coating manually applied; the mechanical operation should be more reproducible from day to day than the manual operation of the gun. A mechanical device was, therefore, constructed and employed for coating experiments. The device and its operation have been described in Part I.

To determine the value of mechanized spray-coating, ten panels of molybdenum were coated by means of the mechanical device; the usual grit blasting and diffusion-treating procedures were employed. The single-layer aluminum-chromium-silicon coating was applied, inasmuch as the results with this coating appeared to be superior to the other two coatings in the oxidation tests.

The ten coated panels were subjected to the regular oxidation test at 1800°F. The results obtained are presented in the graph at the extreme left of Figure 21. All ten panels endured for 500 hours at 1800°F without failure. Small defects, however, appeared on the surface of the coating during the 500-hour test. The times at which such defects were first detected are noted on the graph by hatched lines. The defects were pimple-like and became enlarged at a very low rate during the remaining period of testing. Figure 22 is a photograph of the panels after testing.

The results with the ten panels showed that mechanized spraying was a decided improvement over manual spraying, but the flaws that appeared in the coatings were potential failure areas and were, therefore, undesirable.

Grit Blasting

Originally the molybdenum test panels were blasted with aluminum-oxide grit to prepare the surfaces for coating. Occasionally SAE Grade G-25 iron grit was employed. Both types of grit were found to produce satisfactory roughening of the surfaces to facilitate mechanical bonding. Meticulous metallographic examination of coatings which had been subjected to oxidation testing led to the discovery that particles of aluminum-oxide grit often became embedded in the surface of the molybdenum panels and were subsequently covered over by the sprayed metals. The presence of the aluminum oxide interfered with the formation of the diffusion zone between the coating metals and the molybdenum substrate. Since there was some evidence that the diffusion zone was important to the effectiveness of the coating, it was suggested that the grit particles could be a cause of coating failures. Metallographic observations of as-sprayed panels revealed that the iron grit also became embedded in the molybdenum, but no iron grit could be found in coated panels that had been diffusion treated. Failure to find the particles in panels after the diffusion treatment and/or the oxidation tests did not remove the suspicion that they were a cause of coating failure. By experiment, however, it was found that embedded iron grit particles could be removed by treating the grit blasted panel with concentrated hydrochloric acid. No satisfactory method of removing embedded aluminum oxide grit was developed.

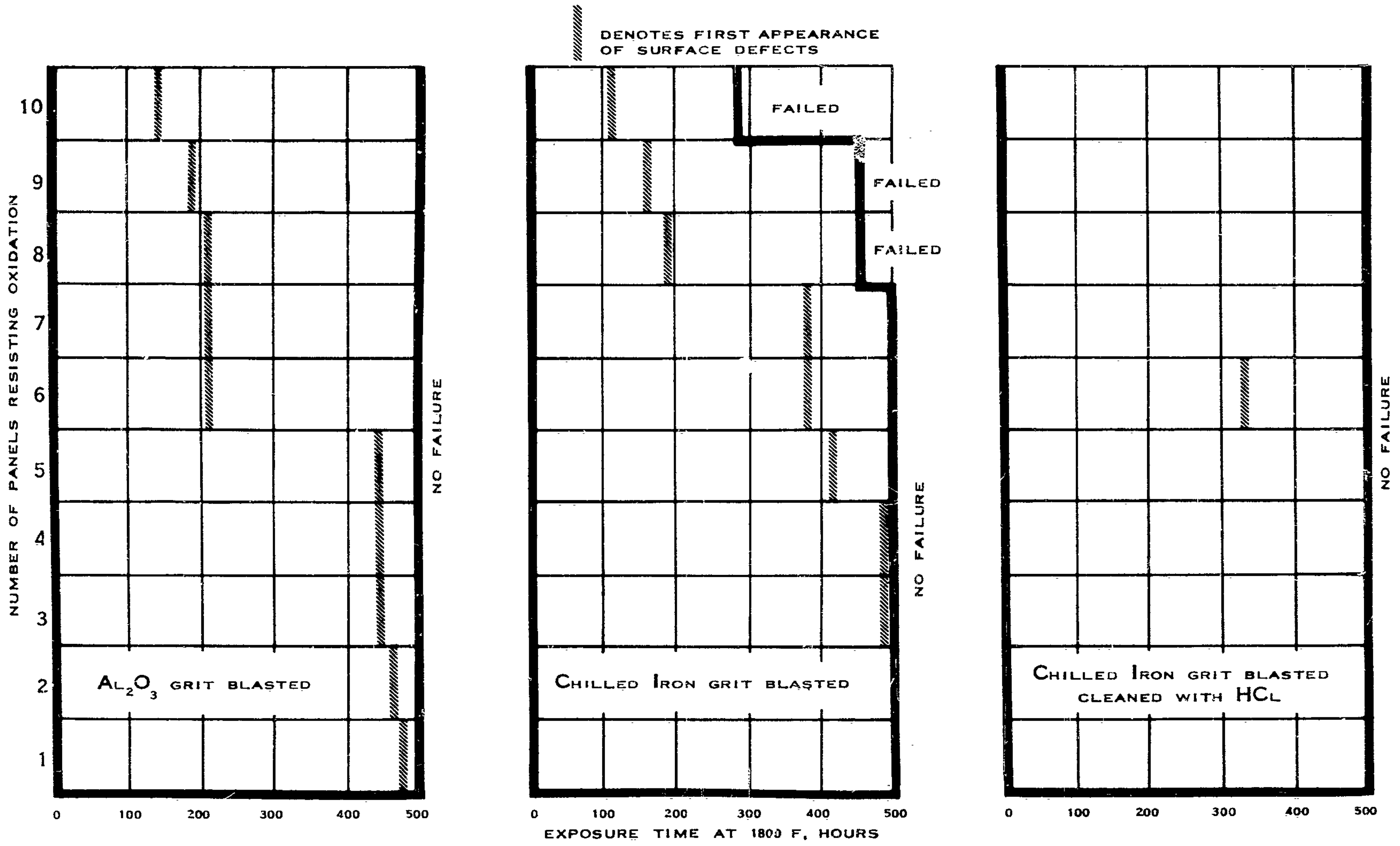
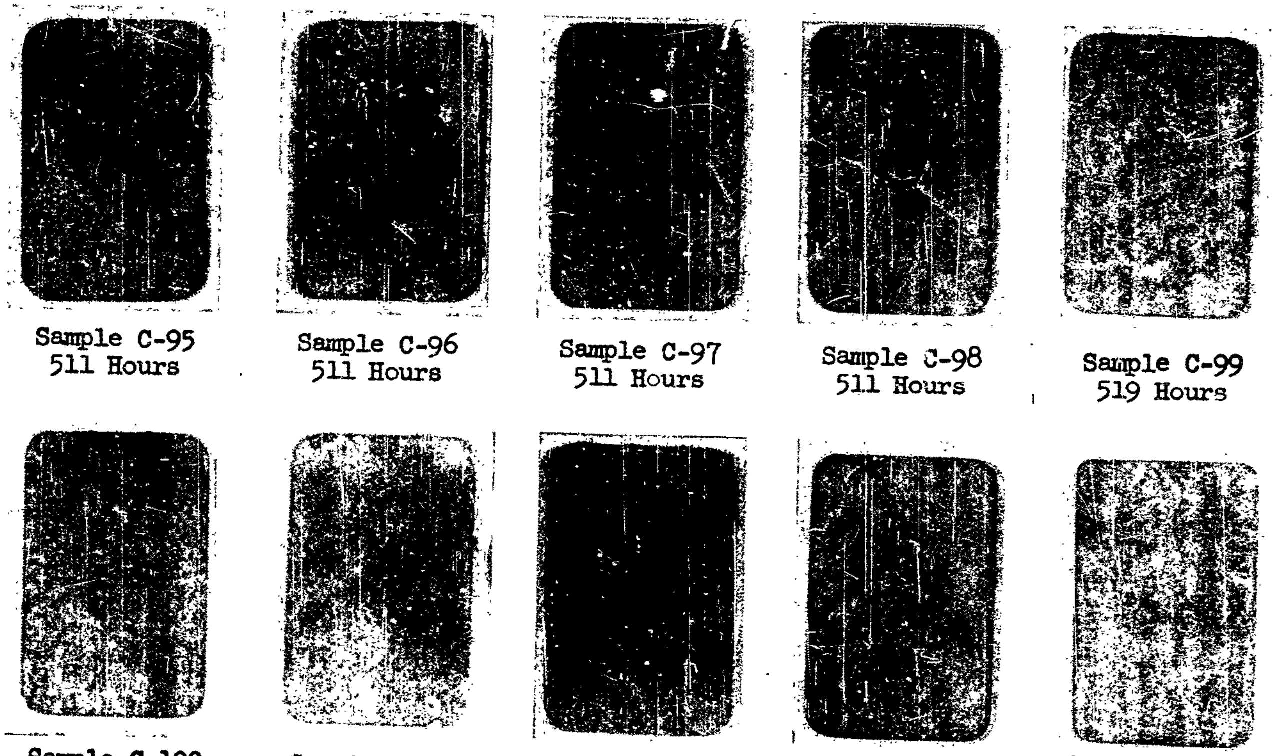


FIGURE 21 — EFFECT OF SURFACE PREPARATION UPON RESISTANCE TO OXIDATION AT 1800 F

ONE LAYER 0.010" AL–CR–SI SPRAY COATING



Sample C-95
511 Hours

Sample C-96
511 Hours

Sample C-97
511 Hours

Sample C-98
511 Hours

Sample C-99
519 Hours

Sample C-100
505 Hours

Sample C-101
505 Hours

Sample C-102
500 Hours

Sample C-103
500 Hours

Sample C-104
500 Hours

FIG 22 (P1101, P1149)

0.8X

PANELS OF Al-Cr-Si COATED MOLYBDENUM AFTER OXIDATION TESTS IN AIR FOR 500 HOURS AT 1800°F, GRIT-BLASTED WITH COARSE-GRADE Al_2O_3 PRIOR TO SPRAYING

To determine the effects of embedded iron grit particles on the frequency of flaws that developed in a coating during the oxidation test, two sets of ten panels were roughened with iron grit. One set was treated by immersion in hot concentrated hydrochloric acid, followed by washing in alcohol and ether before spray coating; the other set received no treatment, but was spray coated immediately after grit blasting. The 20 specimens were spray coated with the single layer, aluminum-chromium-silicon composition, diffusion treated at 2000°F and subsequently subjected to the oxidation test at 1800°F. The results of the oxidation test on these 20 panels and on a similar group which had been grit blasted with aluminum oxide are presented in Figure 21 in graphical form.

From these experiments with grit blasting it was concluded that the best surface preparation consisted in blasting with iron grit, followed by acid cleaning to remove embedded grit particles. In the series of ten panels, treated in this manner, all ten panels endured for 500 hours at 1800°F without failure; only one panel exhibited a flaw in the coating. This flaw was very minor, as can be seen in the photograph of Sample C-115 in Figure 23. A photograph of the other group of ten panels that had been iron-grit blasted but not acid cleaned is shown in Figure 24.

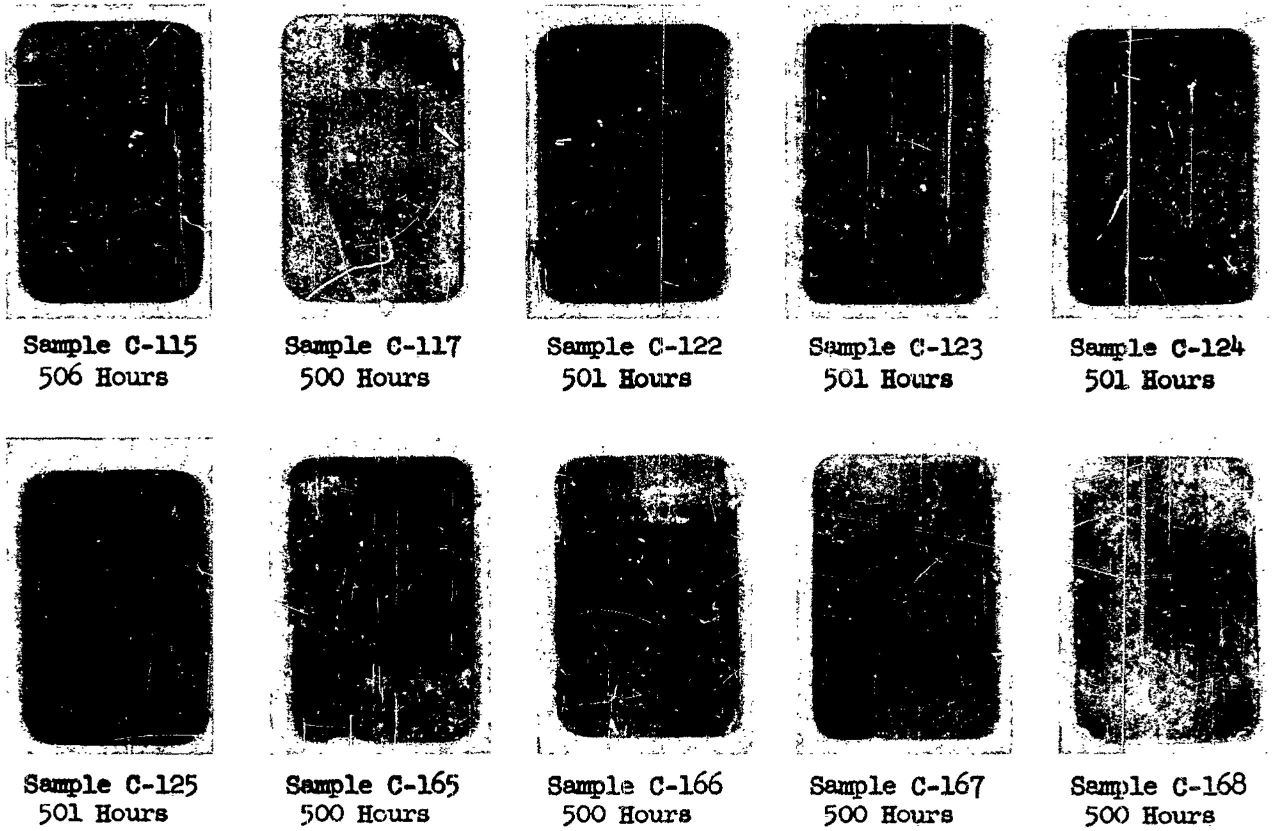
On the basis of these experiments, the techniques of mechanical spraying and of roughening by iron grit, followed by acid cleaning, were proposed as the regular procedure for the preparation of specimens for future spray coating studies. As confirmation of the validity of the proposal, 75 consecutive regular oxidation test specimens which had been prepared by the newly adopted procedure sustained exposure to air for 500 hours at 1800°F without failure. The test specimens had the aluminum-chromium-silicon coating and were prepared in several groups. Only eight of the 75 panels developed detectable flaws in the coatings. These tiny flaws appeared at the edges of the samples after 300-400 hours of exposure. These results attest to the dependability of the process which can be expected to benefit evaluations of other coating compositions.

Mechanically Finished Coatings

Preparation of Specimens

To determine the feasibility of mechanically finishing metal-spray coatings to a smooth surface, five bars of unalloyed molybdenum 5/8-in.-dia by 4-in. long were spray coated with the single-layer aluminum-chromium-silicon coating and five similar bars were coated with Colmonoy No. 5 alloy. The bars were blasted with iron grit, acid cleaned, washed and then sprayed, using the mechanized equipment and the procedure described in Part I.

After diffusion treating the bars for two hours in purified hydrogen at 2000°F, their cylindrical surfaces were ground in accordance with the procedure given in Part II until a coating 0.005-in. thick remained; the resulting surfaces had a smooth appearance.



Sample C-115
506 Hours

Sample C-117
500 Hours

Sample C-122
501 Hours

Sample C-123
501 Hours

Sample C-124
501 Hours

Sample C-125
501 Hours

Sample C-165
500 Hours

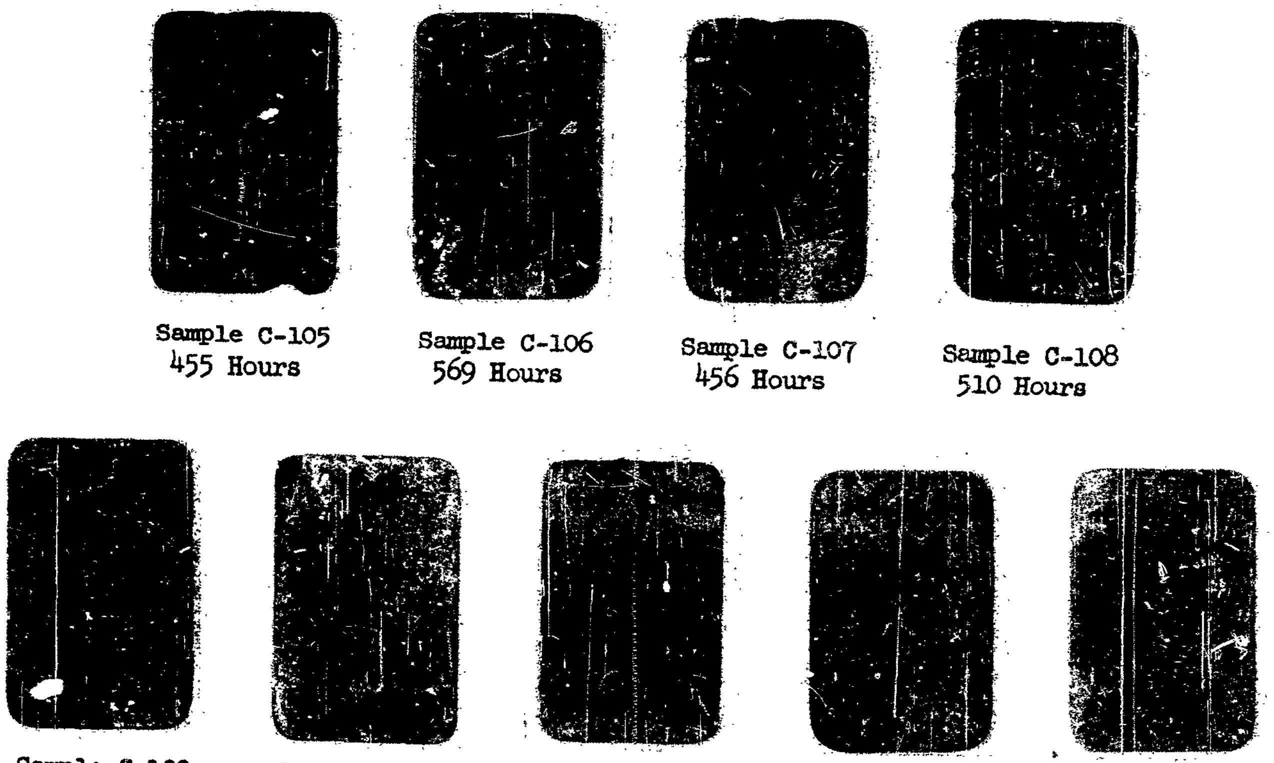
Sample C-166
500 Hours

Sample C-167
500 Hours

Sample C-168
500 Hours

FIG 23 (P1103, P1148) 0.8X

PANELS OF Al-Cr-Si COATED MOLYBDENUM AFTER OXIDATION TESTS IN AIR FOR 500 HOURS AT 1800°F, GRIT-BLASTED WITH SAE GRADE G-25 IRON GRIT AND CLEANED IN ACID PRIOR TO SPRAYING



Sample C-105
455 Hours

Sample C-106
569 Hours

Sample C-107
456 Hours

Sample C-108
510 Hours

Sample C-109
510 Hours

Sample C-110
510 Hours

Sample C-112
514 Hours

Sample C-113
514 Hours

Sample C-114
514 Hours

FIG 24 (P1102, P1175)

0.8X

PANELS OF Al-Cr-Si COATED MOLYBDENUM AFTER OXIDATION TESTS IN AIR FOR 500 HOURS AT 1800°F, GRIT-BLASTED WITH SAE GRADE G-25 IRON GRIT PRIOR TO SPRAYING

Oxidation Tests with Mechanically Finished Coatings

The bars were subjected to the regular oxidation test procedure in air at 1800°F. The five bars of each coating endured for 500 hours without failure, their surfaces remaining very smooth (80-100 microinches on Profilometer). The condition of the bars after the oxidation test is illustrated in the photographs of Figures 25 and 26.

After the 500-hour exposure at 1800°F, four bars from each set were tested in air at 2000°F. The results presented in Table 5 show that the first failure with the aluminum-chromium-silicon coating occurred in 283 hours at 2000°F; two bars failed in 451 hours; one bar endured for 500 hours without failure. The first failure with the Colmonoy No. 5 coating occurred after 83 hours at 2000°F; one failure was exhibited after 175 hours; two bars endured for 500 hours without failure.

Examination of the surfaces of the bars after testing at 2000°F revealed that the aluminum-chromium-silicon coatings were still quite smooth, but contained small flaws in the coating at unfailed areas. The Colmonoy coatings had a wrinkled surface and were considerably rougher than the aluminum-chromium-silicon coatings. The roughness was first noted after about 80-100 hours of testing.

The tests with the round bars showed that smooth surfaces can be produced on the aluminum-chromium-silicon and Colmonoy No. 5 coatings by a conventional grinding procedure and that these coatings, only 0.005-in. thick, remain smooth for at least 500 hours in air at 1800°F. Both coatings also had the capacity to protect molybdenum from oxidizing at 2000°F for considerable lengths of time.

PART IV

ELECTROPLATED CHROMIUM COATINGS

Electroplating of molybdenum with nickel, chromium, and "nickel plus chromium" for protection against oxidation at elevated temperatures has been investigated to a limited extent. The most promising results were obtained with chromium plating. Nickel coatings were not as oxidation resistant as chromium coatings. The "nickel plus chromium" coatings in many cases blistered during the initial period of oxidation testing; with the panels that did not blister, oxidation test results, however, were still inferior to those obtained with chromium plating.

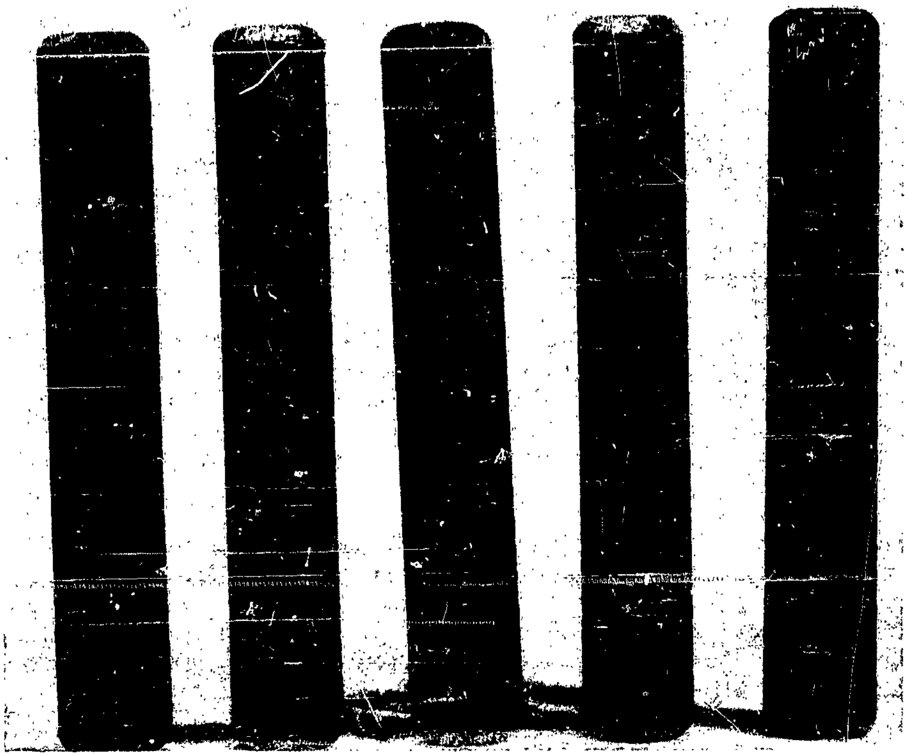


FIG 25 (P1138) 1X

MOLYBDENUM BARS HAVING 0.005 IN. THICK MECHANICALLY FINISHED Al-Cr-Si COATING, AFTER EXPOSURE TO AIR FOR 500 HOURS AT 1800°F

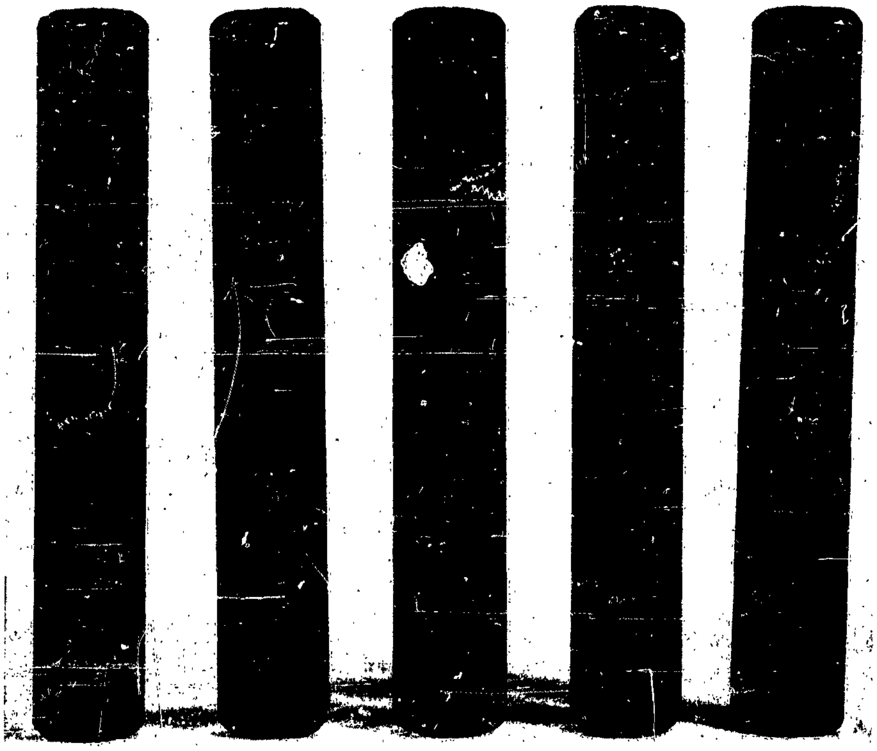


FIG 26 (P1139) 1X

MOLYBDENUM BARS HAVING 0.005 IN. THICK MECHANICALLY FINISHED COLMONOY NO. 5 COATING, AFTER EXPOSURE TO AIR FOR 500 HOURS AT 1800°F

TABLE 5

RESULTS OF OXIDATION TESTS IN AIR AT 1800° AND 2000°F WITH 0.005-IN. THICK MECHANICALLY FINISHED COATINGS

Coating Composition	Specimen No.	Life of Coating 1800°F	Life of Coating 2000°F
Single-layer Al-Cr-Si	1	500 hr[1/]	not tested
	2	500	283 hr
	3	500	500[1/]
	4	500	451
	5	500	451
Colmonoy No. 5	6	500	175
	7	500	500[1/]
	8	500	500[1/]
	9	500	83
	10	500[1/]	not tested

1/ Tests were discontinued after 500 hours' exposure; specimens had not failed

Specimens and Equipment for Electroplating

The plating of the molybdenum specimens was performed by several commercial electroplaters. The molybdenum specimens electroplated were flat panels 2 in. by 2 in. by 0.050 in. or were bars approximately 1/2 in. dia by 2 in. long. Considerable difficulty was experienced in plating both types of specimens because of the necessity of maintaining electrical contact points on the specimens while in the plating bath. The most satisfactory method developed for plating flat panels consisted of using a special rack equipped with "bleeders" to prevent plating build-up on edges. The rack provided three electrical contact points. During plating, the contact points were shifted so that the molybdenum at the original contact points could be plated.

Shifting of contact points on the panels during plating was not entirely satisfactory; there was a tendency to leave thin spots in the plating at the contact points. The necessity for shifting of contact points during the plating of the round bar specimens was avoided by brazing a stainless steel terminal wire on one end of the bar. Electrical contact was maintained continuously through the terminal wire. This method was later found to be unsatisfactory in oxidation tests with the plated bars because of the resultant selective oxidation of the specimen at the brazed joint.

Oxidation Test Results

The initial work with molybdenum panels electroplated with chromium was conducted with 19 specimens having plating thicknesses in the range 0.00035-0.006 in. Oxidation tests conducted in air at 1700°F showed that a plate 0.003 to 0.006 in. thick was capable of protecting molybdenum for 500 hours, but the results were not consistent. Inconsistency was attributed to pinhole porosity in the plating. An attempt was made to eliminate pin-hole porosity by subjecting the specimens to a diffusion treatment of four hours at 2000°F in dry hydrogen before testing. The treatment was neither beneficial nor deleterious. The results obtained were similar to the results for the untreated samples.

Eleven of the 19 specimens had plating thicknesses in the range 0.003-0.006 in. Six of the eleven specimens failed in 5-480 hours; the remaining five sustained exposure to oxidation at 1700°F for 500 hours; three of this group of five sustained an additional 500-hour exposure at 1700°F (total of 1000 hours at 1700°F). Those which endured the 1000-hour exposure at 1700°F were subjected to oxidation at 2000°F; failures occurred in 25, 80 and 148 hours, respectively.

The preliminary results with the chromium plated panels were encouraging and established the technical feasibility of protecting molybdenum from oxidation with electroplated chromium, but it was recognized that certain plating variables, or combinations of variables, would have to be studied and closely controlled if satisfactory coatings were to be produced consistently. Metallographic examination of numerous chromium plated panels revealed the network of cracks characteristic of many electrodepositions of chromium; therefore, it was assumed that failures in the oxidation test were attributable to these cracks. Crack-free chromium plates were desired for tests and an industrial plating laboratory offered to prepare a group of eight specimens by special processes, attempting to tailor the processes to molybdenum. The specimens were 1/2 in. dia and 2 in. long; for electrical contact a stainless steel wire 1/8 in. dia was attached to one end of each specimen by brazing with Colmonoy No. 6. The specimens were immersed in the plating bath so that the top end of the cylindrical specimen was 1/8 in. below the surface of the bath. The brazed joint and 1/8 in. of the wire, therefore, were also plated with chromium. The plate on all specimens was 0.004 in. thick.

The specimens were subjected to the regular oxidation test in air at 1800°F in the as-plated condition. Daily inspection at 75°F revealed that after less than 24 hours' exposure the molybdenum at the brazed joint of all specimens was being oxidized; the rest of the specimen was protected. A proper protective envelope apparently was not obtained at the brazed connection. This was probably due to the presence of three different metals--stainless steel, Colmonoy No. 6 alloy, and molybdenum--at the brazed area, each metal having a different plating characteristic.

Since the plating at all other areas appeared to be protective, the brazed end of each specimen was cut off, about 1/4 in. of the specimen being removed. The exposed molybdenum was sprayed with the single-layer aluminum-chromium-silicon coating. The oxidation testing of the chromium plating was resumed after the sprayed coating was diffusion treated for two hours in purified hydrogen at 2000°F.

The eight specimens resisted oxidation for 500 hours of testing at 1800°F. Oxidation tests were then continued at 2000°F until the coatings failed. The results of the tests are presented in Table 6. The specimens sustained exposures at 2000°F for periods of time in the range 23-171 hours before failure occurred.

The results are sufficiently promising to justify further evaluation of chromium-plated specimens in future tests.

TABLE 6

RESULTS OF OXIDATION TESTS IN AIR AT 1800° AND 2000°F WITH CHROMIUM-PLATED MOLYBDENUM BARS 1/2-IN. DIA BY 2-IN. LONG (APPROXIMATELY 0.004 IN.-THICK PLATING)

Specimen No.	Life in Oxidation Tests, hr 1800°F	 2000°F
1	500[1/]	55
2	500	79
3	500	23
4	500	55
5	500	23
6	500	56
7	500	171
8	500	171

[1/] Oxidation tests were discontinued at 1800°F after 500 hours' exposure; testing to failure was resumed at 2000°F

SUMMARY OF RESULTS

It has been shown that the spray coating of molybdenum with oxidation-resistant alloys by means of commercial metallizing equipment is a practical method of preventing the oxidation of molybdenum in air for at least 500 hours at 1800°F. The coating can be applied without impairing the elevated-temperature properties of molybdenum-base alloys. The method involves the following steps:

(1) The molybdenum article is prepared by slightly rounding edges and corners, blasting with iron grit and acid cleaning to remove embedded iron particles; this provides a roughened surface to facilitate mechanical bonding of the coating to the molybdenum.

(2) A coating 0.010-0.015-in. thick is applied with a metallizing gun; the gun is moved mechanically to insure application of a uniformly thick coating.

(3) The sprayed article is heated in purified hydrogen at 2000°F for two hours to consolidate the coating and to obtain a metallurgical bond of the coating to the molybdenum.

Twelve different alloys have been found to be promising as coating materials. Molybdenum panels coated with these alloys have been subjected to oxidation in flowing air at 1700° and 1800°F for 500 hours without evidence of oxidation of the molybdenum. With the exception of the Colmonoy materials, the powdered alloys were mixed with aluminum for spraying because of their relatively high-melting points. Aluminum served as a binder for the alloy. A list of the alloys follows:

(1) Cr-Si Alloy
(2) Cr-Mo-Si Alloy
(3) Fe-Si Alloy
(4) Ni-Si Alloy
(5) Si-Fe-Cu-Mg Alloy
(6) Fe-Cr-Si Alloy
(7) Mo-Ni-Si Alloy
(8) Aluminum Alloy 13 (wire)
(9) Aluminum Alloy 43 (wire)
(10) Si+Al Powder Mixtures
(11) Colmonoy No. 5 Alloy
(12) Colmonoy No. 6 Alloy

On the basis of spraying characteristics, appearance of the coating and oxidation protection, the following coatings were selected for more extensive testing:

(1) Single layer: 0.010 in. 20% Al + 80% Cr-Si alloy

(2) Three layer: Layers 1 and 3 - 0.003 in. Aluminum Alloy 13
Layer 2 - 33% Al + 67% Cr-Si alloy

(3) Single layer: 0.010 in. Colmonoy No. 5 alloy

Specimens with the above three coatings were subjected to additional tests with the following results:

(1) Ductility Tests. Elevated-temperature creep tests, used to evaluate the capacity of the coatings to sustain plastic deformation showed that the three coatings had the capacity to withstand 2-5% elongation in 100 or 500 hours at 1800°F while continuing to protect molybdenum from oxidation in air.

(2) Gradient-Temperature Oxidation Tests. Data obtained in the ductility tests demonstrated that the three coatings could protect molybdenum from oxidation in air for 500 hours at temperatures up to 1800°F.

(3) Thermal Shock Tests. A special apparatus devised to repeat automatically a 90-second cycle in which three coated specimens are heated rapidly in a gas flame to 1800°F and cooled in an air blast to 80°F was employed to test the three coatings; the following results were obtained:

Coating	No. of Cycles before Failure No. 1	No. 2	No. 3
(a) 3-layer Al-Cr-Si	36	44	40
(b) 1-layer Al-Cr-Si	571	569	509
(c) 1-layer Colmonoy No. 5	218	225	133

Originally the panels were grit blasted with aluminum oxide to facilitate mechanical bonding of the sprayed coating and the coating was applied by manual movement of the gun. When these procedures were used, out of 20 consecutively coated specimens, only five endured exposure for 500 hours at 1800°F; the others failed in exposures lasting from 234-450 hours.

Metallographic examinations revealed that small particles of aluminum oxide grit remained embedded in the surface of the molybdenum panel and prevented the formation of an essential diffusion bond between the coating and the base metal. Manipulation of the metal spraying guns resulted in nonuniform coating thickness. To avoid these difficulties, iron grit was substituted for aluminum oxide in the blasting process, and the roughened panels were treated with concentrated hydrochloric acid to remove any embedded particles of iron. An automatic, mechanical apparatus was constructed to regulate the movement of the spray gun to assure uniform and reproducible coating applications. When these modified procedures were used, 75 consecutively coated specimens sustained exposure to moving air at 1800°F for 500 hours without failure.

The single-layer Al-Cr-Si coating and the Colmonoy No. 5 coating were applied to round bars to determine the feasibility of grinding the coating to smooth surfaces. Tests with five bars of each coating demonstrated that smooth surfaces could be obtained by grinding and that coatings 0.005-in. thick protected the molybdenum on all bars from oxidizing for 500 hours at 1800°F. At the end of the test, all bars still had very smooth surfaces (80-100 microinches on Profilometer).

Four of the five bars of each coating were subjected to additional oxidation tests at 2000°F, with the following results:

Al-Cr-Si Coating:

1 specimen failed after 283 hours of testing
2 specimens failed after 451 hours of testing
1 specimen did not fail in 500 hours of testing

Colmonoy No. 5 Coating:

1 specimen failed after 83 hours of testing
1 specimen failed after 175 hours of testing
2 specimens did not fail in 500 hours of testing

The tests were discontinued at 500 hours. At the end of the 2000°F test, the surfaces of the Colmonoy No. 5 specimens were slightly wrinkled and scaly. The Al-Cr-Si specimen had a smooth surface, but contained small coating defects.

Oxidation tests at 1700° and 1800°F with molybdenum specimens electroplated with chromium showed that consistent results can be obtained if plating conditions are carefully controlled. This was demonstrated in oxidation tests at 1800°F, using eight specimens plated with chromium to a thickness of 0.004 in. All specimens sustained exposure for 500 hours without failure.