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A STUDY OF CERAMIC COATINGS FOR HIGH-TEMPERATURE PROTECTION OF MOLYBDENUM

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National Bureau of Standards

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SUMMARY

The high melting point (4750° F) and comparatively large potential supply of molybdenum suggest that this metal may be useful at temperatures above the melting points of most metals and alloys. In order to use it at high temperatures in the presence of oxygen, however, the molybdenum must be protected against oxidation, and hence it is logical to apply a protective ceramic coating. Several such coatings were developed and applied in the form of water suspensions or "slips" to specimens of molybdenum, by dipping or spraying, after which the pieces were dried and fired at a temperature of 2150° F in oxygen-free atmospheres. Tests of the coated pieces included (1) heating in a gas-oxygen flame, (2) heating at constant temperature in an air atmosphere, (3) thermal-shock tests, and (4) service testing of parts that were finished with a selected ceramic coating in the blast of ram-jet engines.

The results of these various tests indicated that the oxidation of the molybdenum was greatly retarded by the best of the ceramic coatings tried. In an air atmosphere at 1650° F, unprotected 0.040-inch molybdenum sheet was found to decrease to one-half of its original thickness in 1/2 hour. There was no decrease for ceramic coated molybdenum heated for 70 hours under the same conditions.

At a gas temperature approximating 3500° F, giving a surface temperature on the specimen of 2600° F or more, only short-time protection of the molybdenum was attained. The oxidation rate at these high temperatures was found, however, to be sufficiently retarded by the presence of the ceramic coating to make the use of coated molybdenum feasible for special high-temperature applications in which prolonged service is not required.

One current use of these ceramic coatings is to protect molybdenum pitot tubes which are built into the nozzle end of ram-jet engines of a type used for pilotless aircraft. These tubes, which are subjected to a gas temperature of about 3000° F, are expendable and need not last over 5 minutes. Test of a coated tube under simulated service conditions indicated a life in excess of 45 minutes.

INTRODUCTION

The lack of materials having the required properties for operating temperatures in excess of 1800° F is a restrictive influence in the development of ram jets, pulse jets, turbojets, and rockets. If suitable materials were available, design problems for jet engines would be less complicated and greater efficiencies could be obtained.

Most of the usual heat-resistant alloys begin to melt when heated within the temperature range 2400° to 2600° F. Of the metals having melting points greatly exceeding this temperature range, only such scarce metals as platinum and iridium, melting at 3180° and 4260° F, respectively, have sufficient resistance to oxidation at high temperatures to be used without protection. Aside from the question of physical properties, the cost of such metals and the limited supply make their use on a large scale prohibitive.

Other metals that have high melting points, but do not have good oxidation resistance, include titanium (3270° F), thorium (3350° F), zirconium (3450° F), boron (4150° F), molybdenum (4750° F), tantalum (5160° F), and tungsten (6100° F). The last three are of especial interest from the standpoint of potential applications in very high-temperature service. Preliminary tests have indicated that both tungsten and tantalum may be coated to protect against oxidation at elevated temperatures; however, more complete tests have been conducted on molybdenum and are reported herein.

Molybdenum is used as a major constituent of important alloys and is available commercially in substantial quantities. In addition, there are comparatively large ore deposits in the United States. The one characteristic of the unprotected molybdenum metal which precludes its use in high-temperature applications for which its strength would be adequate is its poor resistance to oxidation. A number of applications might be forthcoming, however, if this fault could be overcome by a protective coating that would sufficiently retard the rapid disintegration of the molybdenum in oxidizing atmospheres.

The present report describes some results that have so far been obtained on ceramic coatings for molybdenum. Although these results are of a preliminary nature, a coating was developed for molybdenum that has met an actual service demand. The investigation is being conducted at the National Bureau of Standards under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics.

FUNDAMENTAL CONSIDERATIONS

When unprotected molybdenum is raised to a dull red heat in an air atmosphere, the volatile oxide $\left(MoO_3\right)$ forms slowly (reference 1). As the temperature is increased, the production of oxide becomes more rapid until the metal burns vigorously with a voluminous production of white fumes of MoO_3.

In the application of a ceramic coating to molybdenum this tendency toward rapid oxidation must be considered. If the coating were applied and the firing done in an air atmosphere, a substantial amount of oxide would form before the coating had fused and would prevent proper adherence of the coating to the metal. Firing must therefore be done in a nonoxidizing atmosphere. Furthermore, the expansion coefficient of the coating must be adjusted to that of the metal.

One source of difficulty that can be expected in coating molybdenum is the gas absorbed in the metal. Appreciable quantities of gas (reference 1) may be present in relatively pure molybdenum sheet, and if gas is evolved when the metal is heated to high temperatures, it tends to cause blistering of the coating. In order to minimize serious disruption of the coating as a result of this blistering, the consistency of the ceramic coating during firing and use should permit sufficient flow to reseal the areas punctured by escaping gases. A preferable alternative, if attainable, would be to use metal that is substantially gas free.

Finally, any coating intended to protect molybdenum from oxidation in air at high temperatures should be substantially impervious to air. The coating, therefore, must be rich in glassy phase or, if entirely crystalline, must be so constituted and fired as to produce a dense, nonporous mass, free of shrinkage cracks.

SOURCES OF MOLYBDENUM USED

A supply of 0.040-inch rolled-sheet molybdenum and 0.040-inch-diameter molybdenum wire was obtained from one commercial source, and a second lot of rolled sheet, from another.

A spectrochemical analysis made on these samples of the metal showed the principal impurities to be chromium, copper, and iron, each of which was present in amounts between 0.01 and 1.0 percent. Minor impurities (less than 0.01 percent) present in all three samples were silicon, titanium, nickel, calcium, beryllium, and aluminum.

FORMULATION OF COATINGS

In order to obtain coatings having a combination of high refractoriness, impermeability, and adherence, the approach chosen was to apply first a base coat having a high content of glassy phase, then a very refractory cover coat having little or no glassy phase, and finally to seal the pores of the cover coat with a top coat of the same characteristics as the base coat, each coating being separately fired.

Since the coefficient of thermal expansion of molybdenum is only about half that of ordinary low-carbon steel and about one-third that of many high-temperature alloys, it was necessary to seek a frit composition having much lower expansion coefficient than the frits suitable for incorporating in coatings for the high-temperature alloys. (See reference 2.)

Another characteristic required of the frit constituent of coatings for molybdenum is a much higher viscosity than was required for the frits previously developed for coatings of the heat-resisting-alloy type.

This combination of requirements made it logical to seek a suitable composition for the frit constituent of a coating among available types of commercial glasses, with the intent of formulating and preparing a series of progressive modifications for comparison with the initial composition. For this purpose a glass was chosen having the composition shown as 402C in table 1.[1] Variations from this base frit were formulated and prepared and these are listed in table 1 as 402M to 410M.

The smelting temperature of all these frits was high, ranging from 2650° to 2750° F, but in all cases no appreciable undissolved material was present at the time of pouring.

Qualitative comparison was made of the characteristics of base coats prepared by ball milling frit 402C with zirconium oxide (zirconia "A", reference 3) in amounts of 0, 10, 20, 30, and 40 parts of zirconium oxide to 100, 90, 80, 70, and 60 parts by weight, respectively, of frit 402C. Five parts of Florida kaolin were incorporated in each batch. From observation of the performance of these base coats when applied to small specimens of molybdenum and heated at 2000° and 2100° F in an electric furnace, a tentative selection of the combination having 20 parts zirconium oxide and

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[1] A quantity of glass of this composition, designated as N-51a, was supplied by courtesy of the Kimball Glass Co.

80 parts frit was made for use in further work. Accordingly, base coats were prepared in these proportions from each of the frits given in table 1. These base coats were applied in thickness approximating 0.007 inch to specimens of sheet molybdenum and tested at a metal temperature of 2000° F. For reasons described under the heading entitled "Heating Tests in an Electric Furnace with Air Atmosphere," the results so far obtained have not provided an adequate basis for comparison of the efficacy of these frits as constituents of base coats for molybdenum. In most of the subsequent experiments reported herein the commercial glass 402C was used as the frit constituent, since it gave good promise and was available in an adequate supply.

The characteristics of greatest importance in the cover coat were deemed to be (a) refractoriness, (b) appropriate thermal expansion, and (c) a suitable physical structure under firing and service conditions. A suitable physical structure requires a balance between a vitreous seal to prevent oxygen permeating from the atmosphere to the metal and, at the same time, a porous structure to prevent gases that escape from the metal from forming large blisters. Such blisters upon bursting might expose so much of the metal surface that rapid oxidation would occur and make healing impossible.

A variation in the physical structure of the cover coat at high temperature was attained by using as the principal constituents calcined kaolin and zirconium oxide. In all the coatings sufficient raw kaolin was added to act as a bond and maintain a workable consistency of the water suspension or slip, in which form the coatings were first applied.

Table 2 lists five coatings used on the specimens referred to in this report and also indicates milling time, firing temperature, and thermal-expansion coefficient.

The only difference between mill batches of cover coats M-8 and M-33 consists in the fineness of the zirconium oxide used. Coatings of the M-8 type tended to crack during firing, probably as a result of shrinkage. This tendency was considerably reduced by use of the coarser material.

The details of preparation of the coatings for molybdenum were substantially the same as for the ceramic coatings for heat-resistant alloys reported previously (reference 2).

APPLICATION AND FIRING OF COATINGS

The coatings were applied in the form of water suspensions, or slips, to the sandblasted molybdenum by either spraying or dipping.

After drying, the test specimens were fired, many of them in a fused-silica tube furnace with controlled atmosphere. A sketch of this gas-fired furnace is shown in figure 1. Temperatures up to 2550° F inside the tube could be attained by supplementing the air supply with a slight amount of oxygen. Without extra oxygen, temperatures of 2400° F could be reached. The temperature was controlled during firing to ±20° F by manual adjustment of the gas valve. Most of the specimens used in this study were fired at 2150° F by introducing into the hot furnace, heating for about 5 minutes, removing from the furnace, and cooling in air.

In the firing operations a positive gas pressure was maintained within the furnace tube by allowing the gas to bubble through a $\frac{1}{2}$-inch depth of water after passing through the firing chamber. In most cases, carbon dioxide from commercial cylinders was used as the atmosphere. No steps were taken to dry or purify the gas before its entry into the furnace.

Some of the specimens that the tube furnace would not accommodate were fired in a Hayes, Globar heated, controlled-atmosphere furnace, having a working chamber of 16 by 10 by 6 inches and a maximum safe operating temperature of 2500° F. The gas and air inputs to the combustion chamber of this furnace were adjusted to give, in the working chamber, a substantially oxygen-free atmosphere containing 11.4 percent of carbon dioxide, 1.0 percent of carbon monoxide, and the remainder nitrogen. Temperature control was achieved with a recorder-controller operating from a radiation pyrometer.

Most of the coatings were applied in total thicknesses ranging from 0.008 to 0.030 inch. This thickness was normally attained by several applications with separate firing operations between coats. Experience indicated that to allow for escape of gases the base coat should be applied at between 0.0015 and 0.0025 inch. Later coats could be applied in considerably thicker layers and, for best quality of finish, at a firing temperature of about 100° F lower than that used for the first coat.

Nichrome supports were used during the firing of all experimental parts.

TEST PROCEDURES AND RESULTS

Heating Tests in an Electric Furnace with Air Atmosphere

Although a test for the protective properties of the various coatings when the specimens were heated for prolonged periods at various constant temperatures in an air atmosphere was desirable, the difficulties involved in carrying out a test of this type were such as to make it a problem to obtain reliable data. Specimens 2 inches in length and 1/2 inch wide, prepared from 0.040-inch-thick molybdenum sheet and coated as described, were tested at various temperatures in an electric furnace. In many cases during these tests oxidation proceeded rapidly from the spot where the support wire passed through the hole in the molybdenum, while in other cases, failure occurred at an edge or corner on an otherwise sound specimen. Because of the volatile nature of the molybdenum oxide, any small break in the coating allowed progressive oxidation to take place, and in several prolonged tests all the metal disappeared, leaving a hollow shell of the coating material.

Regardless of these difficulties, the test gave some indications of the durability of the coating, especially at the lower temperatures. In a few tests at 2000° F coated specimens were heated for as long as 20 hours with no apparent deterioration of the metal. One specimen still showed good protection after 70 hours of heating at 1650° F. A section cut through this specimen is shown as C in figure 2. The base coat M-5, which was applied to this particular piece, differed from the other coatings described herein. It consisted of 75 parts of -325 mesh, fused zirconium oxide, 25 parts of frit 402M, and 5 parts of Florida kaolin. This was fired at 2550° F to give a slightly porous porcelain-like structure. This structure was subsequently sealed by two applications of M-3 (see table 2) fired at 2150° F.

Specimen A, in figure 2, illustrates the uncoated molybdenum metal while specimen B shows a section of the same metal after 30 minutes of heating at 1650° F. It will be noted that specimen B, with no coating, has been reduced to one-half of its original thickness in only 30 minutes of heating while specimen C has maintained its full thickness throughout 70 hours of heating.

Oxygas Flame Tests

Flame tests were made of coated molybdenum specimens 3/4 by 2 by 0.040 inch using the apparatus shown in figure 3. The welding torch, positioned as shown in the photograph, was operated from controlled pressures of both oxygen and natural gas and, in all cases, was adjusted to give a strongly oxidizing flame.

The temperature of the specimen surface was measured with a calibrated optical pyrometer rigidly clamped so as to be focused on the hottest part of the specimen. In determining the temperature, the emissivity for the coatings was taken as 0.50.

In making a test, the torch was first lighted at a distance of about 4 inches from the specimen. The torch assembly was then slowly moved in toward the specimen until a surface temperature of 1800° F was attained. This temperature was held constant for 5 minutes, after which the torch was again moved closer until the surface temperature was 400° F higher. This procedure of raising the temperature 400° F and holding for 5 minutes was continued until either failure of the coating occurred or until a test at 3400° F was completed.

The temperatures obtained in this way apply to the surface of the coating only, and owing to the insulation effects the temperature of the metal was considerably lower. In order to obtain an indication of the metal temperature under the test conditions, the M-13-33 coating on the back of one specimen was ground off at two small spots directly behind the test area. Small holes 1/4 inch apart were next drilled into the metal. A 22-gage platinum wire was peened into one of these holes and a 22-gage platinum and 10-percent-rhodium wire, into the other. The back of the specimen was recoated to give a smooth surface and the specimen placed in position for flame testing. The temperatures of the metal obtained by this procedure for a coating thickness of 0.033 inch and for the various temperatures of the test surface are given in table 3. These data, showing the temperature of the metal to be approximately 360° to 900° F below that of the surface of the coating, indicate qualitatively that important insulation effects may be obtained with ceramic coatings.

The results obtained from these oxygas flame tests are shown in table 4. Little or no effects were noted at 1800° F on any specimen. At 2200° F small blisters formed at the hottest area of the glazed surface of all specimens, but these quickly rehealed as the heating continued. At 2600° F the coating at the hottest area had apparently become more stable and blister formation in the seal coat was noted on only one specimen, while at 3000° F no blisters were present. At 3400° F the two specimens of coating M-13-35 failed by localized melting of the ceramic. Coating M-13-33, which had a high zirconium-oxide content (see table 2), showed neither melting nor blistering after the 5-minute heating at 3400° F.

Figure 4 shows three M-13-33 coated specimens that had been heated 1/2 hour, instead of 5 minutes, at 2600°, 3000°, and 3400° F. No thickness loss was indicated for any of these three coated specimens. A specimen of uncoated molybdenum sheet was subjected to the same flame condition that had given a surface temperature of 3400° F on the coated specimen. During the heating, the uncoated specimen reached a temperature of 2800° F. Intense fuming of the oxide was noted under these conditions. Within 3 minutes a hole had been burned through the unprotected metal specimen, which is shown with the coated specimens in figure 4. Figure 5 shows a heavy deposit of the crystalline molybdenum oxide formed in a symmetrical pattern by sublimation on the cooler portions of the refractory supports during the heating operation.

Thermal-Shock Tests

For the thermal-shock tests use was made of the previously described oxygas flame-test equipment. In making a test, the flame was lighted and adjusted so that the surface temperature could be raised to 2600° F in approximately 30 seconds. This temperature was then held for an additional $1\frac{1}{2}$ minutes. The gas was next turned off for 1 minute. During this period the specimen was cooled in the stream of oxygen, the surface dropping below a visible red heat in less than 15 seconds. After 1 minute of cooling, the metal temperature, determined with a thermocouple attached as previously described, was approximately 400° F. This cycle was repeated until either failure occurred or a total of 10 cycles was accumulated. The results of these tests for coatings M-13-33 and M-13-35 are shown in table 5.

In some respects these results fall into the conventional pattern whereby increasing resistance to thermal shock goes with decreasing thickness of coating and with decreasing thermal-expansion coefficients of the coating material, but in one important respect they do not. Since the exterior of a specimen normally is both heated and cooled more rapidly than the interior, it is necessary for the coating to have a lower coefficient of thermal expansion than the underlying metal in order to maintain an approximation of equality in the rates of expansion and contraction of the metal and the coating. Minimizing the differential rate of dimensional change correspondingly reduces the development of stresses leading to failure of the coating from sudden temperature changes. The results obtained with coating M-13-33 and M-13-35 at 0.030-inch thickness are in harmony with these considerations. At the 0.030-inch thickness, coating M-13-35 withstood 10 quenches without damage while coating M-13-33 failed before one cycle was completed. The thermal-expansion coefficients of 6.22×10^{-6} per degree centigrade for M-33 and 4.25×10^{-6} per degree centigrade for M-35, as given in table 2, are entirely consistent with this result, since the one value is above and the other below that of molybdenum $(5.5 \times 10^{-6}$ per degree centigrade$)$. The improvement in thermal-shock resistance obtained on the M-13-33 coating as the thickness of the coating was decreased to 0.017 inch is also in conformity with normal expectations.

The unusual feature of the results in table 5 is that the thinner coatings of M-13-35 failed under conditions that the heavier coatings withstood. The key to this unusual behavior lay in the blistering characteristics of the M-35 cover coat as compared with the M-33. The M-35 showed a greater tendency to blister, probably because it more readily entrapped gases escaping from the metal. The quantity of this evolved gas is, however, a function of the temperature of the metal. The thinner coatings of both types would be expected to permit the metal to become hotter under the test conditions than the thicker coatings, but only the M-13-35 coating developed serious blistering. The raised portions of the coating, being insulated from the underlying metal, changed temperature much more rapidly than the surrounding material, and hence failed more readily because of the resulting large dimensional changes.

Service Tests of Coated Tubes

In figure 6 are shown two molybdenum pitot tubes approximately 10 inches long, the white one of which has been given a ceramic coating, except for a distance of 1 inch at the end not heated in service. These tubes had $\frac{1}{4}$-inch outside diameters and $\frac{1}{16}$-inch walls. The coating was applied to both inside and outside surfaces by submersion of the specimen into the slip, followed, after drying, by a spray-coat reinforcement at the end exposed to high temperature. After the spray coat was dried, the specimen was fired at 2150° F on a Nichrome supporting rack in the oxygen-free atmosphere of the previously mentioned Hayes furnace.

The coated tubes were used for instrumentation purposes in ram jets. Each tube was positioned with the curved end directly in the blast at the nozzle of the jet and was subjected to a computed gas temperature of approximately 3000° F. Protection for a period of about 5 minutes was all that was required of these tubes.

Flame tests[2] with propane fuel, made of one coated tube, showed that with an air-fuel ratio of 18.6:1.0 (18.5 percent excess air) and a gas temperature of 3500° F protection was practically unimpaired after 5 minutes. When the air-fuel ratio was dropped to 13.3:1.0 (no excess air) giving a gas temperature of 3600° F, the tube was found to be still serviceable after an additional 33 minutes. It should be pointed out, however, that the tube operated at temperatures considerably below those of the gas. Temperature measurements on the tube with an optical pyrometer gave values of about 2450° and 2650° F with air-fuel ratios of 18.6:1.0 and 13.3:1.0, respectively. There was no distortion of the tubes during test, and the damage to the coating was confined to that caused by blistering.

Twenty-four of the tubes as shown in figure 6 were given exterior and interior coatings of the M-3-8 type and one with coating M-13-35. These were used in ram jets attached to the wings of aircraft. One tube with each type of coating was returned after undergoing this service and examined with a binocular microscope. Neither tube had failed in service, except for breaking near the end that was welded to a steel tube and which operated at a relatively low temperature.

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[2] These tests were made under the supervision of Dr. Ernest F. Fiock in charge of combustion research at the National Bureau of Standards.

On the M-3-8 tube (coating thickness, 0.006 in.) which had been in service for 15 minutes there were numerous areas where the outer layers of the coating had flaked off, but the microscopic examination showed plainly that a thin protective coating still remained and there was little or no evidence of oxidation of the metal, which was still in good condition.

The M-13-35 tube (coating thickness, 0.008 in.) had undergone 45 minutes of service without any considerable oxidation of the metal except at two spots. One of these spots, shown as O at the upper end of the tube in figure 7, was originally not so well protected as on the M-3-8 tube inasmuch as it had not been reinforced with extra coating at the tip. As a result, the protection at this point terminated during the test and considerable oxidation occurred. The dark area indicated as O at the central section of the tube was believed to have resulted from damage to the coating during installation. Oxidation had progressed sufficiently at this area to halve the thickness of the tube wall. No serious damage had occurred elsewhere, although several small spots appeared to have lost the coating, possibly near the end of the 45-minute test period.

The speckled appearance of the coating on the tube at B in figure 7 is caused by healed blisters in the coating. There is evidence also of flow of the coating, which is apparent at F in the photograph as ripples in the surface. This flow was believed to have occurred at the moment the blisters formed. The blisters caused added obstruction to the smooth flow of the high-velocity gases. The flow of the coating reduced this obstruction.

DISCUSSION

The primary cause of failure of the coatings for molybdenum described in this report when operated at gas temperatures approaching 3500° F was gas evolution from the metal leading to the formation of blisters in the coating.

It is known that the molybdenum metal contained large quantities of gas. Some of this gas was expelled during the coating operation, but considerable amounts were still being evolved during the subsequent heat treatments. This residual gas came out slowly during the high-temperature treatment and in so doing caused blisters to form in the coating. Even though the blisters rehealed after breaking, the metal was momentarily exposed to oxidation. The effect of this behavior was probably cumulative because the fluxing action of the molybdenum oxide absorbed by the original coating as the blisters healed caused a deterioration of the coating. Also, the laboratory tests indicated that the tendency of a coating to entrap escaping gases as blisters may in some measure govern its resistance to thermal shock.

Efforts to eliminate the gas from the metal prior to coating proved ineffective. In one experiment molybdenum wire was heated for 15 minutes at about 3000° F in vacuo. After cooling, the wire specimens were removed from the vacuum and coating M-3 applied. No decrease in blistering tendency was noted. It is possible, however, that more refractory coatings, applied at temperatures considerably above the expected operating range, might considerably reduce blistering in service. Preliminary experiments have indicated some promise in this direction.

The relatively short-time protection afforded by the presently developed coatings at high temperatures automatically restricts their use to expendable items in which a high melting temperature is essential for a short period. In addition to such applications as the pitot tubes shown in figures 6 and 7, coated thermocouples and resistance thermometers made of high-melting-point metals furnish examples of possible uses in which even short-time protection can be valuable.

Although the test results illustrated by figure 2 demonstrate definite potentialities, the extended use of coatings for protection of molybdenum at operating temperatures in the range from 1300° to 1800° F does not appear probable, as long as suitable heat-resisting alloys for these temperatures are available. There is no assurance, however, that the high-cobalt alloys will be available in sufficient quantity to meet a greatly expanded demand. If this demand should develop, these alloys could probably be supplemented by high-molybdenum alloys for use at temperatures beyond those now feasible provided suitable protection against oxidation could be effected by means of a ceramic coating.

All tests so far performed have indicated the great importance of complete and sustained coverage. The oxide which forms on the metal surface is highly volatile at temperatures as low as 1650° F and therefore an uncoated molybdenum specimen will completely disappear when heated for sufficient time to high temperatures in an atmosphere containing appreciable amounts of oxygen.

Little published information is available regarding the high-temperature strength of molybdenum, but from data on wires at temperatures up to 1600° F (reference 4) indications are that molybdenum has considerably more strength than platinum. This expected greater strength of coated molybdenum as compared with platinum, together with its higher melting point and lower cost, would favor its use in certain high-temperature applications.

The thermal shock involved in service operations with the pitot tubes, consisting of one heating and one cooling, did not appear to be an important source of failure since coatings of both higher and lower thermal-expansion coefficient than the metal gave adequate protection. There was evidence, however, that the cooling of the higher-expansion coating (M-3-8) after service resulted in damage which would have been important in additional cycles of use of the same coated tube. For service conditions involving repeated heatings and coolings, it would be advisable to use only coatings of suitable low thermal-expansion coefficient.

CONCLUSION

The results obtained with the ceramic coatings on molybdenum specimens have demonstrated that short-time (10 to 45 min) protection of molybdenum in oxidizing atmospheres at gas temperatures up to 3500° F is possible. Even such limited duration of protection meets certain current service requirements for expendable items having very short operation periods, for example, the protection of instruments such as pitot tubes, thermocouples, and resistance thermometers for which even a brief period of operational life is of value in obtaining much-needed data. The results point to the need for continued research to prolong the period of protection which can be achieved at these high gas temperatures.

National Bureau of Standards
Washington, D. C., December 31, 1947

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TABLE 1.- COMPUTED OXIDE COMPOSITIONS OF FRITS PREPARED FOR USE IN MOLYBDENUM COATINGS

Oxide \ Frit	402C (1)	402M	403M	404M	405M	406M	407M	408M	409M	410M
SiO_2	73.3	74.7	74.0	74.0	74.0	74.0	74.0	74.0	70.0	66.0
B_2O_3	9.1	9.6	10.0	10.0	10.0	10.0	10.0	10.0	14.0	18.0
Al_2O_3	6.6	5.6	5.0	2.5	-----	2.5	-----	3.0	5.0	5.0
ZnO	----	0.1	-----	-----	-----	2.5	5.0	-----	-----	-----
CaO	0.8	0.9	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
BaO	2.1	2.2	2.5	5.0	7.5	2.5	2.5	2.5	2.5	2.5
Na_2O	6.7	6.4	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0
K_2O	0.7	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
MgO	----	-----	-----	-----	-----	-----	-----	2.0	-----	-----
Total	99.3	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[1] By chemical analysis.

TABLE 2.- MILL BATCHES, MILLING TIMES, FIRING TEMPERATURES, AND THERMAL EXPANSIONS OF SEVERAL CERAMIC BASE COATS AND COVER COATS AS DEVELOPED FOR APPLICATION TO MOLYBDENUM

Coating (1)	Coating type (2)	Mill batch in parts by weight (3)		Milling time (hr) (4)	Firing temperature (°F)	Expansion coefficient (5)
M-3	Base coat	Frit 402M ZrO_2(-325) Fla. kaolin Sodium nitrite Water	80 20 5 0.1 42.5	4	2150	5.14×10^{-6}
M-8	Cover coat	ZrO_2(-325) Fla. kaolin Water	95 5 50	1/2	2050	(6)
M-13	Base coat	Frit 402C ZrO_2(-40,+80) Fla. kaolin Sodium nitrite Water	80 20 5 0.1 42.5	4	2150	5.26
M-33	Cover coat	ZrO_2(-40) Fla. kaolin Water	95 5 35	$2\frac{1}{2}$	2050	6.22
M-35	Cover coat	Calcined kaolin[7] Fla. kaolin Water	94 6 46	$2\frac{1}{2}$	2050	4.25

[1] Coating designations such as M-13-35 refer to cover coat M-35 over base coat M-13 with a thin top coat of M-13 as a glaze.

[2] The compositions listed as base coats were used also as seal coats, applied as a glaze over the cover coats.

[3] Designations such as (-325) refer to grain size. (-40,+80) means that the material passes a No. 40 sieve but is retained on a No. 80. ZrO_2 refers to partially stabilized fused zirconium oxide (zirconia "A", reference 3).

[4] Milling time applies to a 1000-gram dry charge in a 1-gallon-size ball mill operating at 60 rpm with a charge of 4000 grams of 1-inch-diameter porcelain balls.

[5] Values are given as linear expansions per degree centigrade over range 20° to 500° C and were determined by interferometer measurements.

[6] Values assumed to be nearly the same as that for coating M-33 which is the same as M-8 except for fineness of zirconia.

[7] Combination of refractory clays calcined at approximately 2600° F and ground to pass a 100-mesh sieve.

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TABLE 3.- TEMPERATURES OF COATING SURFACE AND CORRESPONDING TEMPERATURES OF METAL WHEN A SPECIMEN OF 0.040-INCH MOLYBDENUM HAVING A 0.033-INCH CERAMIC COATING (M-13-33) WAS HEATED WITH AN OXYGAS TORCH

Temperature of coating surface (°F) (1)	Temperature of metal (°F) (2)
1800	1440
2200	1725
2600	2115
3000	2365
3400	2505

[1] Determined with calibrated optical pyrometer using an emissivity of 0.50.

[2] Determined from thermocouple formed by peening 22-gage platinum and platinum and 10-percent-rhodium wires into small holes in the metal, drilled 1/4 inch apart, on the back side of the coated specimen.

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TABLE 4.- EFFECT OF OXYGAS-FLAME HEATING ON TWO CERAMIC COATINGS FOR MOLYBDENUM APPLIED AT COMPARABLE THICKNESSES

Specimen	Coating (1)	Thickness of coating (in.)	Effect of 5-minute surface heating at - (2)				
			1800° F	2200° F	2600° F	3000° F	3400° F
1	M-13-33	0.033	SPB,R	BF,R	NB	NB	NB
2	M-13-33	.038	NB	BF,R	NB	NB	NB[3]
3	M-13-35	.030	NB	BF,R	BF,R	NB	CM
4	M-13-35	.032	NB	BF,R	NB	NB	CM

[1] Both coatings consisted of 0.005 inch of M-13 as a base coat, with either M-33 or M-35 as a middle coat, and with M-13 applied at 0.002 inch as a blaze coat. Thus, specimen 1 consists of a ground coat of 0.005 inch of M-13, 0.026 inch of M-33, and finally a glaze of 0.002 inch of M-13.

[2] Letter notations indicate the following: NB, no blistering; BF, blisters forming; R, rehealing; CM, coating melted; and SPB, scattered pinpoint blisters. Temperatures by calibrated optical pyrometer using an emissivity of 0.50.

[3] On continued heating at 3400° F, specimen 2 developed a large blister over the hottest area. This blister broke at the center but a thin layer of coating remained on the metal beneath, and after 1/2 hour of further heating very little damage to the molybdenum had occurred.

TABLE 5.- RESULTS OBTAINED IN FLAME-TYPE THERMAL-SHOCK TEST WITH COATINGS M-13-33 AND M-13-35 APPLIED AT VARYING THICKNESS

Specimen	Coating	Coating thickness (in.) (1)	Number of thermal-shock cycles for failure (2)
1	M-13-33	0.017	> 10
2		.017	> 10
3		.017	7H
4	M-13-33	.023	2H
5		.023	> 10
6		.023	> 10
7	M-13-33	.030	1H
8		.030	1H
9		.030	1H
10	M-13-35	.016	5H[3]
11		.016	5H[3]
12		.016	4H[3]
13	M-13-35	.023	7H[3]
14		.023	>10
15		.023	>10
16	M-13-35	.030	>10
17		.030	>10
18		.030	>10

[1] Each specimen was prepared with an M-13 base coat of 0.007 inch and an M-13 seal coat of 0.001 inch with the cover coat, in each case, making up the remainder of the thickness.

[2] Thermal-shock cycle consisted in heating an area about 1/2 inch on the face of the $\frac{3}{4}$- by 2-inch specimen to a surface temperature of 2600° F in approximately 30 seconds, holding for an additional $1\frac{1}{2}$ minutes, and then quenching to a metal temperature of 400° F in 1 minute in a stream of oxygen. The letter H indicates that failure occurred during the heating part of the cycle.

[3] Failure by shattering of blisters formed during earlier treatment.

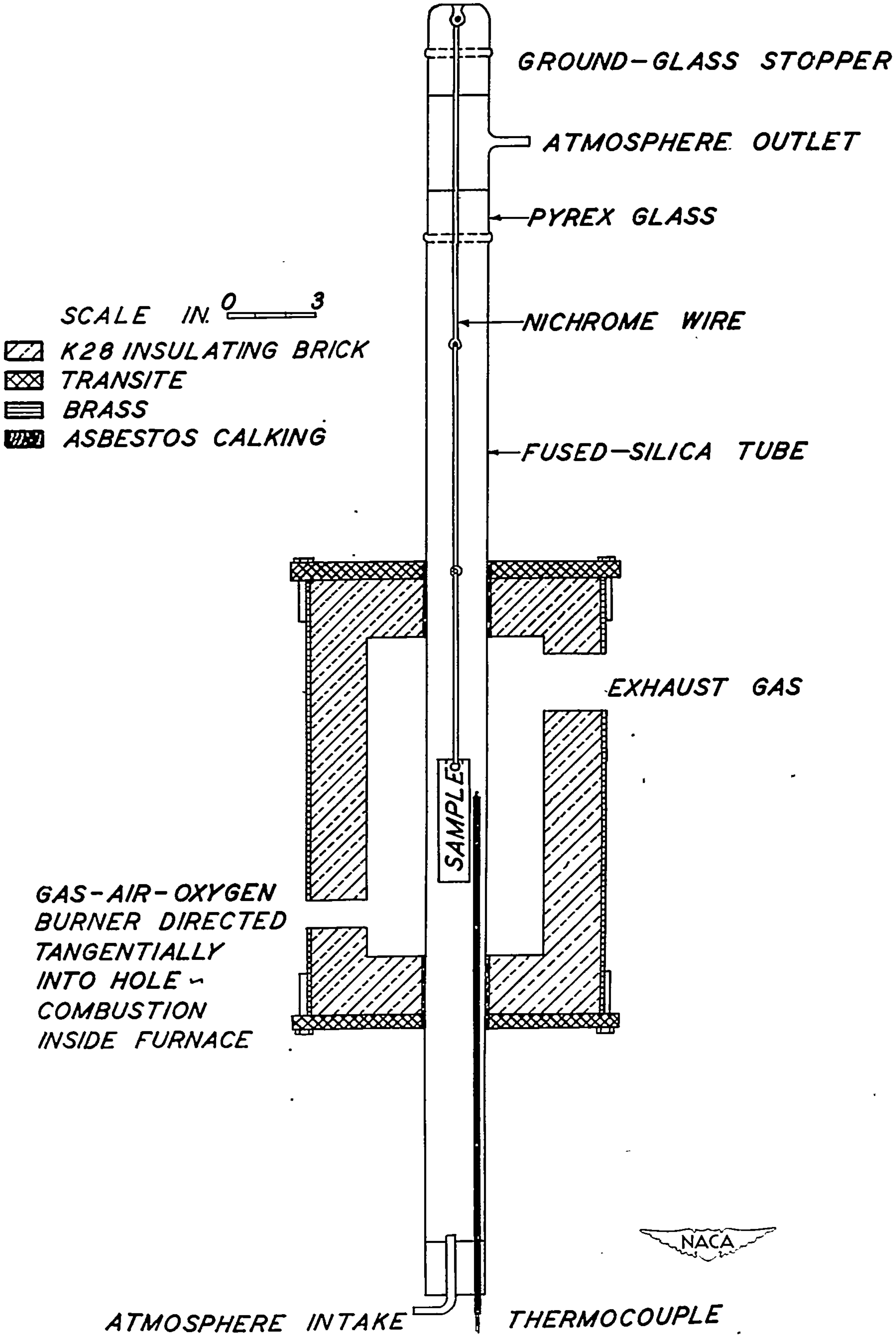

Figure 1.- Schematic diagram of fused-silica tube furnace used for controlled-atmosphere firing of ceramic coatings on molybdenum.

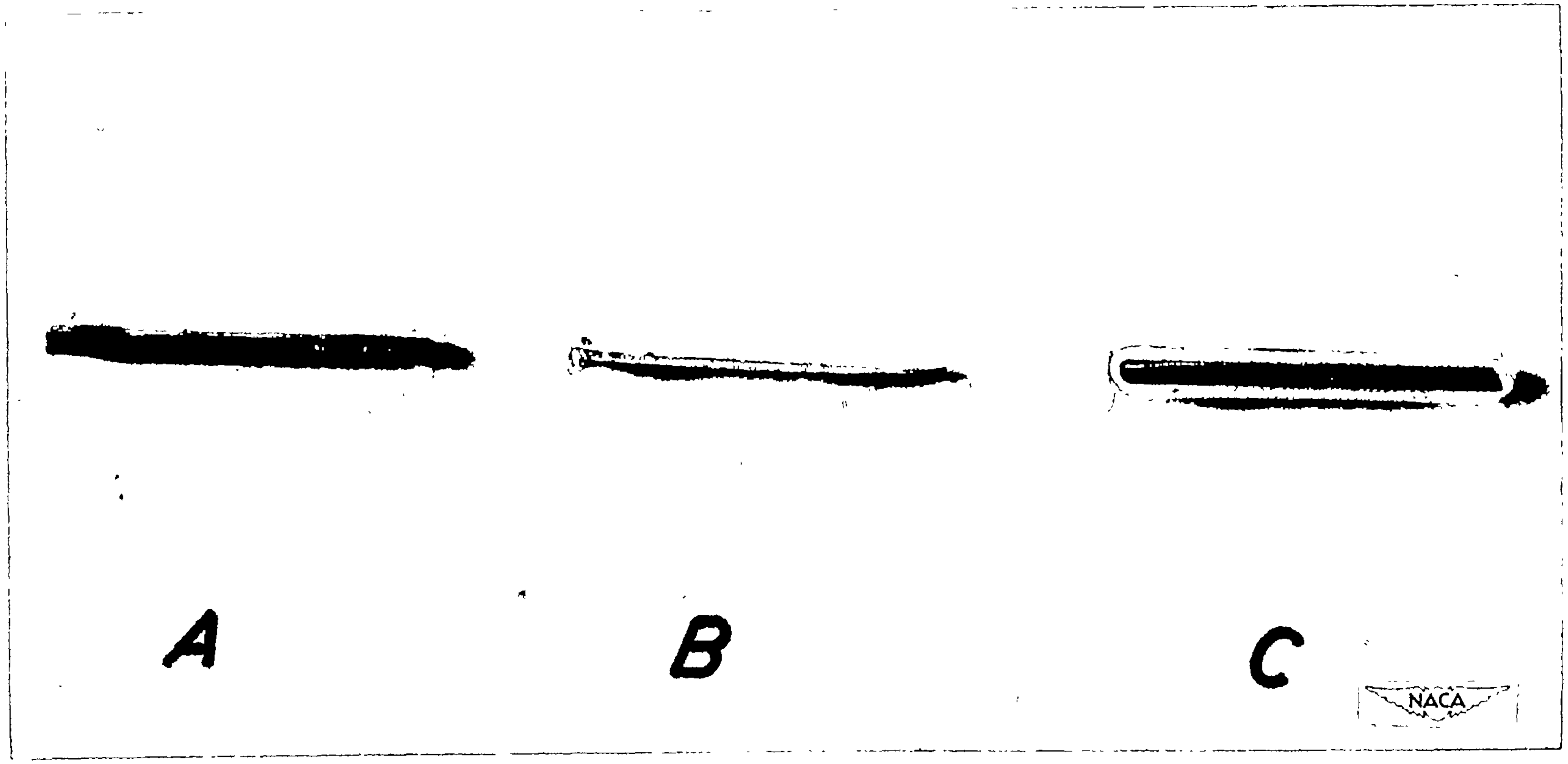

Figure 2.- Enlarged photograph (2.3X) of sections cut through coated and uncoated sheet molybdenum. Specimen A is the original uncoated molybdenum 0.040 inch thick. Specimen B is similar to A except that it has been heated for 1/2 hour in air at 1650° F, losing approximately half its thickness. Specimen C which has had a ceramic coating applied at a thickness of 0.028 inch has undergone 70 hours of heating in air at 1650° F with no evidence of oxidation of the metal.

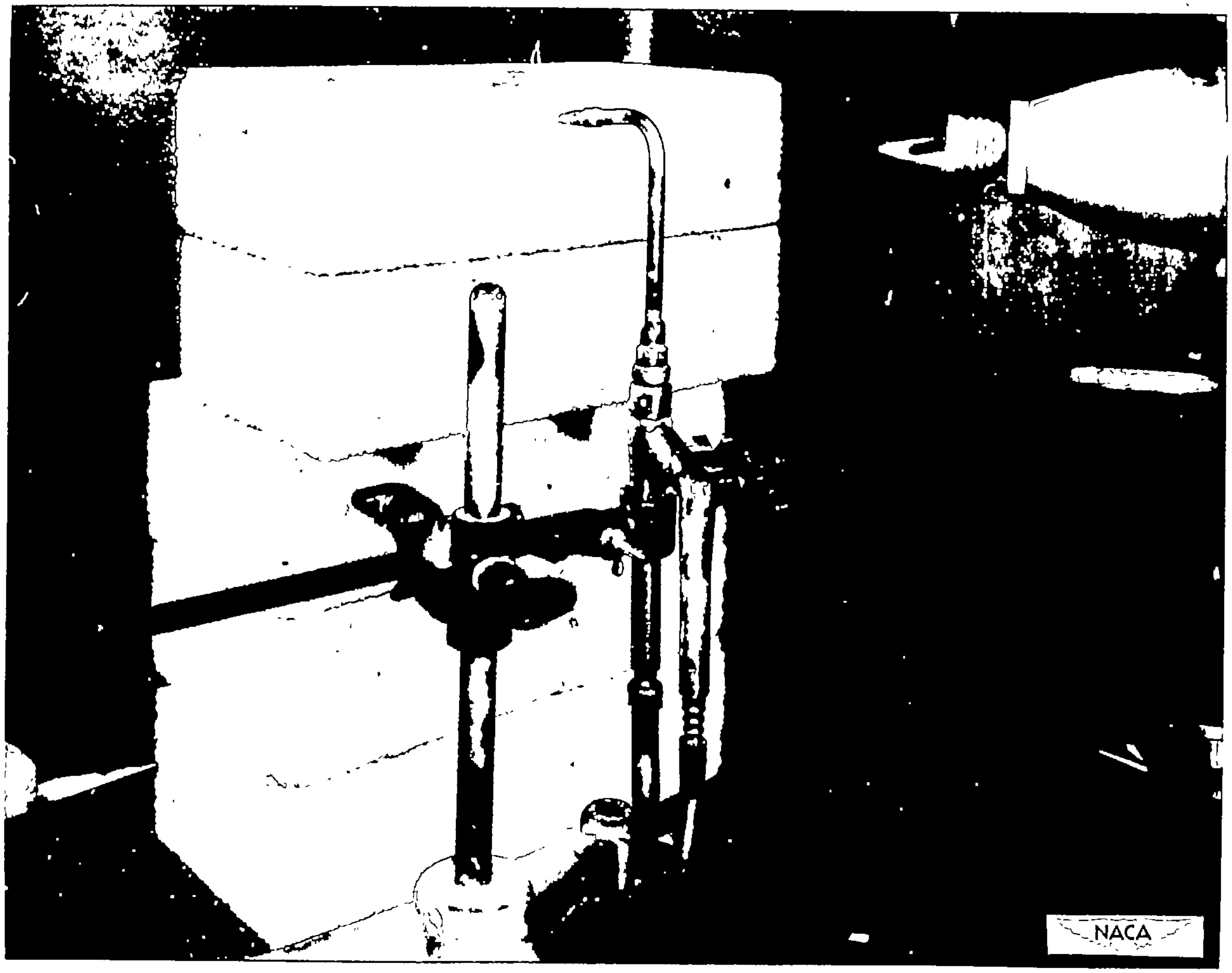

Figure 3.- Arrangement used for flame testing of coated molybdenum specimens. The welding torch operates from controlled pressures of oxygen and natural gas. Surface temperature, which is measured with a rigidly clamped optical pyrometer, is regulated by a movement of the torch toward or from the specimen and adjustment of oxygen and gas input.

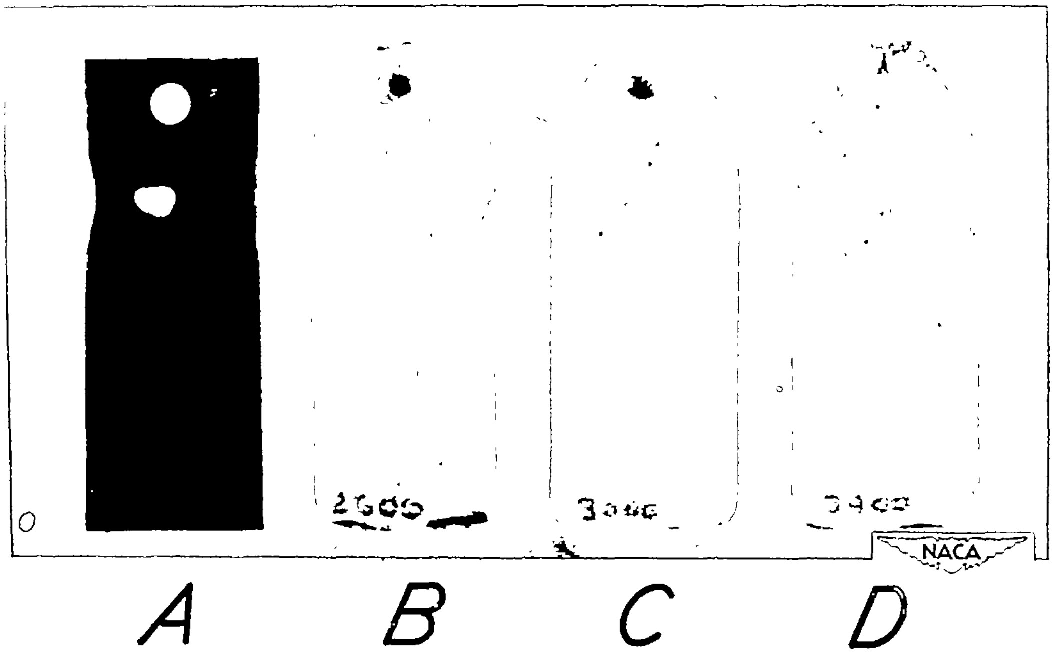

Figure 4.- Molybdenum specimens after exposure to flame testing. Specimens B, C, and D have been coated with M-13-33 at a total thickness of approximately 0.033 inch and have been treated for 30 minutes at surface temperatures of 2600°, 3000°, and 3400° F, respectively. Specimen A is uncoated and the hole was burned through it when it was treated for 3 minutes under the same flame adjustment as for D.

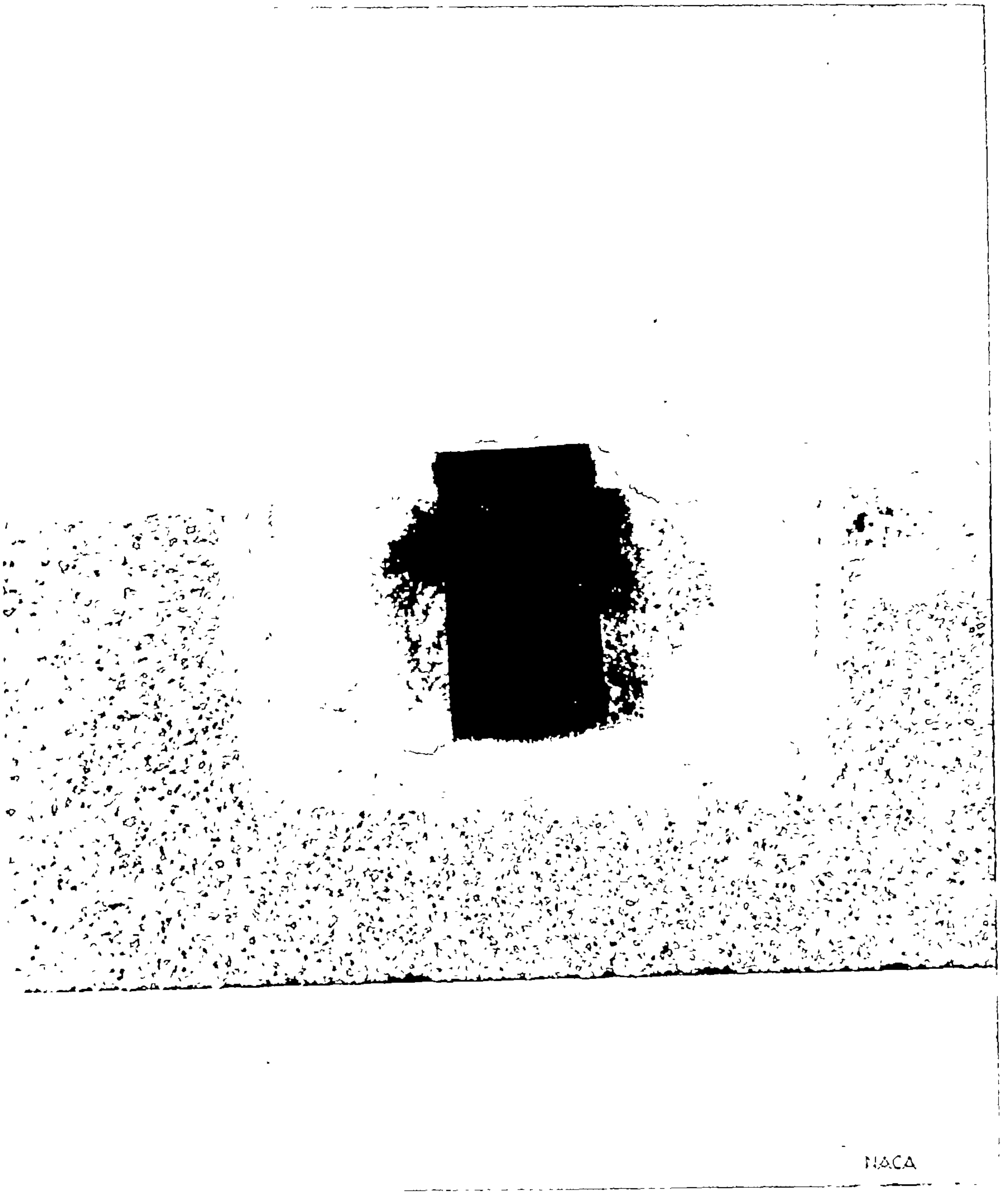

Figure 5.- Molybdenum-oxide condensate formed in a symmetrical pattern on cooler portions of refractory supporting structure by sublimation during 3 minutes of heating of an uncoated molybdenum specimen at 2800° F by oxygas flame. The test involved a voluminous production of white fumes of the volatile oxide.

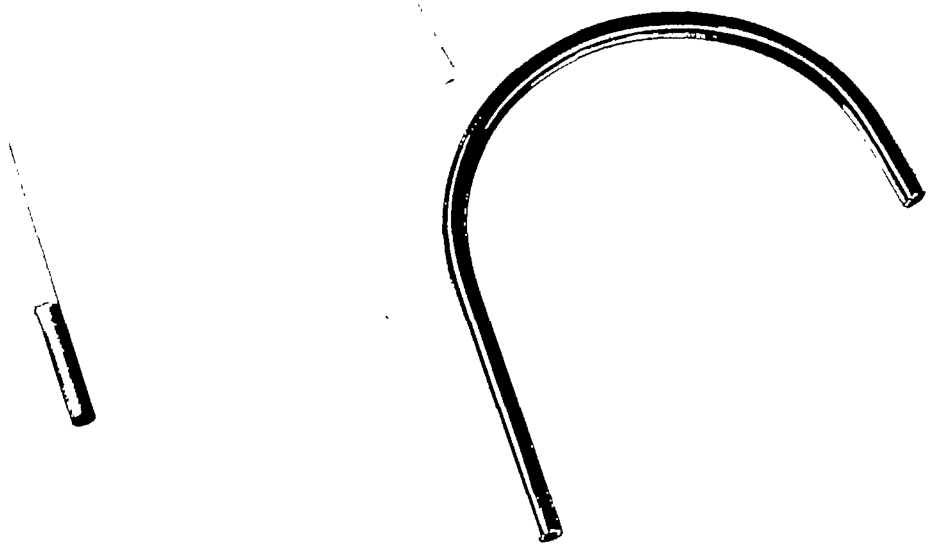

Figure 6.- Uncoated and coated molybdenum pitot tubes approximately 10 inches long, of a type used for recording pressures in the 3000° F blast of a ram-jet engine. The white tube has been given a ceramic coating except for a distance of 1 inch at the end not heated in service.

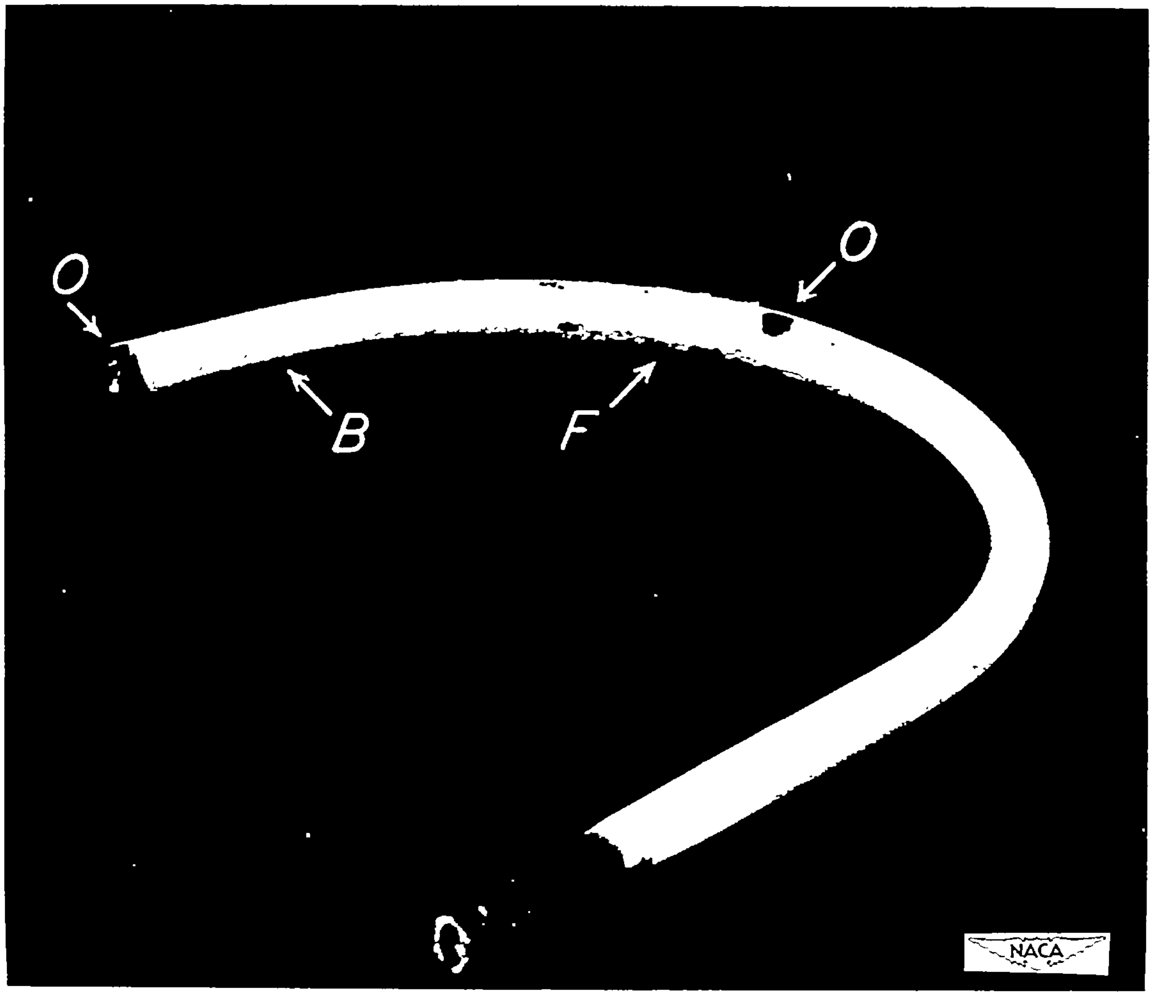

Figure 7.- Coated pitot tube of the type shown in figure 6 after 45 minutes of service operation in blast of ram jet at computed gas temperature of 3000° F. Although deterioration of the coating has occurred, the tubes have performed satisfactorily under conditions which would have caused serious oxidation of uncoated parts.