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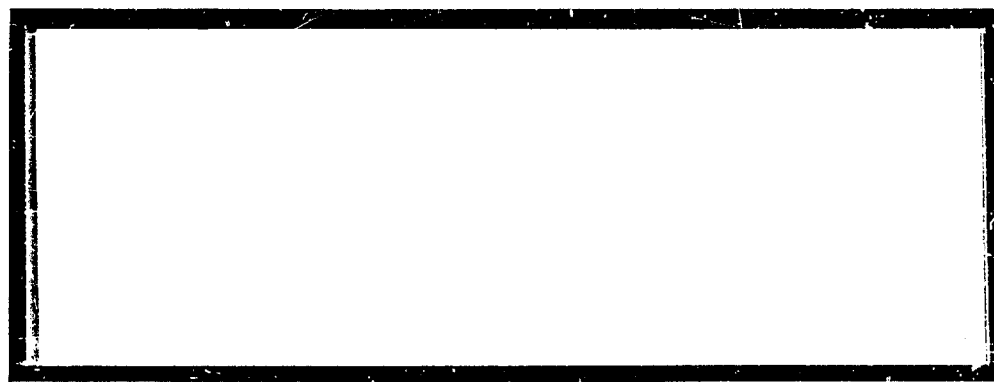


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METALS & CONTROLS INC.

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INCORPORATED

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**STUDY OF DUCTILE COATINGS FOR THE OXIDATION
PROTECTION OF COLUMBIUM & MOLYBDENUM ALLOYS**

31 MARCH 1964

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FOURTH BIMONTHLY PROGRESS REPORT

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ABSTRACT

Oxidation loss rates for platinum and platinum-10% rhodium alloy samples were determined to be 1.98 and 2.40 microinches per hour, respectively, at 2550 F in an air flow of 480 ipm. From extrapolation it was found that in the absence of interdiffusion of coating and base metal, 2.5 mils of platinum would protect the base metal for 100 hours at 3000 F in an air flow of 480 ipm.

An increase in dew point from about -40 F to 120 F for the air used in testing was seen to have an insignificant effect on the oxidation rate of pure platinum at 2200 F and 2550 F in an air flow of 24 ipm. This indicates that platinum does not react with water vapor at these temperatures, and an increase in humidity should simply serve to provide an increased percentage of non-reactive gas in the test atmosphere.

Tests on coating-base metal composites showed coated TZM and FS-85 to be attacked differently. Molybdenum from the TZM was found to diffuse through the coating and be removed at its surface as a volatile oxide. Oxygen penetrated the coatings on the FS-85 samples in a discontinuous manner, causing blisters of oxide to be formed which eventually burst through the coating. Details of the diffusion-oxidation mechanisms remain to be determined.

An attempt was made to prepare a platinum-10% rhodium clad FS-85 sample with an intermediate rhenium diffusion barrier layer. The components of the proposed composite were hot roll bonded in an evacuated package. However, the rhenium layer broke up during rolling and the composite was not suitable for testing. Other methods for preparation of this type of composite, such as electrolytic and vapor plating, are being considered.

Samples of platinum coated FS-85 and TZM with boron nitride as a diffusion barrier were prepared through chemical vapor deposition and hot press bonding techniques. Edge protection proved to be a problem in tests on these samples, as they always failed at the edges where no boron nitride had been deposited. Also, in hot press bonding platinum to the composite, the edges of the platinum were subjected to a shearing action which probably caused it to be much thinner there. It will be necessary to solve the "edge protection problem" for this type of composite before any significant test data may be obtained.

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I. INTRODUCTION

The objective of this program is to explore the potential for development of coatings which will afford oxidation protection for 100 hours on columbium and molybdenum alloys at temperatures up to 3000 F. Also, these coatings should be ductile or, at least, flexible, and must not significantly degrade the mechanical properties of the alloys.

One molybdenum and one columbium alloy were selected for these investigations. They are, respectively, TZM (Mo-.5Ti-.08Zr-.02C) and FS-85 (Cb-28Ta-10W-1Zr). These alloys are considered to be two of the more promising refractory metal alloys.

Platinum and platinum-10% rhodium alloy were chosen as coating materials on the basis of their oxidation resistance, ductility, and high melting point.

The principal efforts of the first three bimonthly periods (Ref. 1) included a review of pertinent literature, selection and ordering of materials, setting up equipment for preparation and testing of samples, running oxidation tests on coating materials, preparation and testing of coating-base metal composites, and work on the application of diffusion barriers to the chosen substrate metals. The work of the fourth period consisted primarily of preparing and testing coating-base metal and coating-diffusion barrier-base metal composites. Also, some further oxidation tests were conducted on platinum and platinum-10% rhodium alloy. A detailed discussion of the investigations undertaken and results obtained during the fourth period are presented below.

II. OXIDATION TESTS ON PLATINUM AND PLATINUM-10% RHODIUM ALLOY

Oxidation tests were conducted (using the same test setup as in the third period) to obtain the following information:

1. The rate of weight loss for platinum at 2550 F in a dry (dew point of about -40 F) air flow of 480 ipm.
2. The rate of weight loss for platinum-10% rhodium alloy at 2550 F in a dry (dew point of about -40 F) air flow of 480 ipm.
3. The rate of weight loss for platinum at 2200 F in a moist (dew point of about 120 F) air flow of 24 ipm.
4. The rate of weight loss for platinum at 2550 F in a moist (dew point of about 120 F) air flow of 24 ipm.

The results of the tests at the high air flow rate are presented, along with data at other flow rates from the third period report, in Table I. This table presents the results in a somewhat different

manner than in previous reports, giving rates of oxidation losses both as linear rate of weight loss in $\text{mg}/\text{cm}^2/\text{hr}$ and as thickness loss in microinches per hour.

An interesting comparison can be made between our data and that of General Electric (Ref. 2) and Battelle (Ref. 3), as is done in Fig. 1. The oxidation data obtained in this program compares favorably with that of General Electric at an air flow of about 240 ipm. However, data obtained at an air flow of 24 ipm differs greatly from that obtained by Battelle at a similar flow rate. The most likely source of this discrepancy lies in the difference between the surface areas of the samples used here and those used at Battelle. The samples used in their program had about 10 times as much surface area as the samples used in this program, and about 30 times as much surface area as the samples used by General Electric. Increases in surface area, particularly at low flow rates, will cause corresponding increases in the concentration of oxide vapor in the air layer directly above the sample. This, in turn, brings about a decrease in the rate of weight loss. Both Betteridge and Rhys (Ref. 4) and Hill and Albert (Ref. 5) have emphasized this point.

It is interesting to note that the slopes of the curves plotted in Fig. 1 are quite similar. This indicates that the activation energies are nearly equivalent, as might be expected.

Due to differences in experimental conditions, the platinum oxidation rates obtained by Hill and Albert and those obtained by Fryburg and Petrus (Ref. 6) are not directly comparable with those in Fig. 1. However, if nothing was present to catalyze the reactions, the activation energies obtained from their data should essentially match those obtained from the curves of Fig. 1. This hypothesis is confirmed in Table II, which presents the various activation energies obtained.

Previous studies of the oxidation of platinum metals in flowing air have generally used dry air. No reference was found, however, to indicate whether or not moisture might have any influence on the rate of oxidation of the platinum metals. As the proposed oxidation resistant platinum coatings might be expected to offer protection in air with varying degrees of moisture content, it was decided to determine what effect, if any, humidity would have on high temperature oxidation of platinum. Two tests were conducted, one at 2550 F and the other at 2200 F. The air for each was bubbled through a flask of water before entering the furnace at a flow rate of 24 ipm. The water picked up by the air raised the dew point to about 120 F as compared to the -40 F dew point usually attained. The results showed the increase in humidity to have little or no effect on the rate of oxidation. Apparently, the platinum and water vapor do not react under these conditions. The test results are given in Table III in comparison with results obtained in the dried air.

III. PREPARATION OF PLATINUM AND PLATINUM-10% RHODIUM ALLOY COATED FS-85 ALLOY AND TZM ALLOY SAMPLES

In the past, providing edge protection for samples with roll bonded platinum and platinum-10% rhodium alloy coatings has been a problem. It appears that this problem has now been overcome. This was accomplished by undercutting the base metal at the edges of the sample with an acid mixture ($40\text{HF}-30\text{HNO}_3-30\text{H}_2\text{SO}_4$), then pressing the edges together, using dies and a hydraulic press, and heating the dies and composite to red heat in air.

As it was not initially known what difficulties might be encountered in sealing sample edges by this method, simple and easily obtained dies were desired. Since 1 inch I.D. stainless steel pipe and a 1-1/4 inch diameter blanking punch were conveniently available, they were used in the preparation of the first samples. The punch was used to blank out the samples and two pieces of the pipe served as dies. After encountering difficulties in alignment of the dies, the bottom piece of pipe was replaced with a piece of Inconel rod. Good samples could be prepared using these dies, although samples often stuck to the Inconel rod, causing damage to the coatings. It was found that sticking could be prevented by simply placing a piece of paper between the sample and rod. However, a hole had to be drilled in the rod so that the gases given off by the paper during heating could escape without "blowing up" the sample. Sticking also occasionally occurred between the upper die and the sample edge. This was eliminated by using a little molybdenum disulfide lubricant on that die.

Fig. 2 shows the setup used for preparing most of the samples. These samples were 1-1/4 inches in diameter and, hence, a little too large for the oxidation test furnace. Therefore, they had to be bent before testing. One of these samples is shown in Fig. 3. A new rectangular die is being prepared for making rectangular 1 inch by 3/4 inch samples which would not require bending prior to oxidation testing.

IV. OXIDATION TESTS ON PLATINUM AND PLATINUM-10% RHODIUM ALLOY COATED TZM AND FS-85 ALLOYS

The apparatus used for these tests was the same as that used for determining oxidation rates of the coating metals. The composites used were prepared by roll bonding the coating metal to the base metal, undercutting the sample edges with acid, and sealing the edges by hot press bonding, in the manner described in the preceding section of this report. The coatings were about 3 mils thick.

Several tests were made on each coating-base metal composite at 2550 F, and a single test was made on platinum coated FS-85 alloy at 2200 F.

Most of the samples were tested in an air flow of 24 ipm, although two were tested in a 240-ipm air flow. As seen in Table I, the coatings could offer over a thousand hours protection at either of these flow rates at 2550 F, if there were no diffusion through the coating.

During each test the sample being tested was removed from the furnace, cooled, weighed, and examined for gross surface defects at intervals of 1 to 3 hours. A test would be terminated when the rate of weight change for the sample was definitely seen to be moving away from that expected for the coating metal.

It has been found to be difficult to determine the exact protective life of a given coating. Two criteria, (1) changes in rate of weight change, and (2) surface condition, may be used to indicate how protective a given coating is. However, in many cases, changes in the rate of weight change and surface condition occur gradually. Plots of weight change versus hours tested, given in Figs. 4, 5, 6, 7, and 8, give a better indication of this problem.

Fig. 4 shows a plot of weight loss versus time for a platinum clad FS-85 sample tested at 2200 F. For 55 hours the weight losses from this sample were essentially the same as those expected of pure platinum. After 55 hours the weight of the sample began to increase and open "blisters" formed in the platinum cladding. Except for these blisters the surface of the sample appeared otherwise good. A picture of the general surface condition of the sample is seen in Fig. 9. The grain structure has been revealed by thermal etching but the roll marks are still evident. Fig. 10 shows some of the open blisters on the surface of the sample.

The plots for platinum clad FS-85 tested at 2550 F are given in Fig. 5. Both samples began gaining small amounts of weight at the beginning of testing and it was thought that the coatings might be damaged. The surface appearance of the samples was good, however, and with continued testing each sample eventually began losing weight. In fact, one of the two samples (7-9) even began to lose at a rate similar to that for pure platinum. As the tests progressed the samples again began gaining weight and blisters appeared on their surfaces. When this happened the tests were terminated. There is no definite explanation as to the cause of the first weight gains occurring in the samples, but on the basis of the results obtained at 2200 F, it is felt that the coatings on these samples may have contained defects which escaped visual observation.

Fig. 6 shows the plots of weight loss versus hours tested for samples of FS-85 clad with platinum-10% rhodium. All three of the samples tested initially oxidized at a rate nearly equivalent to that of pure platinum-10% rhodium alloy. Each sample eventually came to a point at which the weight losses rapidly deviated from those of pure platinum-10% rhodium alloy. Blisters, several of which were ruptured, exposing a white powder (probably columbium pentoxide), were again seen on the surfaces of the samples. A photograph of the general

surface condition of sample 8-2 is shown in Fig. 11. Fig. 12 shows the surface condition of the same sample at the edges where the coating overlies no base metal. It is obvious that the difference between the coating where it does and does not overlie base metal is small or non-existent if the few surface blisters are ignored. Fig. 13 shows one of the open blisters in sample 8-2. Fig. 14 is a micrograph of a blister in sample 8-4, and Fig. 15 shows the diffusion layers in sample 8-4 (brought out by etching).

The plots of weight loss versus hours tested for platinum coated TZM are given in Fig. 7. Both samples are seen to have weight losses that are continuously greater than for pure platinum. In the later portions of the tests the rates of weight losses are seen to take rapid increases, indicating that the coatings were quickly losing their protective qualities. While definite changes in the appearance of the coating surface were seen during testing, no gross defects, such as blisters or holes, could be found.

Fig. 8 is the plot of weight change versus hours tested for the platinum-10% rhodium coated TZM samples. Unlike the platinum coated TZM samples, the oxidation rates of these closely followed the rate of pure platinum-10% rhodium alloy for the first few hours. Once having deviated from the rate of pure platinum-10% rhodium alloy, weight loss rates for the samples increased rapidly and the coatings no longer offered sufficient protection. While no gross defects, such as blisters, holes, or cracks, etc., were seen in the samples after these tests, the surface condition was different from that of both the coating alloy alone and from the coating on FS-85. Fig. 16 shows the surface condition at the edge of sample 9-1 after testing, and Fig. 17 shows the coating where it overlies TZM. The differences are easily discerned. A micrograph of sample 9-2, shown in Fig. 18, shows that the TZM has been "eaten out" in a discontinuous manner. No holes are found in the coating itself and it therefore appears that the TZM was "eaten out" through some form of diffusion-oxidation process.

Several tentative conclusions have been drawn on the basis of the data obtained, and are listed below.

1. Oxidation of FS-85 clad with platinum or platinum-10% rhodium occurs through the penetration of the cladding by oxygen and discontinuous formation of oxide beneath the cladding.
2. Oxidation of TZM clad with platinum or platinum-10% rhodium occurs through diffusion of molybdenum to the cladding surface where it is removed as oxide vapor, leaving discontinuous "eaten out" spaces beneath the coating.

A number of questions remain unanswered and some of these are listed below.

1. Norton (Ref. 7) has indicated a very low rate of diffusion of oxygen through platinum at 2600 F - why then, do the platinum-clad TZM samples in Fig. 7 show initial weight losses greater than expected for pure platinum?
2. Through what mechanism does oxygen penetrate platinum and platinum-10% rhodium alloy coatings on FS-85?
3. Why is the formation of oxide beneath the cladding on coated FS-85 samples a discontinuous process?
4. Through what mechanism is the TZM discontinuously removed from coated TZM samples?
5. What basic protective differences, if any, exist between platinum and platinum-10% rhodium coatings?

From the questions that remain unanswered above, it is apparent that our basic understanding of the failure mechanism for these coatings is inadequate. Furthermore, only a limited amount of data has been obtained and tests more closely observed and controlled are desirable.

Due to the extreme differences in hardness and chemical reactivity between the various coatings and base metals, difficulties in metallography have been encountered. Polishing and etching techniques should be optimized, as metallography makes an important contribution to our understanding of the processes taking place during testing.

V. PREPARATION AND TESTING OF DIFFUSION BARRIERS

A. Rhenium Diffusion Barriers

Rhenium was perhaps the best diffusion barrier for refractory metals of those investigated by Manlabs (Ref. 8). Brown Boveri (Ref. 9) has found it to be a useful diffusion barrier between molybdenum and platinum for grid wire in transmitting tubes where the temperature may be as high as 2200 F.

Most of the pertinent work on the mechanical properties of rhenium have been presented in reports from Battelle (Ref. 10) and Chase Brass (Refs. 11 and 12) and in the book Rhenium (Ref. 13). It has high strength over a wide temperature range and is far more ductile than molybdenum. It is difficult to fabricate, however, as it work hardens faster than any other metal. In cold rolling, light reductions are initially applied, gradually increasing to 40% between anneals at 1600 C in vacuum, hydrogen, or cracked ammonia. Hot rolling has been attempted unsuccessfully, due to hot shortness - apparently resulting from rhenium oxide in the grain boundaries.

An attractive means of preparing composites containing rhenium diffusion barriers is the roll bonding technique which has been used in the preparation of the simple coating-base metal composites. Since the formation of a good bond between metals by this method generally requires the use of at least one heavy roll pass, it could not be done cold because of the rapid work hardening. However, it was thought that hot rolling might succeed if the metal were protected from oxidation and the resultant hot shortness. An evacuated package was prepared for this purpose.

The components of a composite consisting of FS-85 base metal 67 mils thick, rhenium diffusion barriers 5 mils thick and platinum-10% rhodium coating metal 15 mils thick, were placed in a molybdenum frame and enclosed by molybdenum cover plates. This frame was, in turn, placed in a stainless steel frame with stainless steel cover plates, and was welded shut except for a hole where an evacuation tube was welded in place. The molybdenum frame was used to hold the composite rigidly in place during rolling and the stainless steel frame was used to protect the hot molybdenum and composite from oxidation during bonding.

The package was evacuated and heated to 1800 F prior to bonding. For bonding it was given an initial reduction of almost 50% on the first pass and after seven more passes, had been reduced almost 85%. The composite obtained had a dark "wavy" surface. Several samples were cut from this piece. Metallographic examination has shown that the rhenium layer broke up during rolling, as seen in Fig. 19. It is believed that during rolling the FS-85 and platinum-10% rhodium tend to "flow," while rhenium, with its high yield strength, cannot and thus breaks up.

Two other methods have been considered for preparation of samples with rhenium diffusion barriers - (1) electrolytic deposition, and (2) chemical vapor deposition. However, as electrolytic deposition techniques have reached a much higher stage of development, preparation of samples by chemical vapor deposition will not be attempted unless electrolytic deposition is shown to be ineffective.

Summit Finishing Co. of Thomaston, Connecticut, has had some experience in rhenium electroplating and has been contacted to determine whether or not they can plate samples for us. If so, platinum and platinum-10% rhodium will be bonded to the plated samples and oxidation tests will be conducted.

B. Boron Nitride

Samples of platinum coated TZM and FS-85 with boron nitride (except at the edges) diffusion barrier layers were prepared. A 1.5 micron thickness of the boron nitride was deposited on heated TZM and FS-85 through decomposition of trichloroborazole.

Sputtering was used to deposit platinum over the boron nitride layer. Only low deposition rates were possible with the platinum and the thickness obtained was approximately 1 micron.

Additional platinum (2 mils thickness per side) was hot press bonded to a platinum-boron nitride-FS-85 sample and it was tested for oxidation resistance. White oxide burst the edges of the sample after a few hours of testing at 2550 F. The rapid failure of the coating is attributed to two sources:

1. The shearing action of hot press bonding causing thinning or possibly even tearing of the sample's edges.
2. Lack of any boron nitride on the edges to retard diffusion there. This new "edge protection" problem must be solved before significant test data can be obtained from these samples.

VI. WORK PLANNED FOR THE NEXT PERIOD

1. Extensive studies of the behavior of coating-base metal composites to obtain more information as to the mechanism through which failure occurs during oxidation testing.
2. Analysis of the experimental results for evidence of oxygen diffusion through the platinum metal coatings.
3. Develop improved techniques for metallography on the composites.
4. Evaluate electrolytic deposition as a means of deposition of rhenium diffusion barrier coatings on TZM and FS-85.
5. Attempt to solve the edge protection problem for samples with boron nitride diffusion barriers.
6. Begin work on the preparation of composites containing aluminide diffusion barriers.
7. Prepare samples with gold diffusion barriers.

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TABLE I

SUMMARY OF OXIDATION LOSSES FOR PLATINUM AND PLATINUM-10% RHODIUM

Temp.	Air Flow	Platinum		Pt-10%Rh	
		mg/cm ² /hr.	Microinches per hr.	mg/cm ² /hr.	Microinches per hr.
2200 F	24 ipm	.0111	0.20	.0066	0.12
	240	.0181	0.33	.0154	0.28
	480	.0284	0.52	.0254	0.47
2550 F	24 ipm	.0447	0.82	.0335	0.61
	240	.0886	1.62	.0804	1.46
	480	.1082	1.98	.1313	2.40
2880 F	24 ipm	.1218	2.23		
3000 F	24 ipm		10.0 (ex)		
	480		25.0 (ex)		

Note: This is equivalent to
2.5 mils per 100 hrs.

(ex) - extrapolated.

TABLE II

THE ACTIVATION ENERGY FOR OXIDATION OF PLATINUM

<u>Reference</u>	<u>Activation Energy kcal/mole</u>	<u>Air Flow Rate</u>
M&C	38.9	240 ipm
M&C	38.7	24 "
General Electric (Ref. 2)	45.7	231 "
Battelle (Ref. 3)	42.4	24 "
Hill and Albart (Ref. 5)	43.9	.2 cu.ft./hr.*
Fryburg and Patrus (Ref. 6)	42.5	**

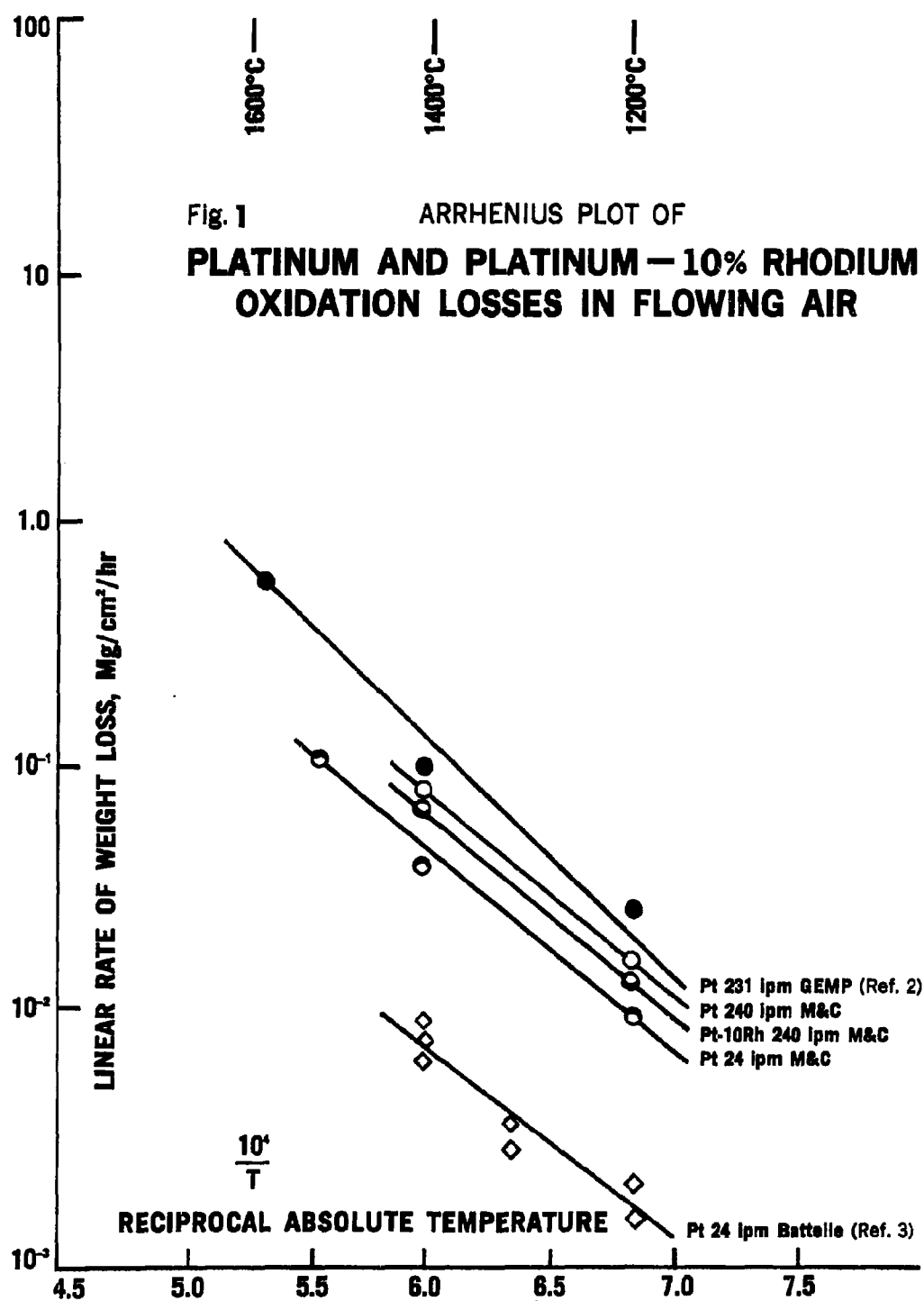
* Flow rate was not given in ipm.

** Flow rate not given.

TABLE III

THE OXIDATION RATE OF PLATINUM IN DRY AND WET AIR
FLOWING AT A RATE OF 24 IPM

<u>Temperature °F</u>	<u>Dew Point °F</u>	<u>Rate of Weight Loss mg/cm²/hr.</u>
2200	-40	.0111
2550	-50	.0447
2200	+120	.0087
2550	+120	.0440



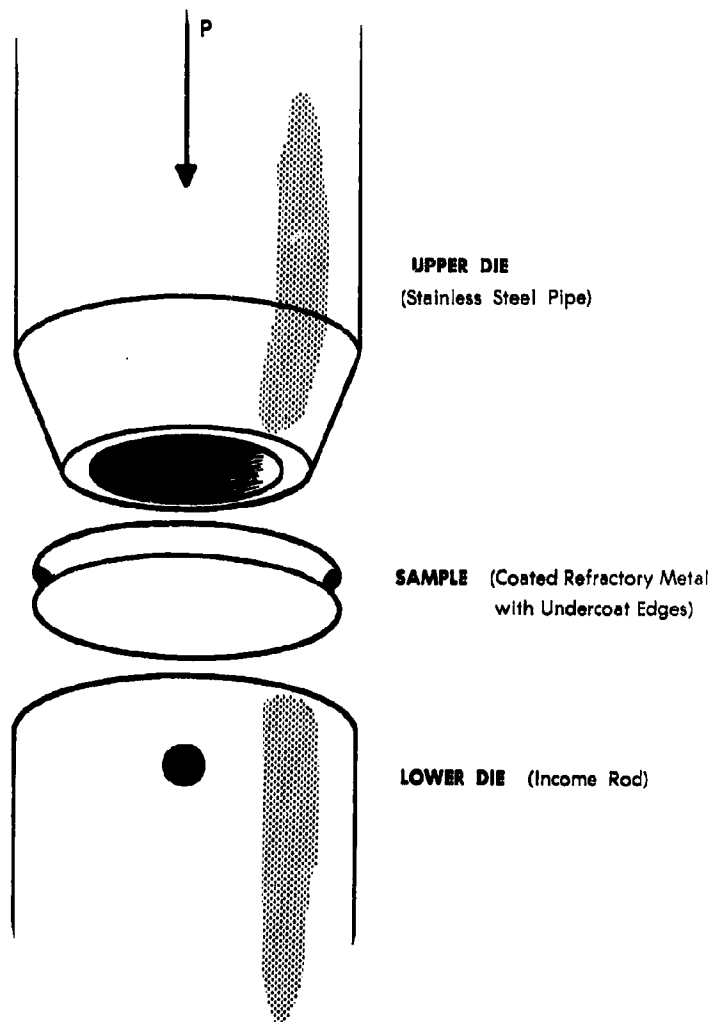


Fig. 2 — Set Up for Sealing Sample Edges by Hot Press Bonding
(Induction Coil for Heating is not shown).

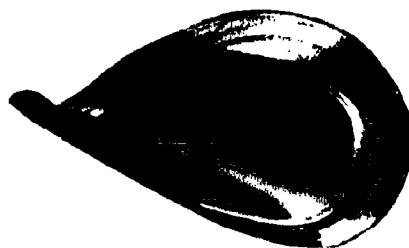


Fig. 3 — Coating-Base Metal Composite Test Sample (a Bent $1\frac{1}{4}$ " Dia. Disk).

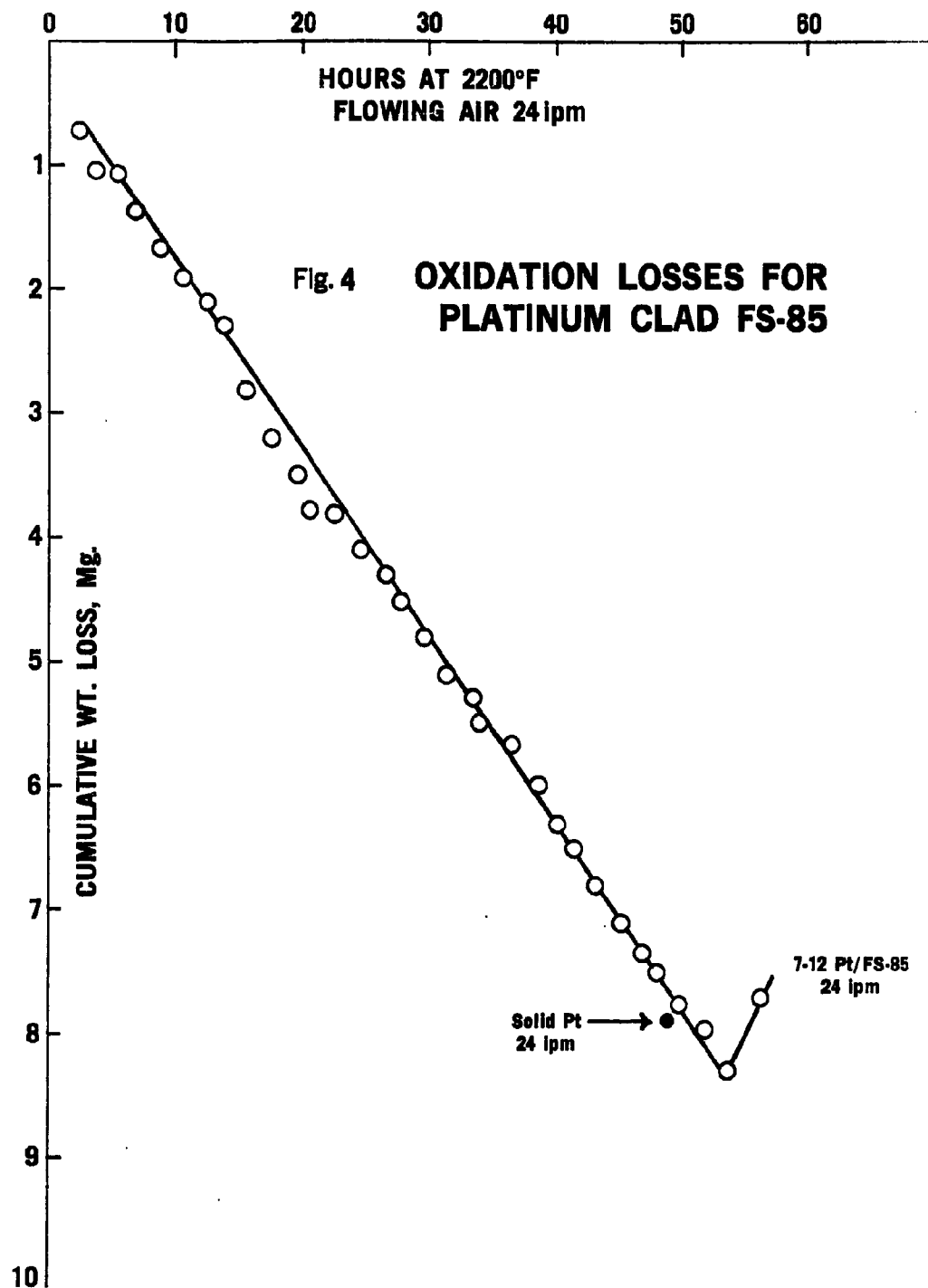
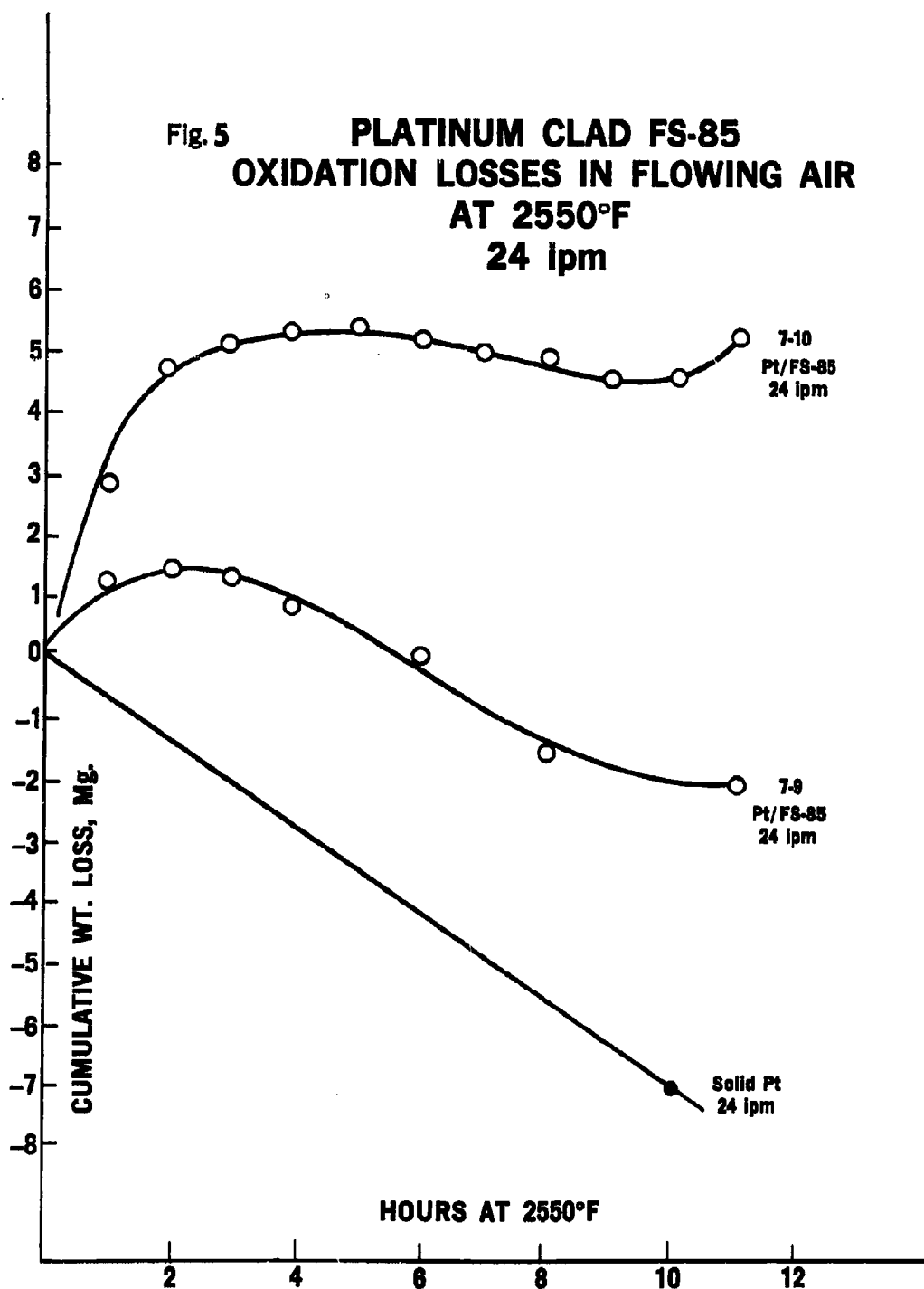
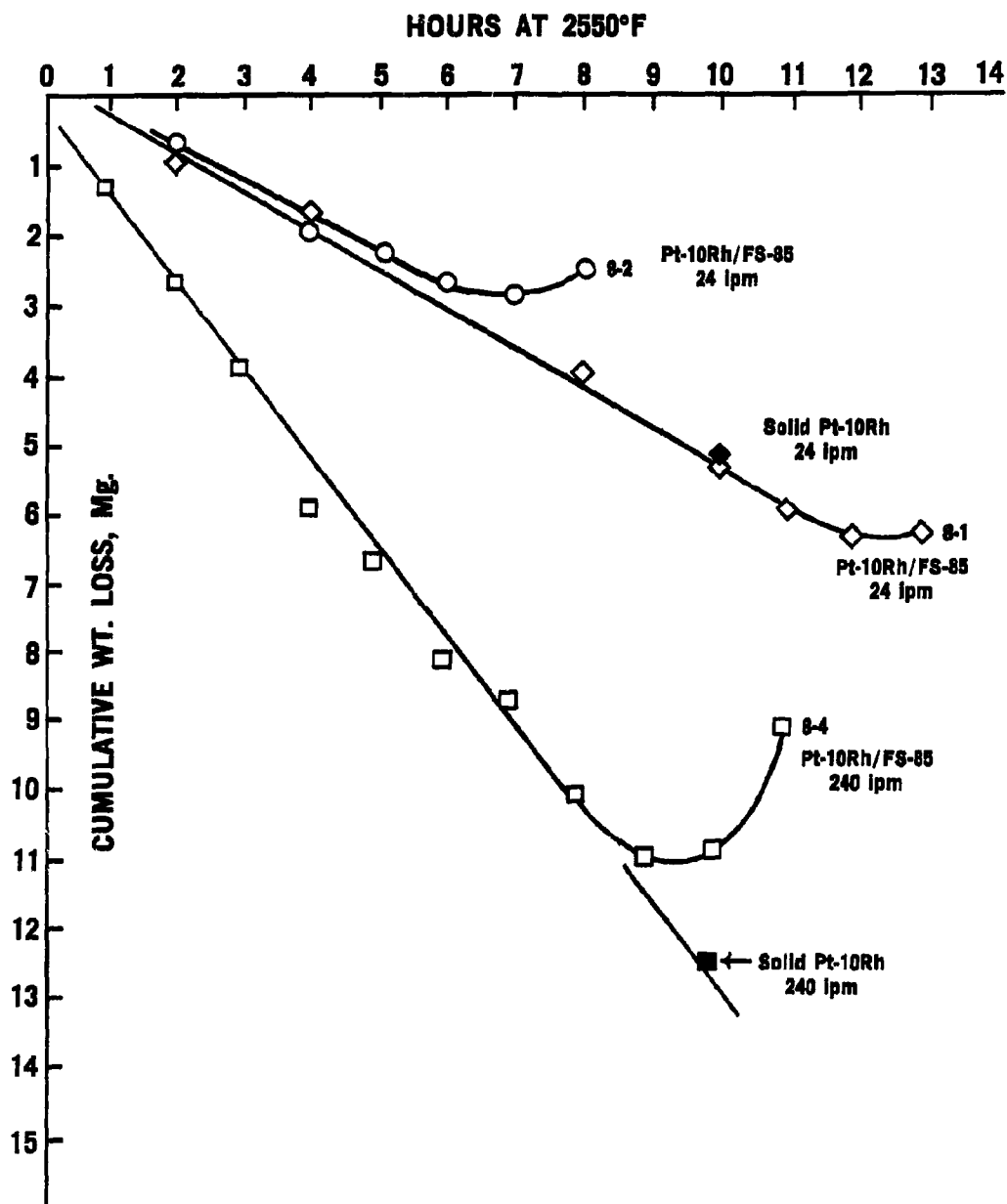


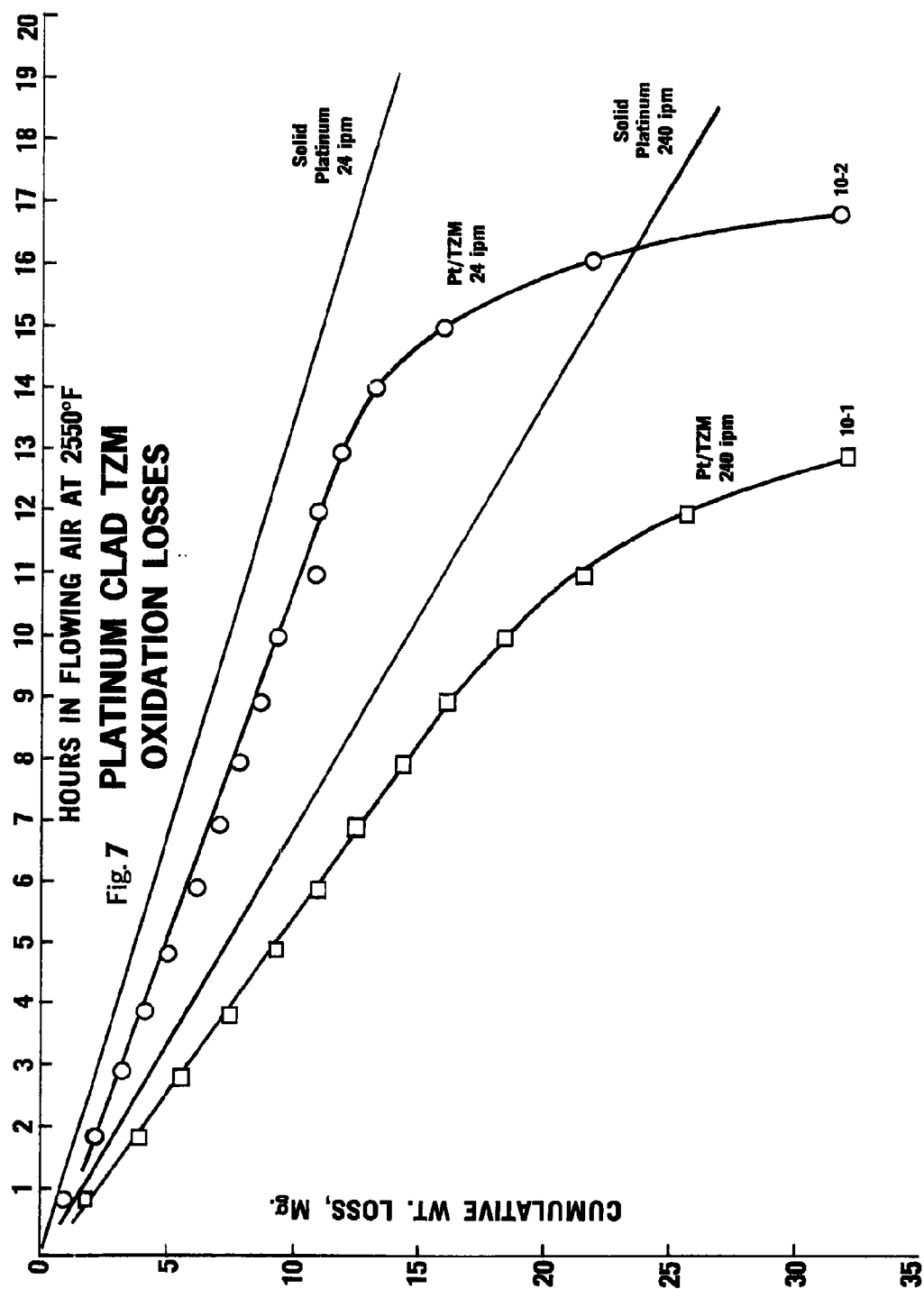
Fig. 5

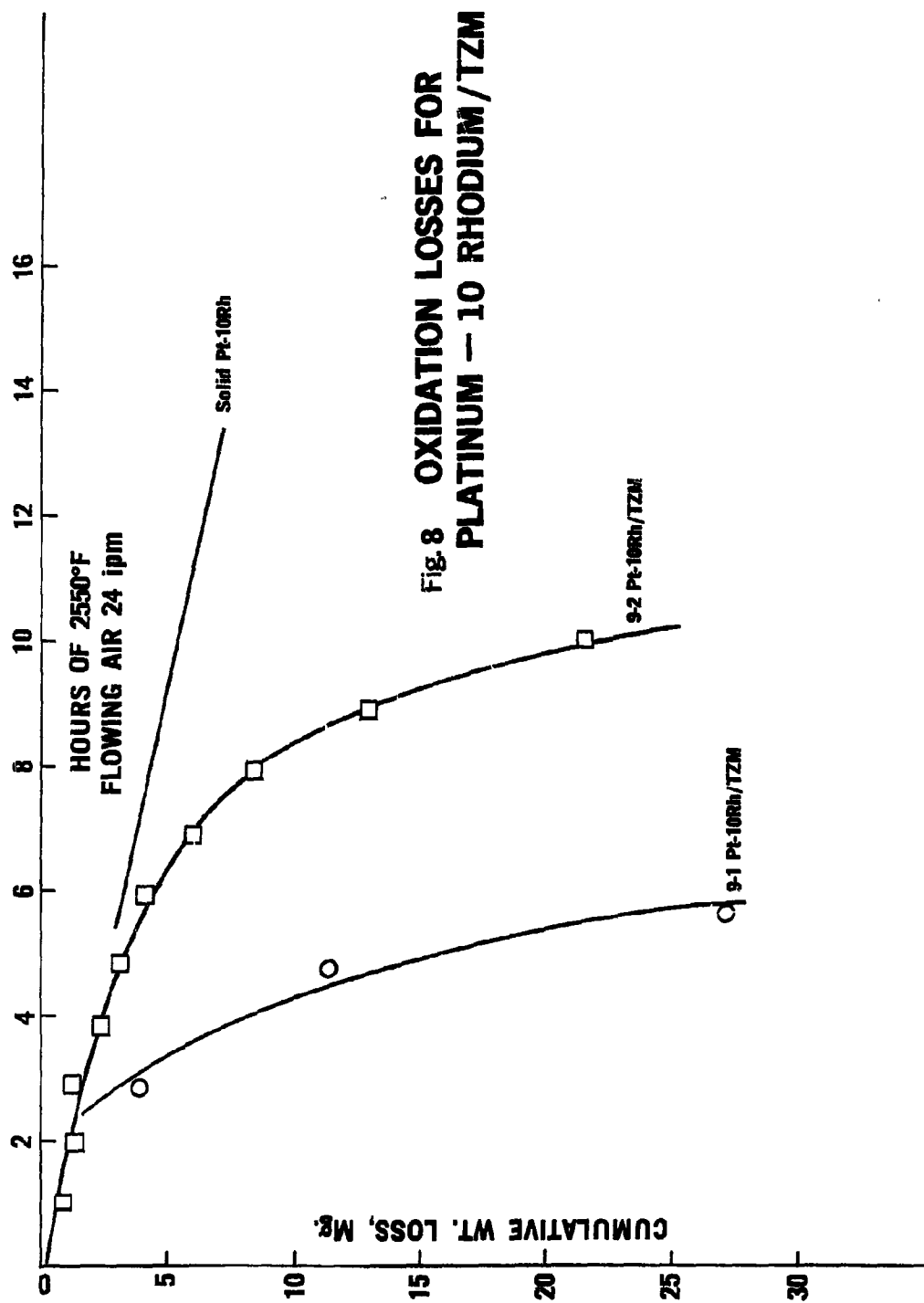
**PLATINUM CLAD FS-85
OXIDATION LOSSES IN FLOWING AIR
AT 2550°F
24 ipm**



**Fig. 6 PLATINUM - 10 RHODIUM CLAD FS-85
OXIDATION LOSSES IN FLOWING AIR**









No. 1494

100X



No. 1495

500X

Fig. 9 — General Surface Condition of Sample 7-12, Platinum Clad FS-85, After Heating in an Air Flow of 24 ipm for 57 Hours at 2200 °F.



No. 1496

50X

Fig. 10 — Blisters on the Surface of Sample 7-12, Platinum Clad FS-85, After Heating in an Air Flow of 24 ipm for 57 Hours at 2200 °F.



No. 1489

100X

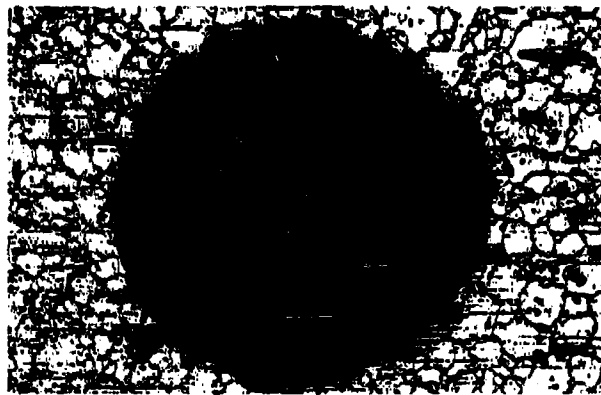
Fig. 11 — General Surface Condition of Sample 8-2, Platinum-10 Rhodium Clad FS-85, After Heating In an Air Flow of 24 lpm for 8 Hours at 2550 °F.



No. 1492

100X

Fig. 12 — Edge (No Base Metal Beneath Coating) of Sample 8-2, Platinum-10 Rhodium Clad FS-85, After Heating in an Air Flow of 24 lpm for 8 Hours at 2550 °F.



No. 1490

100X

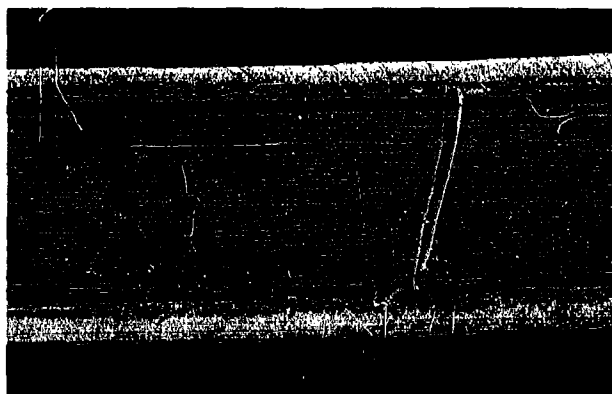
Fig. 13 — Blister on Sample 8-2, Platinum-10 Rhodium Clad FS-85, After Heating in an Air Flow of 24 lpm for 8 Hours at 2550 °F.



No. 1499

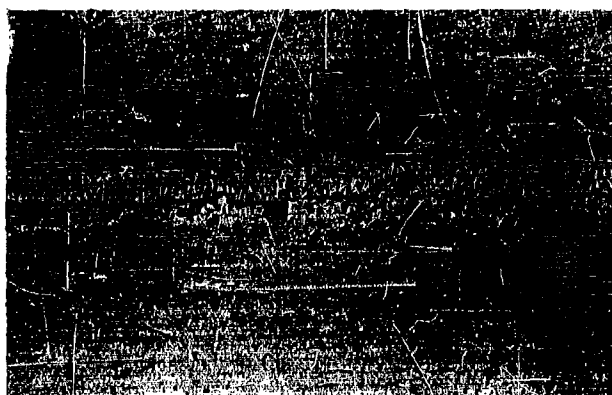
50X

Fig. 14 — Micrograph of a Blister in Sample 8-4, Platinum-10 Rhodium Clad FS-85, After Heating in an Air Flow of 240 lpm for 13 Hours at 2550 °F.



No. 1500

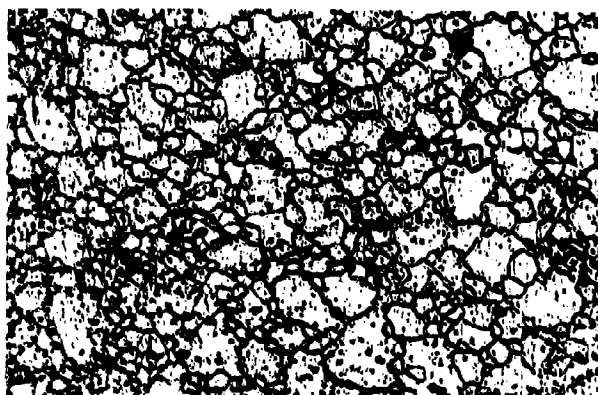
100X



No. 1501

500X

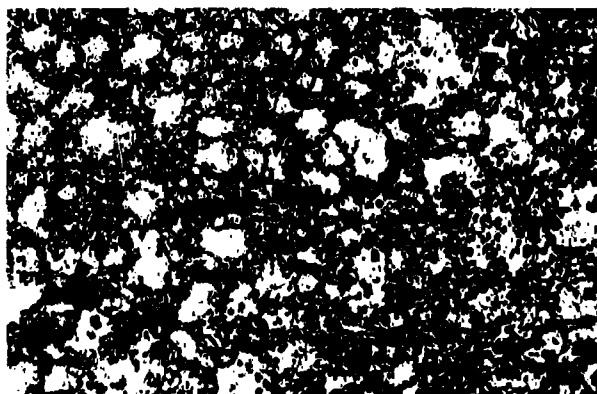
Fig. 15 — Diffusion Zones in Sample 8-4, Platinum-10, Rhodium Clad FS-85, After Heating in an Air Flow of 240 ipm for 13 Hours at 2550 °F.



No. 1487

100X

Fig. 16 — Edge (No Base Metal Beneath Coating) of Sample 9-1, Platinum-10 Rhodium on TZM, After Heating in an Air Flow of 24 lpm for 12 Hours at 2550 °F.



No. 1485

100X

Fig. 17 — General Surface Condition of Sample 9-1, Platinum-10 Rhodium on TZM, After Heating in an Air Flow of 24 ipm for 12 Hours at 2550 °F.



No. 1498

100X

Fig. 18 — Micrograph of Sample 9-2, Platinum-10 Rhodium on TZM, After Heating in an Air Flow of 24 ipm for 17 Hours at 2550 °F.



No. 1497

50X

Fig. 19 — Micrograph of a Hot Roll Bonded Composite Consisting of a Platinum-10 Rhodium Coating, a Rhenium Diffusion Barrier Intermediate Layer (Broken Up), and an FS-85 Substrate.

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