NASA Contractor Report 3680

# Plasma-Sprayed Self-Lubricating Coatings

H. H. Nakamura, W. R. Logan,
and Y. Harada

CONTRACT NAS3-21979
JULY 1983

25th Anniversary
1958-1983

NASA

NASA Contractor Report 3680

# Plasma-Sprayed Self-Lubricating Coatings

H. H. Nakamura, W. R. Logan,
and Y. Harada
*IIT Research Institute*
*Chicago, Illinois*

Prepared for
Lewis Research Center
under Contract NAS3-21979

National Aeronautics
and Space Administration

**Scientific and Technical
Information Branch**

1983

TABLE OF CONTENTS

TABLE OF CONTENTS (cont.)

# 1. INTRODUCTION AND SUMMARY

Plasma-sprayed coatings which are self-lubricating from cryogenic temperatures to 840°C (1600°F) have been developed at NASA/Lewis (Sliney et al.).[1-3] A composition of the plasma-sprayed coat is described in U.S. Patent 3,953,343, "Bearing Materials," assigned to H. E. Sliney, NASA/Lewis, U.S. Government. A particular coat composition covered by this patent, NASA-LUBE PS106, contains three components: silver, nichrome, and calcium fluoride. The purpose of the silver is to function as a low temperature lubricant, the nichrome to improve machinability and impart thermal matching with similar metal substrates, and the calcium fluoride to give high temperature lubrication up to 800°-900°C (1476°-1652°F) range.

One of the most important criterion for acceptable commercial applicaion of such a multiple-phase composition is uniformity and reproducibility. This means that the performance characteristics of the coat--e.g., its lubricating properties, bond strength to the substrate, and thermal properties--can be readily predicted to give a desired performance.

The objectives of these studies involved the improvement of uniformity and reproducibility of the coats, examination of the oxidation behavior at three temperature ranges, the effect of bond coat and the effect of preheat treatment as measured by adhesive strength tests, investigation of coating examination procedures, and physical property measurements.

The following modifications improved the uniformity and reproducibility:

1. Changes and closer control in the particle size range of the raw materials used.

2. Increasing the binder content from 3.2% to 4.1% (dried weight).

3. Analytical processing procedures using step-by-step checking to assure consistency.

This resulted in material balance of the processing parameters showing improved consistency from batch to batch with chemical analyses of the prepared powders all falling within the NASA specified compositional range.

Other significant results developed during the course of these studies are as follows:

1. The development of an etching technique resulted in obtaining excellent results by image analysis and quantitative microscopy of sprayed coats.

2. Coating bond strength measurements showed that the application of a preheat treatment and/or bond coats of NiCr improved the adhesive strengths of the final coat. Greater strength and uniformity were also obtained as a result of the improved processing procedures.

3. Oxidation tests indicated that considerable failure at 1650°F occurred due to bloating and separation from the substrate. These failures appear due to high thermal expansion caused by a combination of reactions; gas release, vapor condensation reaction, and oxidation of the nichrome. More study is needed to substantiate the results. A lower temperature preheat treatment at 1200°F for 100 hr improved the 1650°F high temperature resistance to failure.

4. Thermal expansion and density/porosity measurements were made on a PS106 free-standing body. Thermal expansion data showed high expansion rates above 1100°F (untreated) and above 1450°F (heat treated) specimens.

5. Ten pounds of NASA glass were made and delivered to NASA as required. Wear specimens coated with PS101 (10 coated rings and 20 coated rub blocks) were also sent to NASA according to specifications.

## 2. EXPERIMENTAL PROCEDURE

This section describes the raw materials and specifications, processing parameters for making plasma powder and NASA glass, plasma spraying procedures, and physical/optical methods of evaluations.

### 2.1 POWDER COMPOSITIONS

The coating composition, NASA-LUBE PS106, is specified to fall within the following compositional range:

| | wt., % | Vol., % |
|---|---|---|
| Nichrome | 35 ± 3 | 25 ± 2 |
| Silver | 35 ± 3 | 20 ± 2 |
| $CaF_2$ | 30 ± 3 | 55 ± 5 |

Two plasma powder compositions that are modifications of the basic PS106 powder were also prepared and tested. These are designated as PS101 and modified PS106 (hereafter designated as MPS106). Table 1 gives the weight percentages of the three types of compositions under study. The basic changes were the use of NiCrAl in MPS106 and the addition of NASA glass in PS101.

TABLE 1. COMPOSITIONS OF THREE TYPES OF COATINGS FOR TESTING

| Raw Material | Weight Percent Ingredients Composition Nos. PS106 | MPS106 | PS101 |
|---|---|---|---|
| Ag | 35 | 35 | 30 |
| $CaF_2$ | 30 | 30 | 25 |
| NiCr | 35 | -- | 30 |
| NiCrAl | -- | 35 | -- |
| Glass | -- | -- | 15 |
| | 100 | 100 | 100 |

The silver, nichrome, nickel-chrome aluminide were all commercial powders. Table 2 lists the sources and particle size range of the commercial powders as-received.

TABLE 2. PARTICLE SIZE RANGE AND SOURCES OF COMMERCIAL POWDERS

| Material | Source (Brand Name) | Particle Size, mesh size, μ |
|---|---|---|
| Nichrome 80% Ni, 20% Cr | Cerac, Inc. | -150+325 (-104+44μ) |
| Silver | Cerac, Inc. | -200+325 (-74+44μ) |
| NiCrAl | Metco, Inc. (Metco 443) | -120+325 (-125+44)) |
| $CaF_2$ | Cerac, Inc. | -150+325 (104+44μ) |
| $CaF_2$ | Fisher Scientific | (-5 micron) |

## 2.2 NASA GLASS

### 2.2.1 Composition

An oxidation protective glass whose composition was specified by NASA-Lewis was prepared. Ten pounds of the glass in powder form with at least 80% in the 30 to 150 microns particle size range were delivered to NASA-Lewis as required, and additional glass was prepared for use in subsequent oxidation tests. An extra 2.2 pounds of-400 mesh fines (<37 microns) was also shipped to NASA-Lewis. Table 3 lists the composition of the glass and specifications.

TABLE 3. OXIDATION PROTECTIVE GLASS SPECIFICATIONS

| Compound | wt% |
|---|---|
| Sodium Oxide ($Na_2O$) | 0.2 max |
| Lithium Oxide ($Li_2O$) | 0.1 max |
| Potassium Oxide ($K_2O$) | 13 ± 2 |
| Calcium Oxide (CaO) | 7 ± 2 |
| Barium Oxide (BaO) | 21 ± 2 |
| Silica ($SiO_2$) | Balance |

The chemicals used for glass formation are listed below:

| Materials | Grade/Purity | Company |
|---|---|---|
| Potassium carbonate ($K_2CO_3 \cdot 1\text{-}1/2\ H_2O$) | Analytical reagent | Baker Chemical |
| Calcium carbonate ($CaCO_3$) | Analytical reagent | Mallinckrodt |
| Barium carbonate ($BaCO_3$) | Analytical reagent | Mallinckrodt |
| Silica ($SiO_2$) | Ultra high purity | Orthocast Mfg. Co. |

The silica is from Orthocast Manufacturing Company of New York. It is called Gem-435 Fused Quartz and is made from ultra high purity quartz by electrical fusing. Typical analysis is reported to be:

| | |
|---|---|
| Silica | 99.99% |
| Aluminum | 27 ppm |
| Sodium | 10 ppm |
| Potassium | 6 ppm |
| Iron | 6 ppm |
| Ca | 6 ppm |

The potassium carbonate analysis shows 0.002% sodium, and no lithium. The calcium carbonate shows 0.0026% sodium, no lithium, and the barium carbonate reports hydroxide and alkali carbonate "to pass test." All meet ACS specifications.

2.2.2. Procedure for Glass Formation

Analytically weighed amounts of each constituent were made to yield the composition given in Table 3. Glass melts of approximately 500 gms each were prepared using a 500 cc platinum crucible. The procedural method for glass melting consisted of initially making several small mixes of the desired composition, individually contained in polyethylene bottles. One and two hundred gram batches were made. The contents of each premixed bottle was completely emptied into the platinum crucible and melted before additional batches were added. By this method of using smaller amounts of material, the following advantages were obtained: (1) losses by outgassing of melting mixes were kept

to a minimum, (2) a continuous uniform composition could be maintained; and (3) the maximum amount of powder to fill the platinum crucible could be determined with the least amount of spillage.

A 500 gram melt was obtained by such incremental loading. During melting, the furnace was held at 1350° to 1370°C. When all ingredients had gone into solution, the furnace temperature was raised to 1380°-1420°C. The melt was fired at this temperature for 1-1/2 to 2 hr with periodic stirring with a fused quartz rod to aid in removing bubbles and in improving homogeneity. The crucible was then removed from the furnace, and the glass was poured into a graphite mold and allowed to air cool.

Figures 1 and 2 show the silicon carbide element electric furnace used and the 500 cc platinum furnace. A fused quartz rod was used instead of the stirrer depicted in Fig. 2.

2.2.3 Preparation of Glass Powder Frit

Large lumps of the glass melts were crushed to approximately 1/4 in. in size using an alumina mortar and pestle. A porcelain mill was then filled to approximately one-quarter of the mill volume with glass, and to one-half of the mill volume with balls. Milling time ranged from 1/2 hr to 1-1/2 hr, depending upon initial glass melt size and volume. Sieving was performed frequently to prevent excessive grinding and buildup of fines.

Screening was conducted with ASTM 8 in. diameter sieves on a Ro-Tap Shaker using the following method and screen sizes.

1. Screening through a set of screens containing 100 mesh (149 microns), 270 mesh (53 microns), and 400 mesh (37 microns),
2. Repulverizing the +100 mesh material.
3. Resieving the -270+400 mesh material.

The bulk of the material ranged from 149 microns down to 37 microns. The particle size range of a representative sample from the three bottles of glass was determined with a Leeds and Northrup Microtrac Analyzer, an apparatus that circulates a water-powder suspension past a laser light source and detector. Particle sizes are measured in terms of percent by volume. Table 4 gives the average of four readouts in terms of percent smaller than the listed micron sizes, and also histogram data of the percentage between the listed particle ranges.

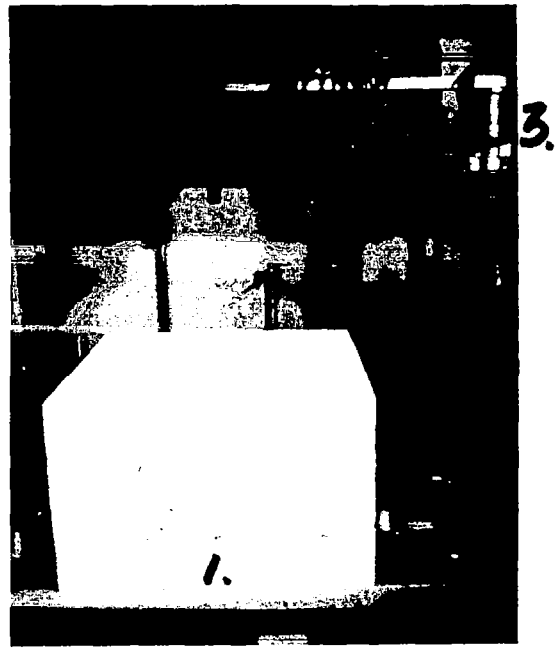



*Figure 1. Glass melt furnace.*

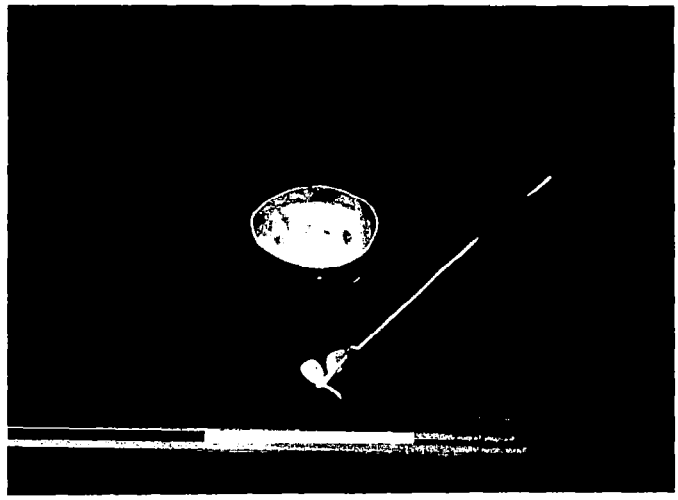


*Figure 2. Platinum crucible and stirrer.*

TABLE 4. PARTICLE SIZE ANALYSIS OF NASA GLASS AS MEASURED WITH L&N MICROTRAC ANALYZER (Average of 4 Readouts)

| Channel Upper Limits, microns | Cumulative Graph, %[a] | Histogram Data, %[b] |
|---|---|---|
| 176 | 100 | 14.6 |
| 125 | 85.3 | 25.6 |
| 88 | 59.7 | 15.1 |
| 62 | 44.5 | 19.0 |
| 44 | 25.5 | 5.5 |
| 31 | 19.9 | 4.9 |
| 22 | 14.9 | 4.2 |
| 16 | 10.6 | 3.1 |
| 11 | 7.5 | 0.7 |
| 7.8 | 6.8 | 0.2 |
| 5.5 | 6.5 | 3.3 |
| 3.9 | 3.1 | 2.1 |
| 2.8 | 1 | 0.7 |
| 1.9 | 0.3 | 0.3 |

[a]Percent smaller than shown.

[b]Percent between listed size and next smaller size.

The data show that the portion smaller than 31 microns averages 19.9%, and the histogram data reveal that the bulk of the material is within the 44 to 149 micron range. The 149 micron is the size of the top screen in our sieving procedure.

The requirement for this program specifies that at least 80% of the glass shall be in the 30 to 150 micron particle size range; thus, the analysis indicates that the prepared powdered glass meets the specifications. The Microtrac analysis indicates that double sieving of the -270 mesh to 400 mesh material did not remove as much material fines as previously presumed.

2.2.4. Chemical Analysis of Glass

A representative sample of "as-melted" glass and a pulverized glass melt (-149+37 micron range) were sent to Coors/Spectro-Chemical Laboratories for chemical analysis. Comparison of the two glasses in weight percent are given below:

| Analyte | "As-Melted" | "Pulverized" |
|---|---|---|
| $SiO_2$ | 60.2 ± 0.2 | 60.0 ± 0.2 |
| BaO | 21.3 ± 0.2 | 21.8 ± 0.2 |
| $K_2O$ | 11.2 ± 0.2 | 11.4 ± 0.2 |
| CaO | 7.3 ± 0.1 | 6.8 ± 0.1 |
| $Na_2O$ | 0.008 ± 0.0008 | 0.0062 ± 0.006 |
| $Li_2O$ | <0.005 | <0.005 |

The results indicate that there was no significant pickup of impurities in the ball milling procedure. The values all met NASA specifications.

## 2.3 PLASMA POWDER PROCESSING

The agglomeration of a multi-phase powder system as represented by composition PS106 was initiated in a previous NASA program, NAS3-2087. This is a fabrication technique whereby a fine $CaF_2$ powder coupled with an inorganic binder (monoaluminum phosphate solution, MAP) cements the silver and nichrome particles into a multi-phase agglomerate.

In the current program, refinements in processing procedures and modifications in existing fabrication parameters resulted in greater uniformity and reproducibility of the final product. Laboratory size batches of 110 gram were made throughout the program.

### 2.3.1 Particle Size Modifications

The first change was to modify and recheck each particle size range of the major ingredients involved. The size range of nichrome was reduced, and all particle ranges (except for the 5 micron $CaF_2$ powder) were resieved. The size ranges are listed below.

PARTICLE SIZE RANGE

| Material | Mesh Size (microns) Phase 1 | Phase 2 |
|---|---|---|
| Nichrome | -150+325 (-104+44μ) | -200+325 (-74+44μ) |
| Silver | -200+325 (-74+44μ) | Resieved |
| Calcium Fluoride | | |
| Addition No. 1 | (5 microns) | (5 microns) |
| Addition No. 2 | -150+325 (-104+44μ) | Resieved |

Resieving was done despite the fact that silver, for instance, was a commercially double-screened product.

2.3.2 Binder Concentration

The inorganic binder used in this process is a monoaluminum phosphate solution (MAP). The commercial product, as-received, is a 50% concentrated solution obtained from the Mobil Chemical Co. This solution is diluted by volume to a ratio of one part concentrated solution to four parts of water. By diluting the MAP and thus lowering the solution viscosity, all particles are readily wetted and more uniformly coated with MAP. Also, a significant volume increase of this diluted solution to the batch composition would give only a small increase in actual binder concentration. This is desirable as the intent is to seek better adhesion of particles and not changes in chemical composition that might affect the plasma coat properties.

For instance, for a 110 gram batch of material the binder solution was increased from 27 cc to 36 cc for this phase of work. Increasing the binder solution by 33% only increased the MAP concentration (dried weight) from 3.2 to 4.3% of the solids in step 1 of the process.

2.3.3 The 5-Step Processing Procedure

The fabrication technique involved the agglomeration of different metal particles with a fine $CaF_2$ powder (5μ range) by use of the inorganic binder (monoaluminum phosphate). A 5-step procedure is described that was effective

in attaining improved quantitative control of the process. Careful analytical procedures for each step minimized material balance losses. Since comparative weight measurements were made (from batch to batch) after each processing control point, any losses were readily observed and adjustments in material additions could be made to correct for any deficiency.

Step 1. The amounts of raw material used was based on the required NASA weight percents of raw materials, previously given in Table 1. For this program, all laboratory size batches contained 110 grams of main ingredients. Tables 5, 6, and 7 give the weights and the particle size range of each ingredient used for PS106, MPS106, and PS101, respectively.

TABLE 5. NOMINAL BATCH COMPOSITION OF PS106 POWDER

| Ingredients | Percent | Weight, grams | Size Range, mesh |
|---|---|---|---|
| (1) NiCr | 35 | 38.5 | -200+325 |
| (2)Ag | 35 | 38.5 | -200+325 |
| (3) $CaF_2$ | 30 | (a) 19.3* | -5 microns |
| | | (b) 13.7** | -150+325 |
| Total | 100 | 110.0 | |

*Add in Step 1.
**Add in Step 5.

TABLE 6. NOMINAL BATCH COMPOSITION OF MPS106 POWDER

| Ingredients | Percent | Weight, grams | Size Range, mesh |
|---|---|---|---|
| (1) NiCrAl | 35 | 38.5 | -200+325 |
| (2) Ag | 35 | 38.5 | -200+325 |
| (3) $CaF_2$ | 30 | (a) 19.3* | -5 microns |
| | | (b) 13.7** | -150+325 |
| Total | 100 | 110.0 | |

*Add in Step 1.
**Add in Step 5.

TABLE 7. NOMINAL BATCH COMPOSITION OF PS101 POWDER

| Ingredients | Percent | Weight, grams | Size Range, mesh |
|---|---|---|---|
| (1) NiCr | 30 | 33 | -200+325 |
| (2) Ag | 30 | 33 | -200+325 |
| (3) $CaF_2$ | 25 | 27.5<br>16.5[a]<br>11.0[b] | <br>-5 microns<br>-150+325 |
| (4) NASA Glass | 15 | 16.5 | -150+325 |
| Total | 100 | 110.0 | |

[a]Add in Step 1.
[b]Add in Step 5.

The three designated amounts for each composition were intimately mixed by ball milling. Nylon balls were used in 8 oz glass jars. Each jar received 100 cycles of end-over-end mixing before it was roll-milled for 1-1/2 hr. Biaxial mixing was a necessary added step in obtaining more uniform mixing. After the milling operation, the nylon balls were removed and weight losses taken before continuing to the next step.

Step 2. The mixed powder was placed in an evaporating dish and the diluted MAP solution then added. (The as-received MAP was a 50% concentrated solution. This was diluted by volume, adding 4 parts of distilled water to 1 part of concentrated MAP solution.) Continuous stirring of the slurry as it is evaporated to dryness on a hot plate aided in giving intimate binder-to-particle adhesion and multi-phase aggregate formation. The agglomerated particles were sieved through a 20 mesh screen. Extra care was taken in cleaning the screen and the evaporating dish to keep material losses to a minimum.

Step 3. The screened agglomerates were oven-dried overnight at 110°-115°C to form a cementitious bond. The weight percent of dried MAP was calculated at this point. The hardened aggregates were carefully reduced in size using mortar and pestle, to pass through a 100 mesh screen. The greatest losses occur in this size reduction operation by the formation of fines. This

loss was minimized by taking only small portions of the oversize and reducing them in several screenings instead of one large screening.

Step 4. The powder was heated to 400°-450°C for final curing of the MAP binder. The material was weighed at this point, and the loss in weight was assumed to be a dehydration loss of MAP. The weight of the cured binder was calculated from this loss.

The agglomerated powder was then classified to -100+325 mesh (-145+44 microns). A weight measurement was taken at this point to determine the amount of loss incurred by the -325 mesh fines. The largest process loss occurred in this step.

The reduction of the agglomerate size range to -100+325 mesh (-145+44 microns) from the previous program range of -70+325 mesh was made possible because the nichrome particle size range had been reduced to -200+325 mesh. The multi-phase agglomerate size range could then be decreased from 174 microns (70 mesh) to 103 microns (100 mesh), a reduction of 40%. This has proven to be quite an effective range decrease in regards to uniformity and strength of the final plasma-sprayed coat.

Step 5. Larger sized $CaF_2$ powder (-150+325 mesh) is added in this step to satisfy the compositional demand. The amount of $CaF_2$ to add is determined by two factors: the amount not added in Step 1 to complete the $CaF_2$ requirement (41.5% of 33 g) of 13.7 g, and also an addition of an extra amount equivalent to the weight loss of the -325 mesh fines incurred in Step 4.

In the case of composition PS101, the glass component (16.5 g of -150+325 mesh size) was also added in this step. To minimize dusting, no balls were added in this step. The mix was hand-cycled end-over-end for 100 times and then roll-milled for at least 10 min.

## 2.4 PLASMA SPRAY SYSTEM

A schematic presentation of the plasma spray process is given in Fig. 3.

Figure 4 shows the Plasmadyne control consol and two powder feeders from the Sylvester & Co. (Beachwood, Ohio). To control the feed rate, a variable speed metering screw is located at the bottom of the sealed container which, in turn, is mounted on a controllable vibratory unit. This vibratory-screw feeder type unit prevents segregation of powder particles, a feature that aids

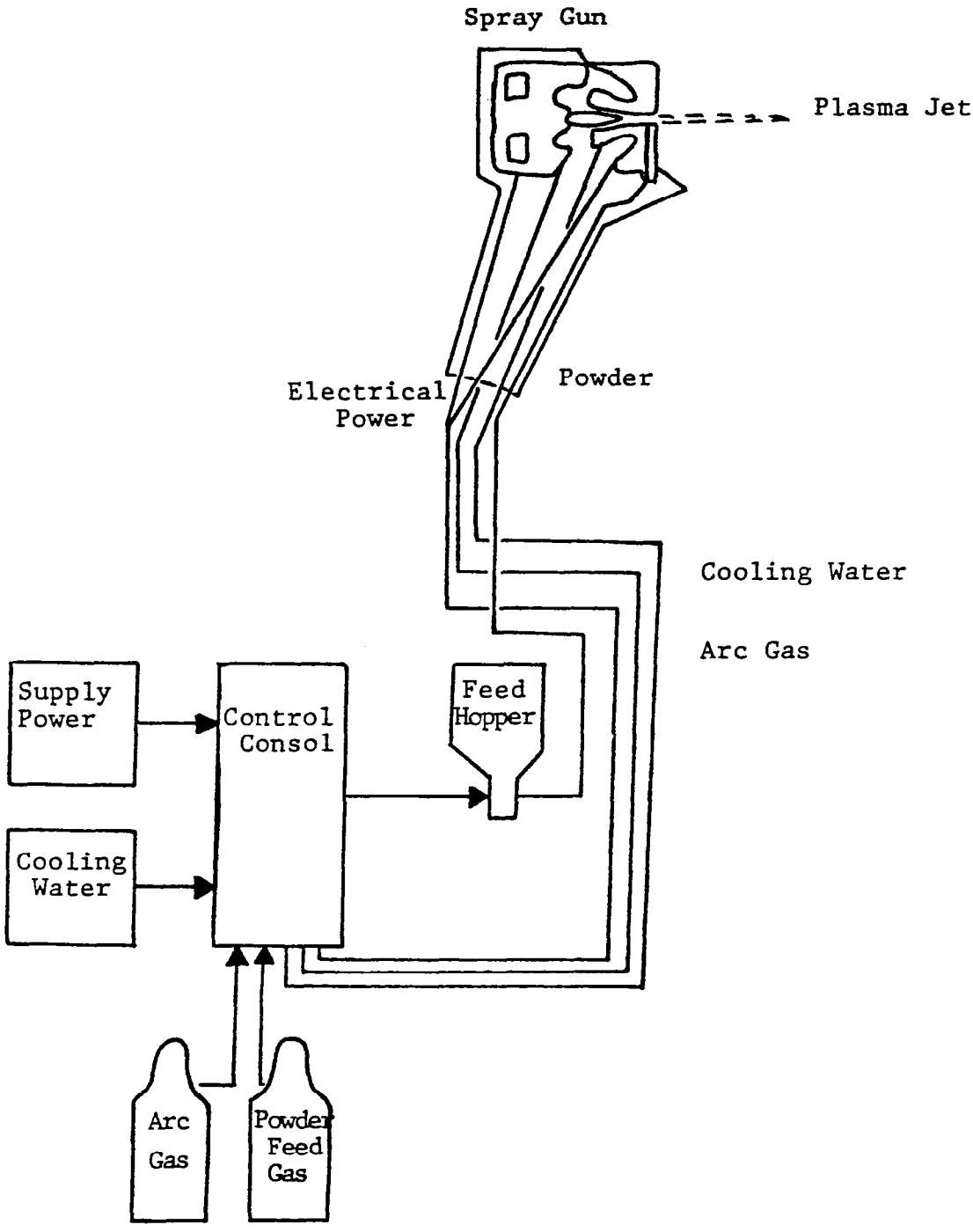
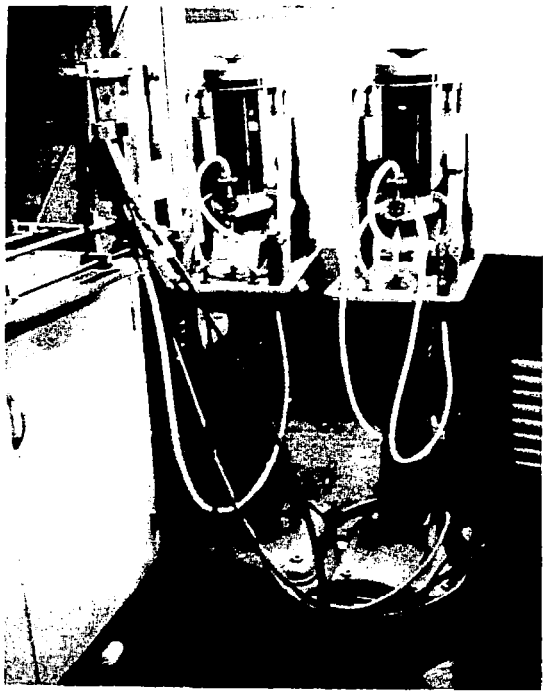
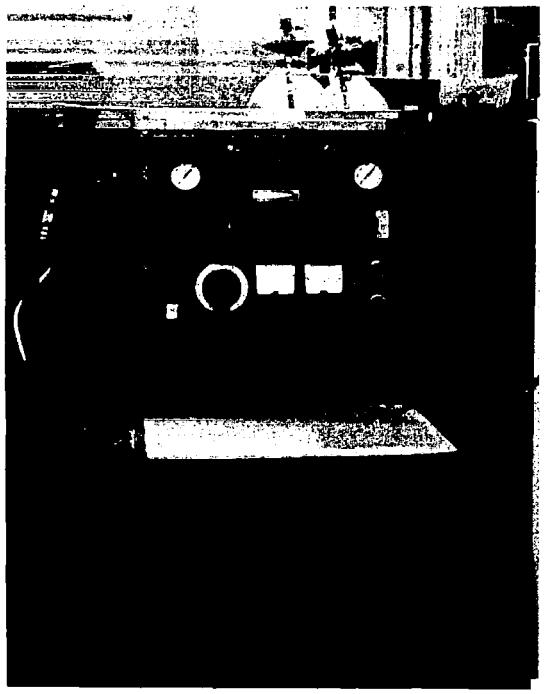



*Figure 3. Schematic representation of the plasma spray process.*



Powder Feeders from Sylvester & Co.



Control Consol from Plasmadyne

*Figure 4. Control consol and powder feeder systems.*

in the uniform spraying of a multi-phase, variable density powder such as the NASA PS106 composition.

Plasma spraying was done with a SG-1B (S1-AS version) gun from Plasmadyne (a division of Geotel, Inc., Santa Ana, Calif.). This gun is designed so that present owners of the SG-1 plasma spray guns might take advantage of the SG-IB features without the added expense of converting to Hi-Frequency auto-start. Figure 5 is a detailed schematic of the SG-1B gun which has two powder ports. The 640A-15 (ref) port enters in the gun in the electrode itself. The S1-20 port shows that the feed enters in a ring in front of the gun. All powders for NASA-Lewis were fed through this front port, S1-20.

### 2.4.1 Fixtures

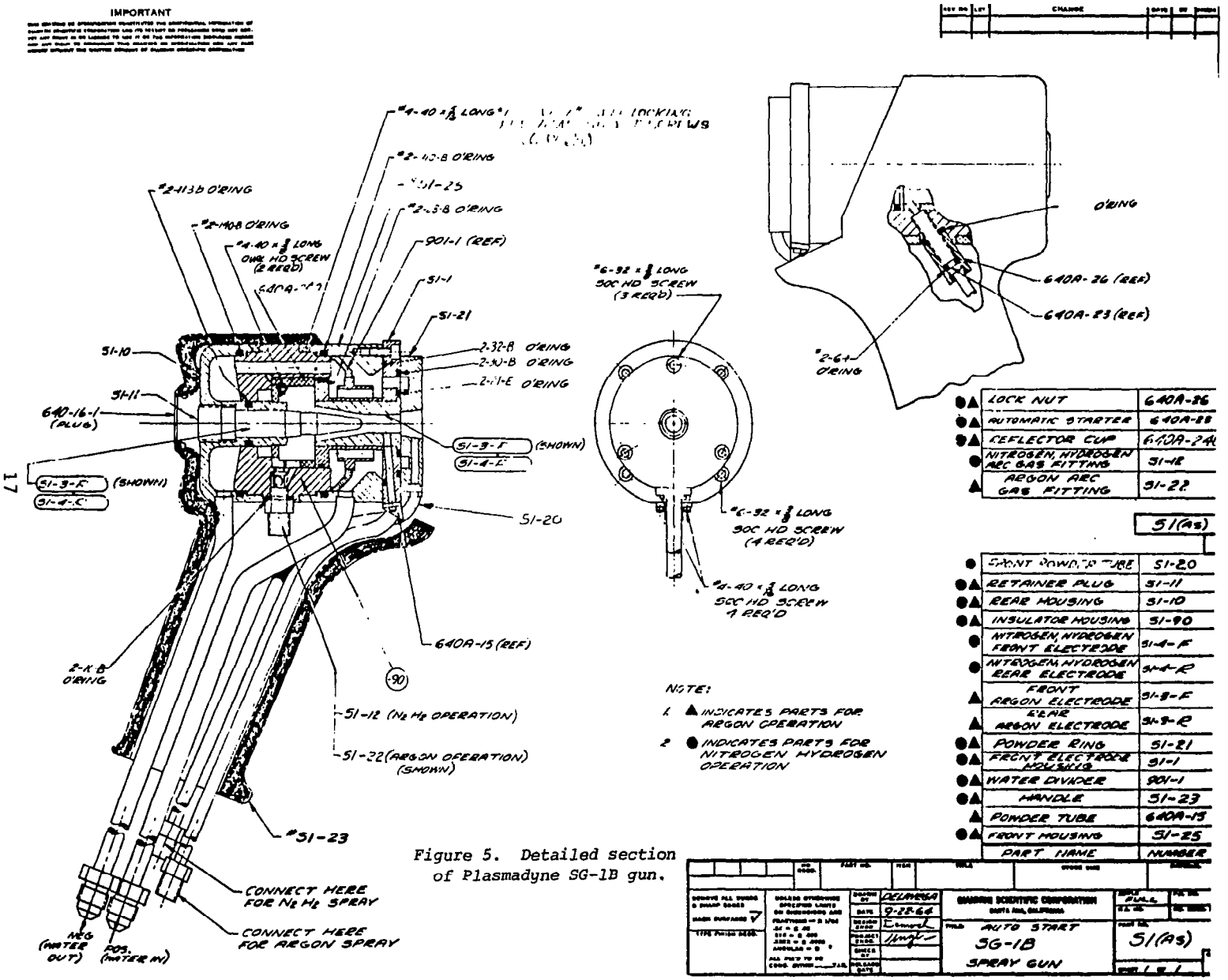
Special fixtures were fabricated for each type of spray configuration. Figure 6 shows the coating fixture arrangement for simultaneously spraying tensile test and microstructural study specimens. Figure 7 gives the setup for holding 2 x 2 in. substrates used in oxidation tests. The fixture in Fig. 8 shows a cylindrical mandrel and rotating drive for spraying cylindrical specimens. The vertical-horizontal sliding frame with the plasma torch attachment is also shown. Located on the top sliding frame and attached to the plasma torch is a counterbalance weight device. This allows the gun and attachment to move up and down on the vertical slide axis smoothly with little effort.

### 2.4.2 Procedures for Spraying

The initial task in the spraying of any coat is to determine the optimum stand-off distance for a specific set of plasma spray gun and powder feed parameters as determined by the physical and chemical variables of the feed powder.

A glass slide test was used to determine this distance. In this method a single pass with the plasma gun is made across a series of upright glass slides spaced 2 to 5 in. away from the plasma gun nozzle, in increments of 1/2 in. Microscopic examination of the particle spray pattern is made and compared. This test showed that a distance of 4 to 4-1/2 in. gave the best single-pass coat, using batch No. PS106-3.

All substrates in this program were made of Inconel 750. Substrates were first washed with a detergent solution of Alconox rinsed with distilled water,




NOTE:
1. ▲ INDICATES PARTS FOR ARGON OPERATION
2. ● INDICATES PARTS FOR NITROGEN HYDROGEN OPERATION

| | | |
|---|---|---|
| ●▲ | LOCK NUT | 640A-26 |
| ●▲ | AUTOMATIC STARTER | 640A-28 |
| ●▲ | REFLECTOR CUP | 640A-24 |
| ● | NITROGEN, HYDROGEN ARC GAS FITTING | 31-18 |
| ▲ | ARGON ARC GAS FITTING | 31-22 |

51(AS)

| | | |
|---|---|---|
| ● | FRONT POWDER TUBE | 51-20 |
| ●▲ | RETAINER PLUG | 51-11 |
| ●▲ | REAR HOUSING | 51-10 |
| ●▲ | INSULATOR HOUSING | 51-90 |
| ● | NITROGEN, HYDROGEN FRONT ELECTRODE | 51-4-F |
| ● | NITROGEN, HYDROGEN REAR ELECTRODE | 51-4-R |
| ▲ | FRONT ARGON ELECTRODE | 51-3-F |
| ▲ | REAR ARGON ELECTRODE | 51-3-R |
| ●▲ | POWDER RING | 51-21 |
| ●▲ | FRONT ELECTRODE HOUSING | 51-1 |
| ●▲ | WATER DIVIDER | 901-1 |
| ●▲ | HANDLE | 51-23 |
| ▲ | POWDER TUBE | 640A-15 |
| ●▲ | FRONT HOUSING | 51-25 |
| | PART NAME | NUMBER |

| | | | |
|---|---|---|---|
| DRAWN BY | DELAMEGA | LINDE DIVISION OF UNION CARBIDE CORPORATION SANTA ANA, CALIFORNIA | SIZE A |
| DATE | 9-28-64 | | |
| TITLE | AUTO START SG-1B SPRAY GUN | | DWG. NO. 51(AS) |

Figure 5. Detailed section of Plasmadyne SG-1B gun.

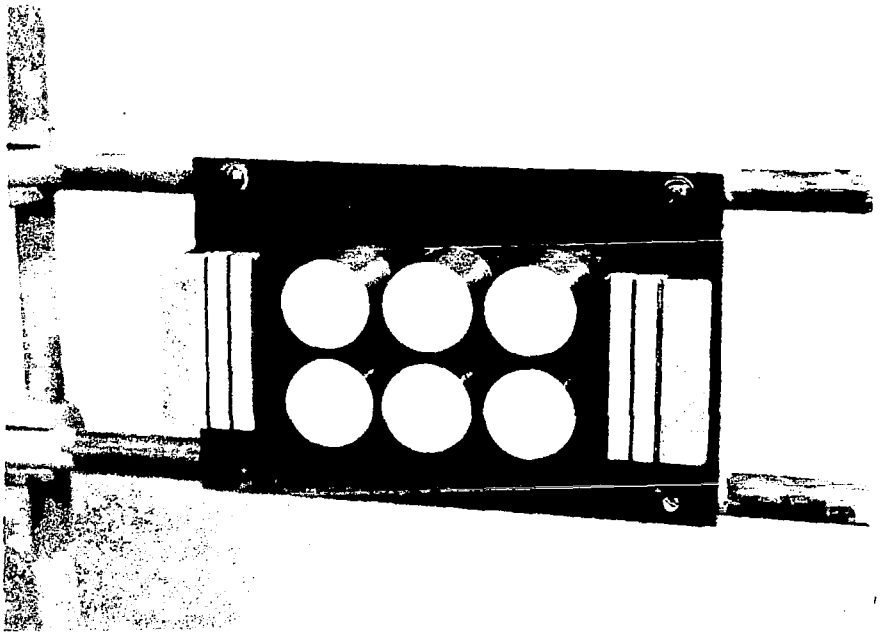


*Figure 6. Plasma spray fixture for simultaneous coating of tensile and microstructure study specimens.*

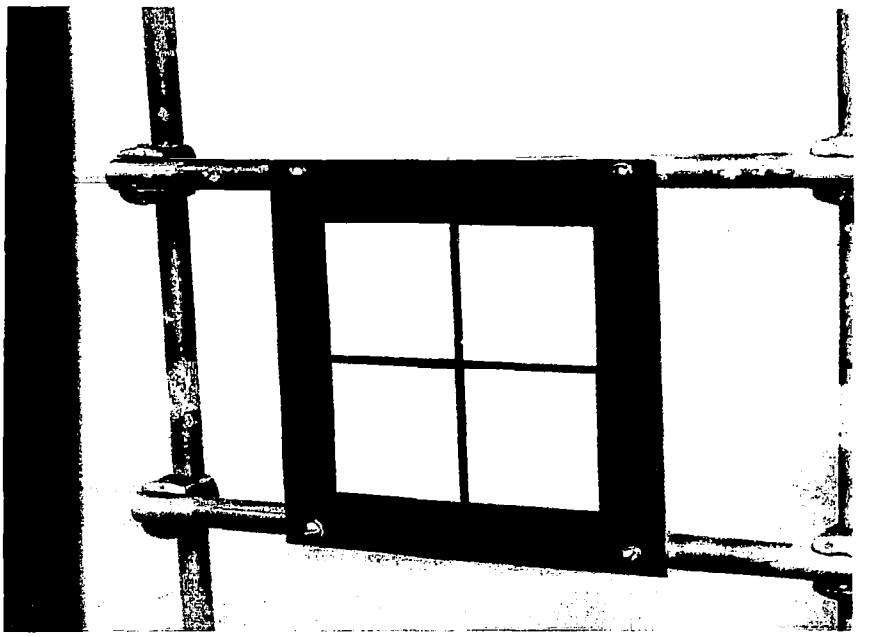


*Figure 7. Plasma spray fixture holding four 2 x 2 in. test coupons.*

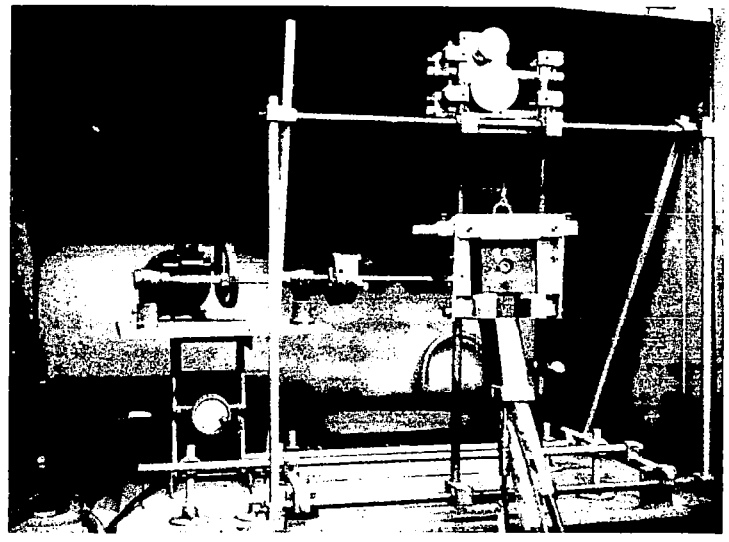


*Figure 8. Fixture for cylindrical specimens.*

then rinsed with acetone. The surfaces to be sprayed were then grit-blasted with No. 20 SiC grit. After grit-blasting the substrates were scrubbed with the detergent solution, washed with distilled water, and given a final acetone rinse. Special techniques are described under appropriate headings.

Once the stand-off distance was determined and specimen(s) placed in the fixture, actual spraying began. Horizontal and vertical passes at a gun travel speed of approximately 1 ft/sec were used. It was found that for the desired final polished coat thicknesses of 0.010 in., an as-sprayed coat thickness of 0.018 in. was appropriate. Figure 9 is a work data sheet giving the plasma parameters used for a 2 x 2 in. substrate using a PS101 type coat composition.

### 2.4.3 Wear Specimens for NASA-Lewis

NASA-Lewis was supplied with ten plasma-spray coated rings and twenty rub blocks made of Inconel 750 according to the specifications shown in Figs. 10 and 11. A 0.020 ±.003 in. coating of PS101 including a 0.002/0.004 in. bond coat was applied to the outer rim (OD surface) of each ring and to the rub surfaces of each block using the best processing achieved under Contract NAS3-21979. All specifications were met. Tables 8 and 9 give the coat measurements of the ring and rub block specimens. The bond coat used was Metco 43C, a nickel-chromium alloy powder.

Sponsor NASA LEWIS Date 11/25/80

Project No. M6051 Test No.

PART

Substrate No. PS-101-1,2,3,4 Type OXIDATION 2x2" (INCONEL)

Fixture No. —

PREPARATION

Pre-blast Cleaning ACETONE

Blasting Grit: Type S.C Size 20 MESH

Post-blast Cleaning ALCONOX & WATER

Masking

EQUIPMENT

Spray Gun SG-1B(S1-AS version) Cathode S1-3-R-05 Anode S1-3-F-05

Powder Injection EXTERNAL

Fixture No.

CONSOLE

Arc Gas Ar (AIR PRODUCTS) psi 50 Flow,CFH(reading) 67(1.6)

Powder Feed Gas S.A.A. psi 30 Flow,CFH(reading) 21(.4)

Amps.DC 510 Volts,DC 26 OCV 84 Arc Time

POWDER FEEDER

Hopper Type: Sylvester Vibratory Screw Feeder

Hopper No. 1 ScrewFeed RPM(Setting) 50(12.5) Vibrator STD.

Amt. Powder Added To Hopper ~220 GRAMS

COATING MATERIAL

Identification PS-101-1

Size Range -100 +325

COATING DATA

Required Thickness .018" Thickness After Spray .017 TO .022"

Spray Distance 4.250" Spray Rate

No. of Passes: Horizontal 14 Vertical 14

Part Preheat Temp. HEATED Max. Part Temp.

Part Speed Gun Speed 1"/SEC Spray Time

COMMENTS

*Figure 9. Plasma spraying work sheet.*

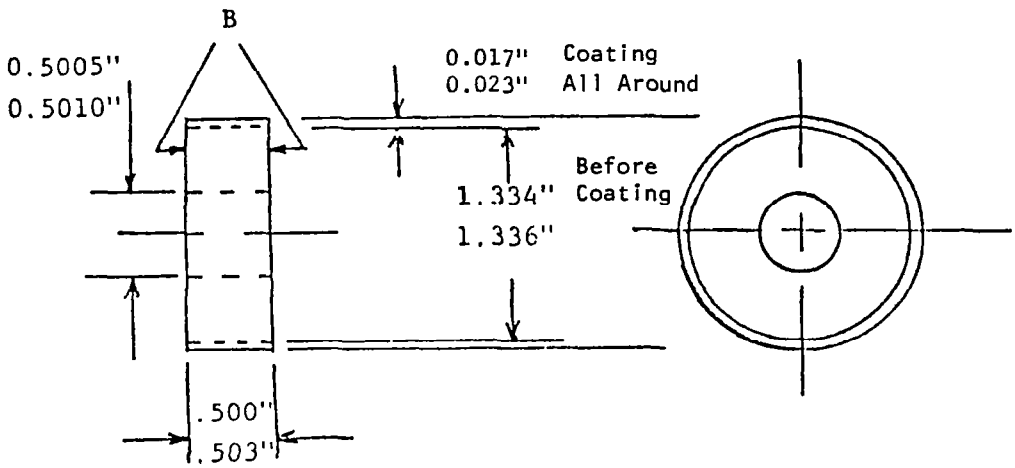



*Figure 10. Ring specimen for NASA line-contact rub shoe wear test machine.*

Notes: Both figures.

1) Bore diameter to be concentric with OD (before coating) and square with B surface within 0.001 in. F.I.R.
2) Break sharp edges on center hole.
3) NASA will machine coatings.
4) 63 maximum all machined surfaces.
5) Sandblast A surfaces before coating.

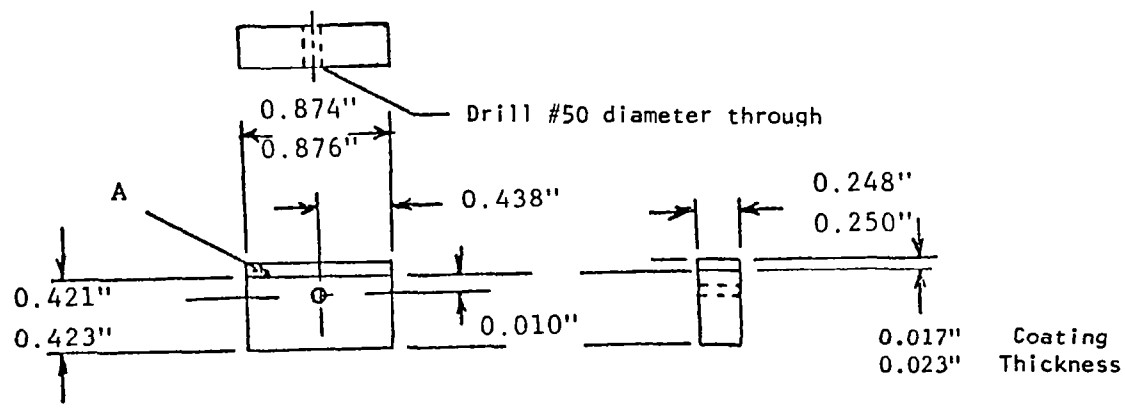



*Figure 11. Rub block specimen for NASA wear test machine.*

TABLE 8. COAT MEASUREMENTS OF RING SPECIMENS

| Specimen No. | Diameter, in. | | | Thickness, in. | |
|---|---|---|---|---|---|
| | Substrate | Substrate/ Bond Coat | Substrate/ Bond Coat/ Top Coat | Bond Coat | Bond Coat/ Top Coat |
| 1 | 1.336 | 1.340 | 1.377 | .002 | .021 |
| 2 | 1.336 | 1.340 | 1.379 | .002 | .022 |
| 3 | 1.336 | 1.340 | 1.376 | .002 | .020 |
| 4 | 1.335 | 1.339 | 1.375 | .002 | .020 |
| 5 | 1.336 | 1.340 | 1.377 | .002 | .021 |
| 6 | 1.336 | 1.341 | 1.375 | .002 | .020 |
| 7 | 1.336 | 1.341 | 1.374 | .003 | .019 |
| 8 | 1.336 | 1.340 | 1.374 | .002 | .019 |
| 9 | 1.336 | 1.340 | 1.375 | .002 | .020 |
| 10 | 1.336 | 1.341 | 1.375 | .003 | .020 |

Substrate: Inconel 750
Bond coat: Metco 43C
Top coat: PS101

TABLE 9. COAT MEASUREMENTS OF RUB BLOCK SPECIMENS

| Specimen No. | Thickness, in. | | | | |
|---|---|---|---|---|---|
| | Substrate | Substrate/ Bond Coat | Bond Coat | Substrate/ Bond Coat/ Top Coat | Bond Coat/ Top Coat |
| 1 | .423 | .426 | .003 | .441 | .018 |
| 2 | .423 | .427 | .004 | .445 | .022 |
| 3 | .424 | .427 | .003 | .445 | .021 |
| 4 | .432 | .425 | .002 | .442 | .019 |
| 5 | .424 | .426 | .002 | .441 | .017 |
| 6 | .424 | .427 | .003 | .441 | .017 |
| 7 | .424 | .427 | .003 | .444 | .020 |
| 8 | .422 | .425 | .003 | .442 | .020 |
| 9 | .423 | .425 | .002 | .442 | .019 |
| 10 | .423 | .426 | .003 | .440 | .017 |
| 11 | .424 | .426 | .002 | .441 | .017 |
| 12 | .424 | .426 | .002 | .444 | .020 |
| 13 | .424 | .427 | .003 | .444 | .020 |
| 14 | .423 | .426 | .003 | .442 | .019 |
| 15 | .424 | .427 | .003 | .442 | .018 |
| 16 | .424 | .427 | .003 | .441 | .017 |
| 17 | .424 | .427 | .003 | .444 | .020 |
| 18 | .424 | .427 | .003 | .444 | .020 |
| 19 | .424 | .427 | .003 | .445 | .021 |
| 20 | .423 | .426 | .003 | .4442 | .019 |

Substrate: Inconel 750
Bond coat: Metco 43C
Top coat: PS101

## 2.5 COATING EXAMINATION PROCEDURES

For microstructural studies, bars of Inconel 750 were plasma-spray coated with PS106. The plasma-spray scheme consisted of bars 2 x 0.21 x 1/4 in. thick separated by 0.052 in. wide spacers to give a composite spraying area of approximately 2 x 2 in. In this manner, individual bars can be cut up, etched differently, analyzed, and still be compared since the coats were similarly sprayed.

### 2.5.1 Grinding and Polishing

A Buehler (model No. 45-1502) grinding/polishing wheel with two speeds (low, 155 rpm; high, 233 rpm) and an 8 in. diameter wheel was used for all polishing. The low speed (155 rpm) was used for all stages. The following method was used to obtain suitably polished surfaces for microstructural studies.

| Stage | Abrasive | Lubricant | Cloth |
|---|---|---|---|
| 1. Fine grinding | 600 grit SiC[a] | Water | -- |
| 2. Rough polishing | 6 micron diamond[b] | Lapping oil[c] | Polishing cloth[d] |
| 3. Fine polishing | 1 micron diamond[d] | Lapping oil | Polishing cloth |

[a]Carbimet paper discs, Buehler, Ltd.

[b]Metadi diamond compound, Buehler, Ltd.

[c]Metadi fluid, Buehler, Ltd.

[d]Texmet No. 40-7618, Buehler, Ltd.

In stage 1 a light pressure is used to minimize the chances of "disturbed metal formation" which is literally a smearing of the topmost surface metal. Use short time periods of polishing (3 to 6 sec). For specimen PS106-3-21C it was found that 8 to 10 mils removal was sufficient.

Between each grinding and polishing period (each period consisting of several 3 to 5 sec intervals), the specimens were rinsed with distilled water, lightly scrubbed with a detergent solution, rinsed with distilled water, rinsed with ethyl alcohol, and then dried with a heat gun. Many time periods for each stage and great care are required for good sample preparation.

A 5-minute ultrasonic wash in Alconox detergent solution is also done between each stage. Hand washing between stages is also necessary.

In stage 2, most of the 600 grit paper scratches are removed. Slightly firmer pressure can be employed at this time to help minimize the chances for pullout. This is also the reason for using the stiffer cloth with very little nap such as Buehler's Texmet cloth instead of the nylon cloth. Again, only short grinding periods (<10 sec) should be used.

In stage 3, the 6 micron diamond scratches are removed. Short time periods with firm pressure are used. Frequent examination of the surface was made with a microscope during all three stages. It was found that the 1 micron diamond paste fine polish gave a suitable finish for the microscopic examination of the microstructural features. An example of the amount of material removal during the grinding and polishing operation for a non-impregnated coat of PS106-3-22A as follows:

| | | |
|---|---|---|
| 1st stage: | Fine Grinding | approx. 6 mils |
| 2nd stage: | Rough Polishing | approx. 0.4 mils |
| 3rd stage: | Fine Polishing | approx. 0.1-0.2 mils |

Microscopic examination of the polished sample showed uniformity of particles and dispersion of nichrome and silver far superior to the coating for the previous program (NAS3-20827).

For bars coated with PS106-8,9, Table 10 gives examples of coat thickness after each stage, indicating the amount of removal necesary to attain 0.010 in. final thickness. Depending upon the initial coat thickness, the second stage was used to reduce excessive thickness rather than the first stage, because the depth of surface smearing is less. This gives a better chance of seeing the true microstructural surface. This is often a long procedure because the particle size in the diamond paste is only 6 microns. From the table, the average amount of removal in stage 3 is calculated to be 0.0003 in. or 0.3 mil to obtain a satisfactory polish.

### 2.5.2 Etching Procedures

In the previous program etching was done by heating the polished specimen overnight in an oven to attain a discoloration of the silver particles, thus

TABLE 10. COAT THICKNESS AFTER EACH GRINDING STAGE

| Identification No. | Thickness of[a] Sprayed Coat, in. | After[a] Stage 1 | After[a] Stage 2 | After[a] Stage 3 |
|---|---|---|---|---|
| 6-8,9-1 | 0.0259 | 0.0149 | 0.0104 | 0.0103 |
| 6-8,9-2 | 0.0300 | 0.0147 | 0.0102 | 0.0101 |
| 6-8,9-3 | 0.0322 | 0.0161 | 0.0104 | 0.0098 |
| 6-8,9-4 | 0.0305 | 0.0157 | 0.0103 | 0.0100 |

[a]Average of three measurements on each bar (1/4 in. from the left and right end, and center).

differentiating them from the nichrome and $CaF_2$ particles, both of which are not affected by heating to 110°C.

During this program an etching scheme was developed that led to results which aided both the image analyses and the quantitative microscope work. A decorating scheme to differentiate the NiCr particles from the silver particles of a polished specimen of PS106, when viewed microscopically, can be obtained by the use of $H_2S$. $H_2S$ readily discolors silver but shows no attack of nichrome.

The problem was to find a method where $H_2S$ can be quickly generated and easily applied to the specimens. A process that proved effective rquired the use of thioacetamide. This is an organic compound with the chemical forumla, $CH_3\ C\ —\ SH{:}NH$.

This compound hydrolyzes in water, particularly when heated to give $H_2S$ as follows:

$$CH_3\overset{\overset{SH}{|}}{C}{:}NH + 2H_2O \rightarrow CH_3COOOH + NH_3 + H_2S$$

An 8% solution of the compound was made by dissolving in distilled water. If the bottle is stoppered and kept at room temperature, very little reaction occurs. When heated above 50°C, hydrolysis is sufficient to yield a solution saturated with $H_2S$.

In the decorating procedure, approximately 10 cc of the solution was poured into a small evaporating dish which was placed on a hot plate set to 200°F. A thermometer immersed in the solution showed that when the liquid temperature reached 50°C a white gas began coming off. When the temperature reached 55°C the freshly polished surface of PS106 coat was immersed in the liquid. It has been found that a one minute immersion gave a brown discoloration to the silver particles, and that under the microscope the silver particles could be readily differentiated from the nichrome particles.

A series of etchings were studied using 1/2 in. lengths of the previously polished specimens of 6-8,9-1 (which was originally 2 in. in length).

The first series of etchings were done with the thioacetamide 8% solution. Various immersion times were studied: 1 min, 3 min, 6 min, 12 min, and 24 min. Microscopic observations are shown in Table 11.

A series of tests were also made by the heat treatment method. Specimens were placed in a small electric oven at the following temperatures and time: 300°C for 5 min and 10 min, 420°C for 10 min, 520°C for 12 min, 650°C for 10 min, 760°C for 10 min, and 770°C for 60 min. Results are shown in Table 11.

Immersion in a 95% ethyl alcohol-5% HCl solution for 15 sec and 30 sec was also done. A specimen immersed in the 95% alcohol-5% HCl solution was then immersed in the thioacetamide solution. The Ag still discolored to a dark brown. After these tests it was concluded that the thioacetamide immersion method for periods less than 3 min gave the most distinctive details for microscopic analysis.

### 2.5.3 Image Analysis

Polished sections of plasma sprayed coats of composition PS106 were examined by image analysis which is a measuring process in which the percent of a phase in a given area is determined. An IMANCO Quantimet-720 image analyzing computer interfaced with a Leitz Ortholux microscope was employed in the analyses. In addition to the basic standard computer and standard detector, IITRI's Q-720 is equipped with the variable frame and scale module, one function computer, and one classifier collector. IITRI's system also utilizes the vidicon scanner.

Standard, dry reflected light objectives were used on the Ortholux to produce the image for the Q-720. With the objective-ocular combination used,

TABLE 11. COLOR CHANGES OF POLISHED AND ETCHED PS106 SPECIMENS

| Method | Time, min. | Observations |
|---|---|---|
| Immersion in heated 8% solution of thioacetimide | 1 | Silver-light brown; other phases - no change |
| | 3 | Silver-darker brown; others, no change |
| | 6 | Silver-multi colored, blue, red, purple; others, no change |
| | 12 | Silver-mostly blue, some purple; others, no change |
| | 24 | Silver-brown, some grey; others, no change |
| Heat Treatment, 300°C | 5 | Silver-blue, red around edges; others, no change |
| | 10 | Silver-increased blue; others, no change |
| 420°C | 10 | Silver-etched or grainy surface; no change |
| 520°C | 10 | Silver-brown; NiCr, mottled |
| 650°C | 10 | Silver-blue; NiCr, mottled; $CaF_2$ clear but light grey |
| 760°C | 10 | Silver-mottled; NiCr blue and grey |
| | 60 | Silver-white, mottled; NiCr-dark grey-black; $CaF_2$ multi colored |
| Immersion in a 95% ethyl alcohol-5% HCl solution | 0.25 | Slight differentiation of phases |
| | 0.50 | Speckling of Ag phase, NiCr not attacked. |

a total image magnification of 325X was produced. The smallest detectable point in the image (1 picture point) was equivalent to 0.93 μm. Thus, for each 500,000 $pp^2$ field of view (areas) analyzed, 428,657 $\mu m^2$ of sample was examined.

Each of the sample phases could be detected independently in most cases, by selecting the appropriate threshold ranges and settings. Silver and nichrome were somewhat difficult to distinguish from each other, due to their similar reflectance properties. However, careful control of the etching procedure produced samples with sufficient differences in gray level between these two phases to allow separate detections of the silver and nichrome; the silver was made to appear slightly gray in color compared to the highly reflective "white" color of the nichrome. The nichrome was detected on the

"whiter than" threshold range (potentiometer 1) and the calcium fluoride was detected on the "blacker than" threshold with potentiometer 4. The silver was detected in a two-step process with the threshold range set at "slice"--i.e., a gray level between the "white" nichrome and the "black" (brown, actually) calcium fluoride.

A two-step process was required to correct for the "halo error" produced by the standard detector. A "halo" is produced at the intersection of the desired intermediate gray phase with a darker phase, because of the finite resolution of the scanning beam. As the beam reaches the intersection of the two phases, a narrow width perimeter around the dark phase is integrated with a narrow width perimeter around the intermediate gray phase to yield a gray band within the boundaries of the dark phase that are detected at the potentiometer 2 setting. The net effect is that the silver area is overestimated, due to the introduction of the narrow band area being detected in the dark phase. The correct threshold was set for the silver phase on potentiometer 2, and the data were recorded. The "halo" of the silver phase on the juxtaposed edges of calcium fluoride grains was then measured by adjusting potentiometer 3 to just detect the "halo." The measured "halo" area was then subtracted from the silver area data measured on the potentiometer 2 setting to yield the true silver area.

The accuracy of the measurement is dependent upon the clarity of phase differences (polishing technique) and the difference in gray level phase contrasts (etching technique). In order to find the most favorable phase contrast required for accurate measurements, three specimens etched by the thioacetamide method were first tested. The immersion times of these test pieces were 30 sec, 1 min, and 2 min. The coat composition was PS106. For all three immersion times the NiCr remained white, and the $CaF_2$ remained a dark gray to black. Only the silver changed color, becoming light brown (30 sc), dark brown (1 min), and dark brown with some red and/or blue discoloration (2 min). Slight variation in immersion time, dependent upon the polished section may be necessary to obtain the most desirable discoloration. It was found that by making the silver as dark brown as possible without the formation of red and/or blue discoloration, readings of all three phases could be made where the sum of the phase percentages were within the accuracy of the Quantimet 720 (100 ± 2%, summation of the phases).

It was found that thorough rinsing after etching was very important to maintain the degree of discoloration throughout the image analysis period. The following procedure gave satisfactory results:

1. Quickly immerse the specimen in distilled water after it had received a specified etching time. Immediately and vigorously move the specimen back and forth in the water.
2. Remove and rinse thoroughly in running water.
3. Quickly plunge specimen in a second beaker of distilled water with back and forth movement.
4. Quickly remove and rinse with distilled water.
5. Immerse in a third beaker of distilled water and ultrasonically clean for 3 to 5 min.
6. Remove, rinse thoroughly in running water.
7. Rinse with ethyl alcohol.
8. Dry with a heat gun.

By following this procedure the discoloration remained stable throughout the analyses.

2.5.4. Quantitative Microscopy

Measurement of the phases of polished coat sections were made by quantitative microscopy as initiated and fully described in the previous program (Contract No. NAS3-20827). By this method one may determine the compositional uniformity of a plasma-sprayed coat. A metallographically polished section is usually used. The basic idea is that geometrical information about a representative three-dimensional structure, such as a phase volume, may be obtained from suitable analysis of a representative two-dimensional section through the sample. If a grid is superimposed at a statistically sufficient number of places, the volume fraction of the phase of interest ($V_V^{Ag}$, $V_V^{CaF_2}$, $V_V^{NiCr}$) is equal to the fraction of grid points that fall within the phase. Thus,

$$V_V = P_p = \frac{\Sigma \text{ \# points within the phase of interest}}{(\text{Total \# points in the grid})(\text{\# of grid placements})}$$

This is true, independent of any phase size or shape. The limitations are that the structure being examined be sufficiently uniform so that an

arbitrarily obtained section will be representative and that a sufficient number of grid placements be made to get adequate statistical distribution (ITIRI Final Report No. D6146, Contract No. NAS3-20827).

Point counting was done manually in the same manner as previously by superimposing the grid in the eyepiece on the magnified polished section. The same type of scaled eyepiece was used with the end points of the six major division lines acting as grid points. Measurements were made on 0.2 x 2 in. long bars. Instead of making 40 total placements as previously, a total of 80 placements were made. Figure 12 is a schematic of the greater quantity of placements and a view of the grid points at each placement. The bar was moved past the objective lens at 1 mm intervals for a total of 40 placements on one side of a 40 mm length. Another 40 placements were taken with the distance between the first and second 40 placements of approximately 2 mm. The ends of the major scale line gave 12 points for a total counting of 80 placements times 12 points at each placement or 960 total points. (For the previous program the total point count was 480.) The other difference was that a slightly larger area was viewed. Figure 12 shows that the area, currently, was 230 μ x 58 μ; previously it was 180 μ x 56 μ.

## 2.6. COATING BOND STRENGTH MEASUREMENTS

The adhesive strength was determined for plasma-sprayed coatings on Inconel 750 substrates. The test method was according to ASTM designation: C633-69, "A Standard Method of Test for Adhesion or Cohesive Strength of Flame-Sprayed Coatings." In this method the degree of adhesion is determined in tension normal to the surface. One face of a plasma-sprayed substrate fixture is bonded with an adhesive to the face of a loading fixture.

Because of the higher bond strengths obtained for coatings in the current program as compared to those of the previous program, a greater demand is placed on the adhesive used in testing. Consequently, adhesive tests were run on blank bond strength specimens using two epoxy resins under two curing cycles, in order to determine the higher adhesive strength material. Results of the tests, given in Table 12 show that Armstrong A-12 with a 24 hr room temperature (RT) cure followed by a 2 hr post-cure at 165°F gave the highest strength. This is the adhesive cure treatment used for all specimens.

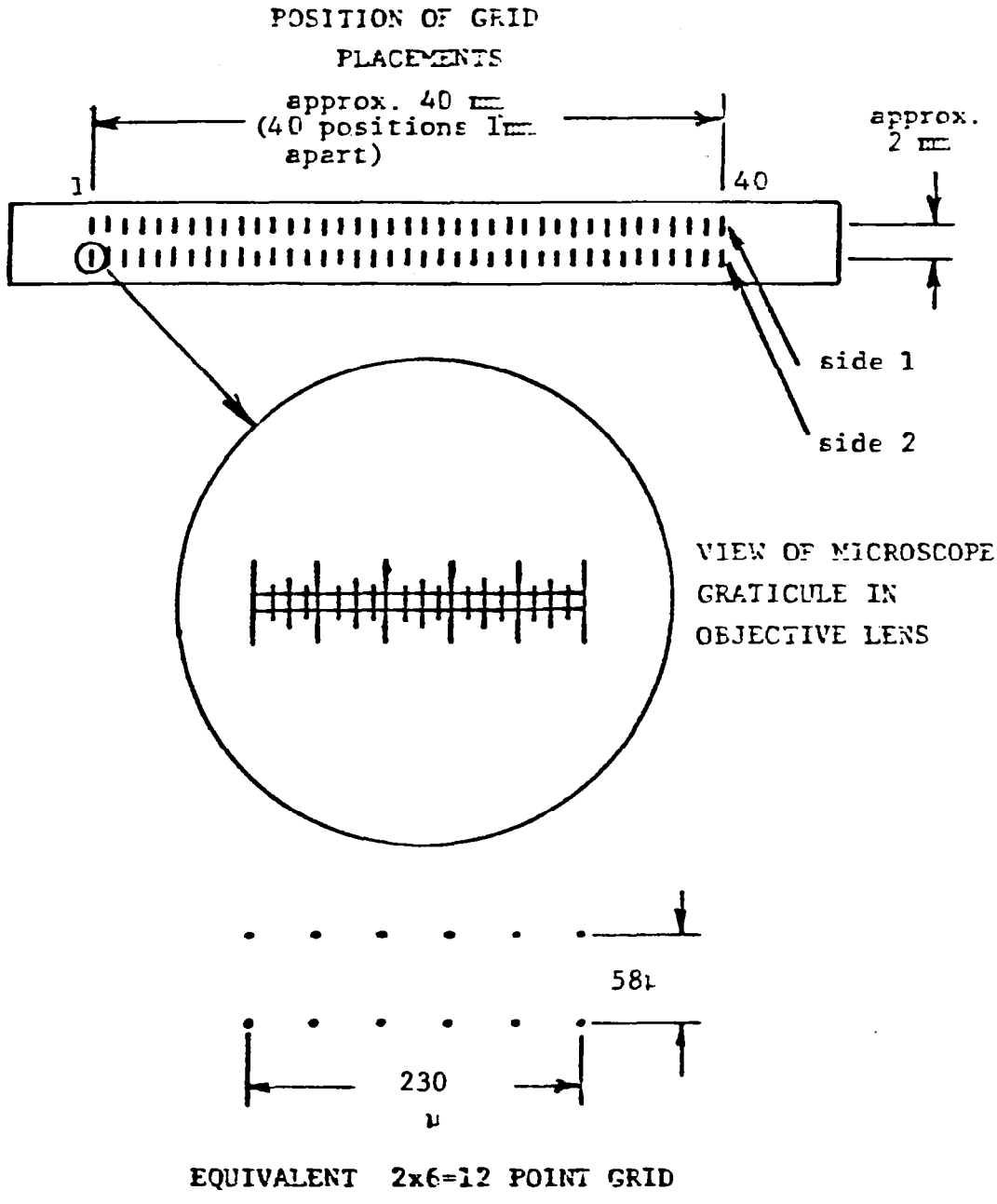



*Figure 12. Scheme for making quantitative microscopy measurements.*

TABLE 12. ADHESIVE STRENGTH TESTS OF TWO TYPES OF EPOXY RESINS

| Cure Treatment | Bond Strength, psi | |
|---|---|---|
| | Hysol Brand IC, White Epoxy | Armstrong A-12 |
| RT, 24 hr cure | 3569 | 4166 |
| RT,24 hr cure 165°F 2 hr post-cure | 4268 | 5414 |

## 2.7. OXIDATION TESTS

Two types of oxidation tests, intermittent and continuous, were made on each of the compositions of PS106, MPS106, and PS101 that were spray coated on test coupons having dimensions of 2 x 2 in. by approximately 0.060 in. thick. In the intermittent mode, weight changes were taken at suitable intervals by removal, cooling, and weighing; in the continuous mode weight changes were monitored continuously. Test durations for both modes were 100 hr at each of the folloiwng temperatures: (1) 1200°F (649°C), (2) 1400°F (760°C) and 1650°F (899°C).

Two specimens of each composition were examined in the intermittent mode, and one specimen of each composition was tested in the continuous mode. Correction factors for substrate oxidation were determined by also making oxidation tests of substrate coupons for each mode.

The procedure for the preparation of metal substrates before plasma-spraying required grit-blasting on both sides to minimize substrate bowing. This was followed by hand-polishing the backside with 400 grit SiC abrasive paper to minimize the surface area available for oxidation. Despite this precaution, coated specimens showed slight bowing. Blank substrate coupons were hand-polished with 400 grit SiC paper on both sides to obtain equivalent surface oxidation.

The plasma spray coats were required to have a final thickness of approximately 0.010 in. An actual as-sprayed coat thickness of approximately 0.018 in. of this multi-phase aggregated powder was needed to satisfactorily grind and lap down to give a smooth surface of 0.010 in.

During the grinding and/or lapping of the coat to the required thickness of 0.010 in., the slight bowing that had occurred due to the grit blasting preparation curtailed the lapping operation. Therefore, the coats were lapped to a 0.010 in. thickness at the peak points and then hand-ground in the bowed or valley portions to obtain the overall 0.010 in. thickness. Grinding was done with 240, 320, and finally 400 grit abrasive SiC paper. Twelve thickness measurements were made over the 2 x 2 in. substrate area. Figure 13 shows the points of measurements by numbered circles.

2.7.1 Weights of NiCr or NiCrAl in Coats

The initial weights of NiCr or NiCrAl were calculated b using the weight of the coat $W_c$ times the fractional amount of NiCr or NiCrAl in the coat.

The initial weight of the coats $W_c$ for all specimens is given in Table 13. The calculated weights of NiCr or NiCrAl in the coats are given in Table 14.

TABLE 13. INITIAL WEIGHT OF COAT, $W_c$ (g) FOR ALL SPECIMENS

| | PS106 | MPS106 | PS101 | Substrate |
|---|---|---|---|---|
| 1200°F (649°C) | | | | |
| Intermittent[a] | 3.4624 | 3.8794 | 3.2188 | 33.8329 |
| Continuous | 3.7933 | 3.7671 | 3.2815 | 34.0980 |
| 1400°F (760°C) | | | | |
| Intermittent[a] | 3.6793 | 3.6205 | 3.189 | 34.188 |
| Continuous | 4.0811 | 3.7315 | 3.2888 | 33.5693 |
| 1600°F (899°C) | | | | |
| Intermittent[a] | (4.3459) | (3.8414) | (3.3434) | 33.9347 |
| 1200W | 3.4098 | 3.8086 | 3.2823 | 33.8949(100) |
| 1400W | (3.5855) | (3.6315) | 3.1740 | 33.7265(100) |
| Continuous | 4.1307 | 3.9411 | 3.1693 | 33.9898 |

[a]Intermittent values are the average of two coats.

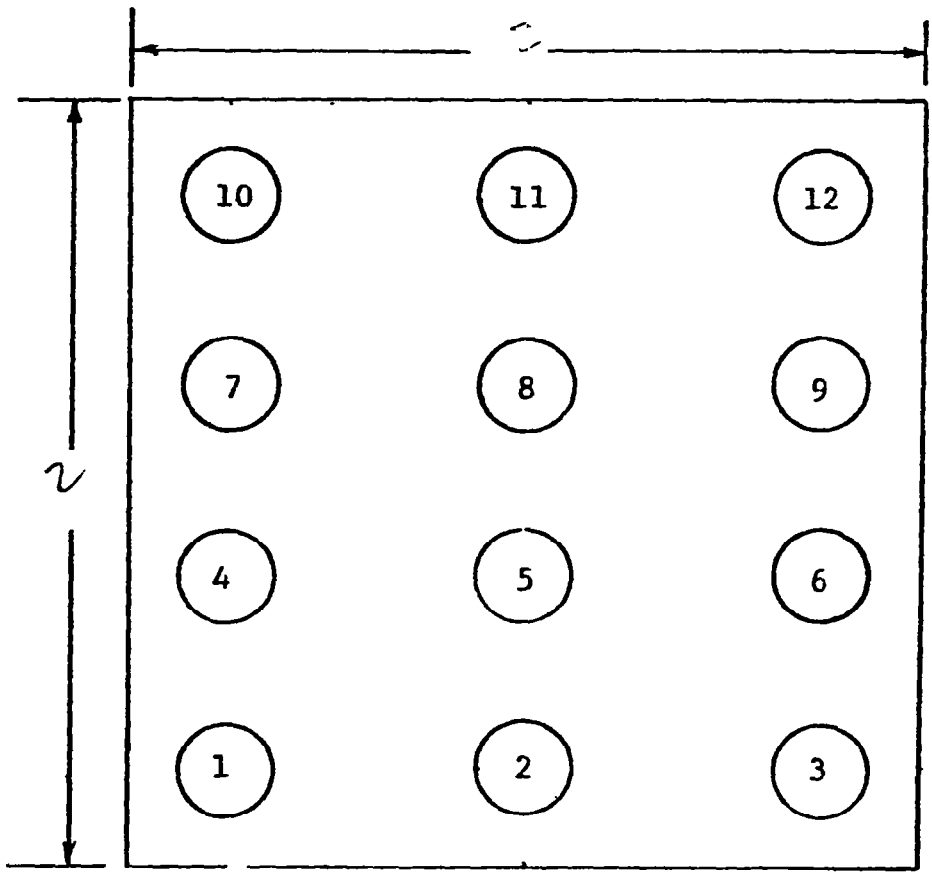



*Figure 13. Location of thickness measurement areas indicated by numbered circles.*

TABLE 14. CALCULATION OF WEIGHT OF NiCr OR NiCrAl IN THE COAT

| | PS106 | MPS106 | PS101 |
|---|---|---|---|
| 1200°F (649°C | | | |
| Intermittent, g[a] | 1.1461 | 1.3811 | 0.9560 |
| Continuous, g | 1.2556 | 1.3411 | 0.9746 |
| 1400°F (760°C) | | | |
| Intermittent, g | 1.2178 | 1.2889 | 0.947 |
| Continuous, g | 1.3508 | 1.3284 | 0.977 |
| 1650°F (899°C) | | | |
| Intermittent, g | 1.4385 | 1.3675 | 0.993 |
| Continuous, g | 1.3673 | 1.4030 | 0.941 |

[a]Intermittent values are the average of two coats.

The values of weight percent NiCr or NiCrAl were obtained from the chemical analyses data of the compositions and were determined to be as follows:

| | | | |
|---|---|---|---|
| PS106[a] | - | NiCr | 33.1% |
| MPS106 | - | NiCrAl | 35.6% |
| PS101 | - | NiCr | 29.7% |

2.7.2. Intermittent Mode

A Thermolyne box-type electric kiln monitored by an off-on control mechanism (Omega Model 150) was used. With this system, a test temperature of approximately ±5° was obtained. Besides the furnace control thermocouple, two thermocouples were positioned just above the surface of the specimen. One led to a strip chart recorder to give a continuous recording of the furnace temperature and the other thermocouple to a digital temperature readout.

The specimens were placed on ceramic setter pins resting on a SiC slab (Fig. 14) to obtain uniform heating on the top and bottom sides, thus closely resembling the type of exposure to be encountered in the continuous oxidation

[a]See Appendix for complete analyses.

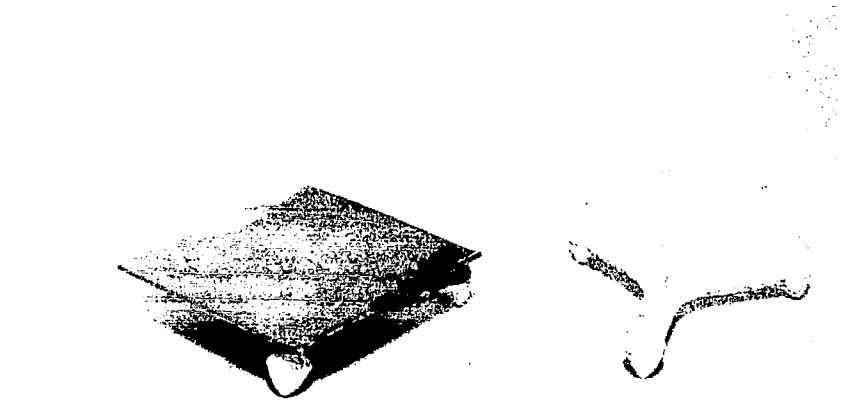


*Figure 14. Oxidation test setup for intermittent mode.*

test where specimens were suspended in the furnace by attachment to a fine wire.

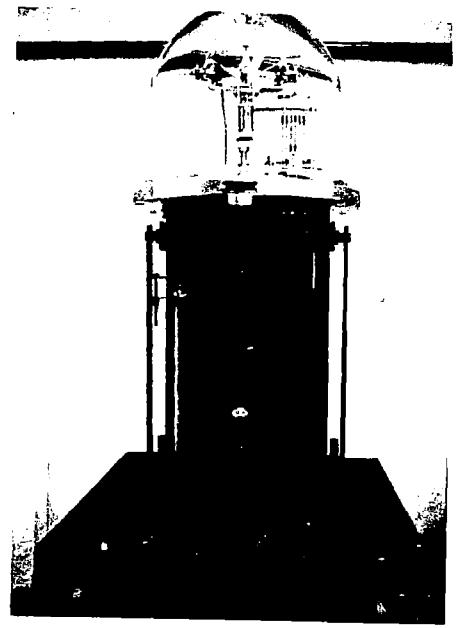
2.7.3. Continuous Mode

The continuous mode oxidation tests were made using an Ainsworth recording balance, Model RV. This balance incorporates an automatic weight-changing mechanism. The final measuring system that gave acceptable oxidation results contained the following components: (1) the Ainsworth balance; (2) the Ainsworth Type AU-2 recorder unit (a two-pen strip chart recorder which records temperature and weight gain or loss); (3) a small wire wound furnace (4 x 4 x 6 in. deep inside dimensions, Huppert Deluxe furnace, Model 434 DL, 120 V, 8.7 amps); and (4) an L&N silicon-controlled rectifier (Model No. 10915) with an L&N digital set-point proportional controller. Three thermocouples monitoring the temperature were located approximately 1/2 in. from the top and extended 1-3/4 in. into the furnace. These were connected to: (1) the controller, (2) the strip chart recorder, and (3) a digital thermometer. Oxidation runs were made with the 2 x 2 x 1/16 in. thick specimens that had a 1/16 in. hole drilled in one corner. These test coupons were suspended in the furnace with a fine nichrome wire from the 1/16 in. hole to an attachment on the Ainsworth balance located 2-1/2 ft above the furnace. Figure 15 shows this system with a glass tube from the balance to the top of the furnace to maintain still air for the suspension system.

Calibration studies for actual specimen temperature for 649°C (1200°F), 760°C (1400°F), and 899°C (1650°F), were conducted by spot welding a fine Chromel-Alumel thermocouple to a suspended blank substrate. Three other thermocouples in the furnace were attached to (1) a digital readout, (2) an L&N set-point controller, and (3) an Ainsworth strip chart recorder.

The actual temperature of the substrate was compared with the temperature given by the digital readout (Table 15). Adjustments of the controller set-point were made to give steady temperature readings. The temperature was held constant for at least 1 hr at each of the three temperature levels.

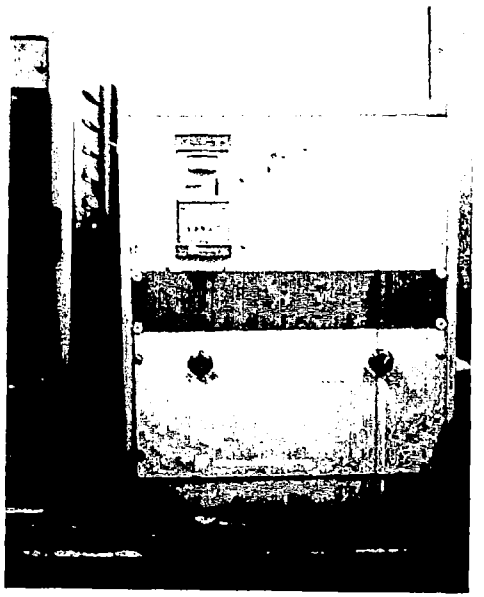
Since no thermocouples could be attached to the specimens in the actual test runs, it was assumed that the coated test specimens were at approximately the same temperature as the substrate blank used for specimen calibration. In the actual test runs the temperature for each range was determined by the



Ainsworth
Balance

Digital
Thermometer

L & N Digital Set Point
Proportional Controller



Two-Pen Recorder Unit

L & N Silicon-Controlled Rectifier

Huppert Furnace with
Suspended Specimen and
Three Thermocouples

*Figure 15. Continuous mode oxidation test system.*

TABLE 15. CALIBRATED TEMPERATURE CONTROL READINGS FOR OXIDATION TEST TEMPERATURES

| Specimen Temperature | Digital Readout | Temperature Difference |
|---|---|---|
| 649°C (1200°F) | 672°C | 23°C |
| 760°C (1400°F) | 784°C | 24°C |
| 899°C (1650°F) | 927°C | 28°C |

digital temperature readings as shown in Table 15, adjusted by the digital set-point proportional controller. Readings of ±1°C were obtained throughout 100 hr at temperature.

## 2.8. FREE-STANDING COAT SPECIMENS

Free-standing cylinders of a PS106 plasma-sprayed coat approximately 1/4 in. diameter x 1 in. in length were prepared by first spraying on a NaCl substrate. To obtain this NaCl substrate, a saturated aqueous salt solution was sprayed on a heated stainless steel mandrel. The rotating mandrel was heated using a Meeker burner so that rapid evaporation of the water portion of the salt solution on contact left a residue coating of solid NaCl particles. Plasma-spraying of the PS106 was done while the mandrel was still hot to obtain a good coating. The salt substrate was subsequently dissolved in water, and a free-standing cylinder was obtained. Figure 16 shows such as specimen.

### 2.8.1. Density/Porosity

Density/porosity measurements were obtained by the liquid immersion method and were made on as-sprayed specimens.

The following procedure was used.

1. Wash specimens in an acetone bath by ultrasonic treatment for 5 min; rinse and dry overnight at 105°C.
2. Obtain dry weight, D.
3. Place specimens in a vacuum chamber. Evacuate and maintain evacuation for 10 min.

*Figure 16. Free-standing cylindrical specimen of a plasma-sprayed coat of PS106.*

4. Completely cover specimens with distilled water.

5. Resume vacuum for 30 min.

6. Measure density/porosity by the water (distilled) displacement method.

7. Use a copper wire, 10 mil diameter to suspend specimen.

8. Use two drops of ethylene glycol to reduce surface tension.

9. Obtain suspended weight, S, by subtracting the weight of the suspending wire, T.

10. With a damp cloth, quickly remove surface water and obtain saturated weight, W.

11. Equations:

(1) Apparent porosity, $\% = \frac{W - D}{W - S} \times 100$

(2) Bulk density $= \frac{D}{W - S}$

D = dry wt, g

W = saturated wt, g

S = suspended wt, g

where W - D = open pore volume, cc ($\rho_{water}$ = 1g/cc)

W - S = volume of exterior portion, cc.

(When the immersion liquid is kerosene, use the following equation for bulk density:

$$BD = \frac{D \times (\text{specific gravity of kerosene})}{W - S}$$

The equation for apparent porosity remains the same.)

### 2.8.2. Thermal Expansion

Measurements of thermal expansion were made with a Model 402 push-rod type dilatometer from the Netzsch Bros., Inc. An alumina sample holder with an alumina push-rod was used for this test. Heating rates of 1°C/min, 2°C/min or 5°C/min are generally used. For the NASA specimens tests were conducted at 2°C/min. A faint greenish tinge was observed on the alumina sample holder, indicating that slight vaporization occurs even for composition PS106 at the higher temperature (1650°F).

# 3. RESULTS AND DISCUSSION

Processing reproducibility and coat uniformity were improved considerably during this present program. This was due to emphasis on quantitative control, improvements in ceramic processing technology, and modification of the particle size range. The resulting materials were evaluated for optical and mechanical properties, oxidation resistance, and for physical properties. The results of these studies are discussed in the following sections.

## 3.1 PROCESSING MATERIAL BALANCES

Quantitative control of powder preparation was conducted by monitoring the material loss measurements from each step in the 5-step process. Table 16 gives the averages and standard deviation of the loss data for seven to nine batches of PS106, and Table 17 gives the averages and standard deviations of six PS101 batches. The data in the two tables indicate that the greatest losses occur in step 4b, and is the result of previous grinding and screening for the removal of fines (-325 mesh material). Since too few batches of MPS106 were made for standard deviation data (2 batches), average weight data of the process are given in Table 18. The greatest loss again occurred in step 4b due to the separation of fines to obtain a -100+325 mesh aggregate size range.

A list of the dates at which batches of PS106 were made is given below, showing the range of time over which batch processing was conducted with consistency.

| Batch No. | Date Processed |
|---|---|
| PS106-4 | 9/27/79 |
| PS106-4 | 10/3/79 |
| PS106-6 | 11/26/79 |
| PS106-7 | 2/12/80 |
| PS106-8 | 6/11/80 |
| PS106-9 | 7/8/80 |
| PS106-10 | 4/27/81 |
| PS106-11 | 12/1/81 |
| PS106-12 | 1/4/82 |

Similarly, processing dates for the six batches of PS101 were from 4/7/80 to 2/5/82. Again, good reproducibility from batch to batch was realized.

TABLE 16. MATERIAL BALANCE OF POWDER PREPARATION PROCEDURE OF PS106 COMPOSITION

| | Avg Wt ( )* | Standard Deviation |
|---|---|---|
| Step 1: | | |
| Initial weight of mix, g | 96.3 | |
| Average weight loss after milling,g | 0.07 (7) | 0.05 |
| Step 2: | | |
| Add 36 cc MAP solution, g | 39.3 (7) | |
| Step 3: | | |
| Dry overnight, 110°-115°C, g | 100.31 (9) | |
| Average weight loss after -100 mesh screening, g | 0.79 (9) | 0.53 |
| Step 4: | | |
| a. Heat to 400°-440°C (3 hr), g | 98.21 (9) | |
| Weight loss (dehydration), g | 1.35 (9) | |
| Weight cured MAP, g | 2.76 (8) | |
| b. Weight loss after -100+325 | 8.56 (9) | 0.74 |
| Step 5: | | |
| Amount $CaF_2$ added | | |
| 13.7 g + weight loss from Step 4 (Average), g | 22.18 (9) | |
| Average calc. percent MAP in final batch | 2.25 (8) | 0.23 |
| Final batch weight, g | 111.82 (9) | |

*(No. of batches)

TABLE 17. MATERIAL BALANCE OF POWDER PREPARATION PROCEDURE OF PS101 COMPOSITION

| | Avg Wt. (6)* | Standard Deviation |
|---|---|---|
| Step 1: | | |
| Initial weight of mix, g | 82.5 | |
| Average weight loss after milling, g | 0.15 | 0.19 |
| Step 2: | | |
| Add 31 cc MAP solution, g | 33.8 | |
| Step 3: | | |
| Dry overnight, 110°-115°C, g | 86.0 | |
| Average weight loss after -100 mesh screening, g | 0.98 | 0.28 |
| Step 4: | | |
| a. Heat to 400°-440°C (3 hr), g | 83.95 | |
| Weight loss (dehydration), g | 1.13 | |
| Weight cured MAP, g | 2.75 | |
| b. Weight loss after -100+325 mesh screening, g | 7.85 | 1.05 |
| Step 5: | | |
| Amount $CaF_2$ added | | |
| 11.0 g + weight loss from Step 4, g | 19.1 | |
| Amount NASA glass added, g | 16.5 | |
| Average calc. percent MAP in final batch | 2.04 | 0.01 |
| Final batch weight, g | 111.65 | |

*(No. of Batches)

TABLE 18. MATERIAL BALANCE OF POWDER PREPARATION PROCEDURE OF MPS106 COMPOSITION

| | Avg Wt., 2 batches |
|---|---|
| Step 1: | |
| Initial weight of mix, g | 96.3 |
| Average weight loss after milling, g | 0.06 |
| Step 2: | |
| Add 36 cc MAP solution, g | 39.3 |
| Step 3: | |
| Dry overnight, 100°-115°C, g | 100.22 |
| Average weight loss after -100 mesh screening, g | 1.68 |
| Step 4: | |
| a. Heat to 400°-440°C (3 hr), g | 97.18 |
| Weight loss (dehydration), g | 1.40 |
| Weight cured MAP, g | 2.49 |
| b. Weight loss after -100+325 mesh screening, g | 7.89 |
| Step 5: | |
| Amount $CaF_2$ added | |
| 13.7 g + weight loss from Step 4, g | 21.59 |
| Average calc. percent MAP in final batch | 2.06 |
| Final batch weight, g | 110.6 |

## 3.2 POWDER CHEMICAL ANALYSES

Chemical analyses were made for several batches of as-processed multi-phase plasma powder. The analyses were done by Coors/Spectro-Chemical Laboratories in the present program. Table 19 compares the chemical analyses results for six batches with analyses of a similar amount from the previous program, as well as the averages of each phase and standard deviations. The improved uniformity and closeness to the specifications is readily apparent.

In the Appendix chemical analyses are presented for four batches as-received from Coors/Spectro-Chemical Laboratories and the conversion of these results to the values of the major components of each composition.

TABLE 19. CHEMICAL ANALYSES OF PS106 PLASMA POWDERS

| | Present Phase of Work | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Batch | | | | | | | Standard |
| | 4 | 5 | 6 | 7 | 8 | 9 | Average | Deviation |
| Nichrome | 41 | 37 | 38 | 42 | 34 | 34 | 38 | 3.4 |
| Silver | 31 | 35 | 35 | 31 | 37 | 36 | 34 | 2.6 |
| $CaF_2$ | 28 | 28 | 27 | 26 | 29 | 30 | 28 | 1.2 |

| | Previous Work | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Batch | | | | | | | Standard |
| | 14C | 15G | 16G | 17G | 18G | 19C | Average | Deviation |
| Nichrome | 53 | 63 | 54 | 38 | 37 | 32 | 46 | 12.6 |
| Silver | 25 | 9 | 16 | 33 | 34 | 39 | 26 | 11.6 |
| $CaF_2$ | 22 | 28 | 30 | 30 | 29 | 29 | 28 | 3.0 |

Specifications: NiCr 35 ± 3; Ag 35 ± 3; $CaF_2$ 30 ± 3 Weight Percents

### 3.3 IMAGE ANALYSES

Three specimens of PS106 were examined by image analyses; IITRI specimens No. 6-8,9-3 and 6-8,9-4 and NASA specimen No. 5141. The IITRI specimens were polished coats with surface dimensions of approximately 2 x 1/4 x 1/6 in. thick. The NASA specimen had a surface dimension of 7/16 in. by 1/4 in. and was imbedded in plastic; the IITRI specimens were not. One side of the NASA specimen, as-received, had been ground down to the substrate surface. As a consequence, only one end of the 1/4 in. wide section could be measured. Each specimen was etched by the thioacetomide method. The NASA specimen was repolished in order to give it a thioacetomide etch.

Table 20 gives the NASA specified range in volume percent as calculated from weight percent. The results of image analysis measurements converted to volume percent is shown in Table 21. The sum totals and sums of the average of all measured data fall very close to within the accuracy of the Quantimet 720 (100 ± 2% for the sum of phases in the given area), indicating that the etching technique gave satisfactory phase contrast.

TABLE 20. SPECIFIED RANGE OF COMPOSITION PS106 IN WEIGHT AND VOLUME PERCENT

| Material | wt% | vol% |
|---|---|---|
| Ag | 35 ± 3 | 20 ± 2 |
| Nichrome | 35 ± 3 | 25 ± 2 |
| $CaF_2$ | 30 ± 3 | 55 ± 5 |

For the IITRI specimens of 2 in. length, measurements were made at approximately 1/4 in. from each end (pts 1 and 7 for specimen No. 3, pts 1 and 5 for specimen No.4); at the center (pt 4 for each specimen). All other points were equispaced between these boundary points. More area points were taken of specimen No. 3 because the first two points taken showed a considerably higher amount of silver although the total count was accurate (99.6% and 99.8%).

The accuracy of the method and the average of the three phases agree well with the specified volume composition range. The accuracy for the total count of the NASA specimen was good (100.6%); however, the amount of $CaF_2$ gave a low count in comparison to the specified range composition.

TABLE 21. RESULTS OF IMAGE ANALYSES DATA
BY USE OF THE QUANTIMET 720 IMAGE ANALYZER

Volume %

NASA 5141

No. of points taken - 3

| | (1) | (2) | (3) | Avg |
|---|---|---|---|---|
| NiCr | 30.0 | 33.2 | 26.5 | 29.9 |
| $CaF_2$ | 42.5 | 43.5 | 45.9 | 44.0 |
| Ag | 26.9 | 25.6 | 27.6 | 26.7 |
| | 99.4 | 102.3 | 100.0 | 100.6 |

Specimen 6-8.9-3

No. of points taken - 7

| | (1) | (2) | (3) | (4) | (5) | (6) | (7) | |
|---|---|---|---|---|---|---|---|---|
| NiCr | 23.3 | 12.6 | 25.5 | 25.3 | 24.2 | 24.7 | 23.9 | 22.8 |
| $CaF_2$ | 51.3 | 57.7 | 56.1 | 54.4 | 55.3 | 57.6 | 59.8 | 56.0 |
| Ag | 25.4 | 26.5 | 17.9 | 20.5 | 20.8 | 18.3 | 17.0 | 20.9 |
| | 99.6 | 99.8 | 99.2 | 100.2 | 100.3 | 100.6 | 100.7 | 99.7 |

Specimen 6-8.9-4

No. of points taken - 5

| | (1) | (2) | (3) | (4) | (5) | |
|---|---|---|---|---|---|---|
| NiCr | 22.9 | 25.5 | 23.9 | 24.6 | 23.8 | 24.1 |
| $CaF_2$ | 55.2 | 53.6 | 59.6 | 56.0 | 58.7 | 56.6 |
| Ag | 20.4 | 22.3 | 19.9 | 20.2 | 19.5 | 20.5 |
| | 98.5 | 101.4 | 103.4 | 100.8 | 102.0 | 101.2 |

Specified volume percent range: NiCr - 25 ± 2; Ag - 20 ± 2; $CaF_2$ - 55 ±5

### 3.4 QUANTITATIVE MICROSCOPY

Three specimens were analyzed by this method. The coated samples of PS106 were all on Inconel 750 bars with polished surface dimensions of 0.2 x 2 in. Two of the bars, Nos. 6-8,9-3 and 6-8,9-4, had also been measured by image analysis. Since the image analysis had required a dark brown discoloration, these specimens were repolished and given a light brown silver discoloration (etching time 30 sec), a more suitable contrast for microscopic analysis. These two specimens were made from a mixture of batches 8 and 9 that were made on June 11, 1980 and July 8, 1980. These batches were combined in the hopper feed just before plasma spraying. The third specimen analyzed was marked PS106-3 No. 21C. This was made from batch No. 3 which was made on September 12, 1979.

Comparison of the results obtained for the three coats are given in Table 22 showing the apparent uniformity of the sprayed compositions despite being made from different batches. These data were obtained using 80 grid placements for a total of 12 x 80 = 960 points over a 0.2 x 2 in. surface area. Previously only 40 grid placements for a total of 480 points were mde for specimens of similar areal dimensions.

TABLE 22. QUANTITATIVE MICROSCOPIC ANALYSIS OF PLASMA-SPRAYED COATS

| | Specimen No. | | | | | |
|---|---|---|---|---|---|---|
| | 6-8, 9-3 | | 6-8, 9-4 | | PS106-3, 21C | |
| Ingredients | Vol% | S.D.* | Vol% | S.D. | Vol% | S.D. |
| Ag | 20 | 1.37 | 22 | 1.26 | 20 | 1.22 |
| NiCr | 25 | 1.61 | 26 | 1.66 | 26 | 1.45 |
| $CaF_2$ | 56 | 1.68 | 52 | 1.66 | 55 | 1.6 |

*S.D. = standard deviation.

Specified range: vol%, Ag 20 ± 2, NiCr 25 ± 2, $CaF_2$ 55 ± 5.
Total Grid Placement = 80
Total number of points = 960

## 3.5 CORRELATION OF OPTICAL EVALUATION DATA

Table 23 gives the average chemical analysis of batches 8 and 9 in weight percent of the three major components NiCr, AG, and $CaF_2$. These are compared with the averages of the image and quantitative microscopy analyses whose data for the two specimens from Tables 19 and 20 were converted from volume percent to weight percent.

The correlation between chemical and optical analyses is good, indicating that the modifications in particle size ranges and procedures, and the quantitative control of processing parameters provide consistency in the powder-to-coat transformation. It also indicates that the plasma spray system with the vibratory-screw feed hopper yields a consistent transfer from powder feed to coat.

Two photomicrographs of polished and etched coated surfaces of PS106 are shown in Figs. 17 and 18, respectively, for IITRI specimen No. PS106-23A2 and NASA specimen No. 5141.

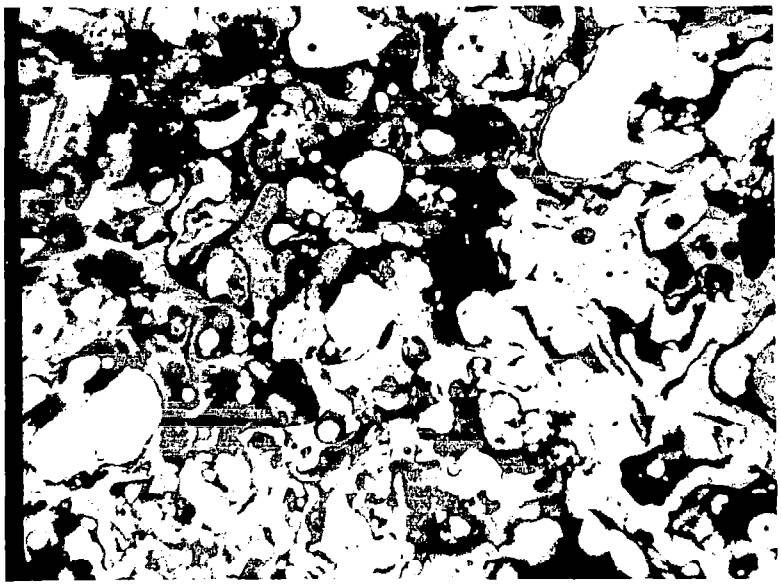
TABLE 23. COMPARISON OF WET CHEMICAL ANALYSIS OF PROCESS POWDER PS106 (BATCH 8 AND 9 COMBINED) WITH IMAGE AND QUANTITATIVE MICROSCOPY ANALYSES OF PLASMA-SPRAYED COAT SPECIMENS FROM THE SAME BATCH MIX

| | Weight Percent | | |
|---|---|---|---|
| Ingredients | Chemical Analysis of Batches 8,9, avg | Image Analysis* | Quantitative Analysis* |
| Nichrome | 34 | 33.2 | 35.5 |
| Silver | 36.5 | 36.6 | 36.3 |
| $CaF_2$ | 29.5 | 30.1 | 28.2 |

Specified Range: NiCr, 35 ± 3; Ag 35 ± 3; $CaF_2$ 30 ± 3.

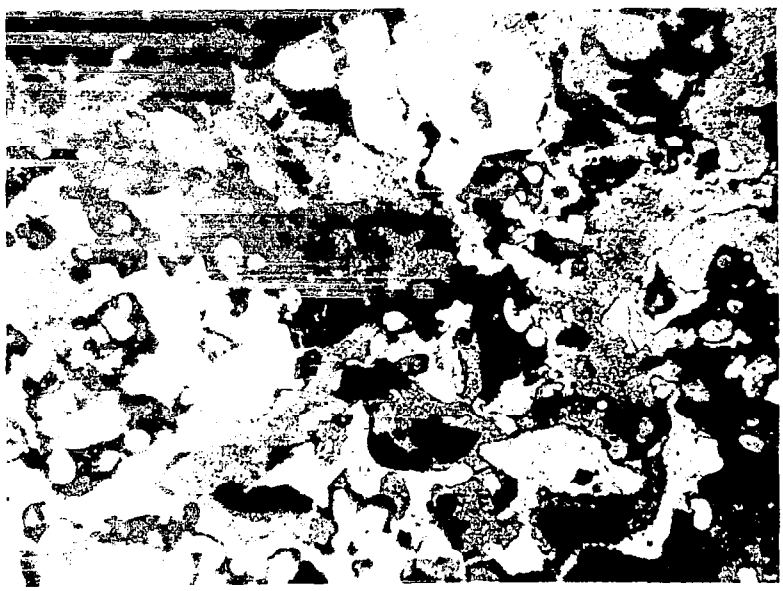
*Average of No. 6-8,9-3 and 6-8,9-4 converted to weight percent.

For each photomicrograph the light colored phase is nichrome, the intermediate gray color is etched silver, and the dark area is calcium fluoride. These photographs were taken at 200 magnification and show the phase shapes and differences.



200X

*Figure 17. Polished and etched section of IITRI specimen No. 23A2, PS106 composition.*



200X

*Figure 18. Polished and etched section of NASA specimen No. 5141, PS106 composition.*

These differences are more readily apparent in Fig. 19 at 80X. A greater overview of the field can be seen between NASA 5141 and specimen No. 6-8,9-3. A greater uniformity is seen in IITRI's No. 6-8,9-3. Figure 20 compares IITRI specimens 23A2 with No. 6-8,9-4. No. 6-8,9-4 was made from the same powder batch mix as No. 6-8,9-3 of Fig. 19 (a mixture of batch 8 and 9) whereas No. 23A2 was made from powder batch No. 4. The small particle dispersion and uniformity of field appears to be quite similar, indicating good uniformity from batch to batch.

### 3.6 BOND STRENGTH TEST RESULTS

Bond strength determinations were made on plasma-sprayed coats on metal substrates of Inconel 750. The substrates were 1 in. diameter cylinders, 1-1/4 in. length. Three sets of samples were tested, with each set consisting of six samples. Set No. 1 had an intermediate bond coat of nichrome (Metco 43C powder) and set No. 2 had an intermediate bond coat of nickel aluminide (Metco 404 powder). The bond coat for each set was in the required 0.003 to 0.005 in. thickness range. Each set of six was then plasma-sprayed with PS106 composition powder. The thickness of the PS106 top coat was 0.015 in. for each set. The six specimens of set No. 3 were composed of PS106 sprayed directly on a sandblasted substrate. Three specimens from each set were heat treated at 1200°F (649°C) for 20 hr.

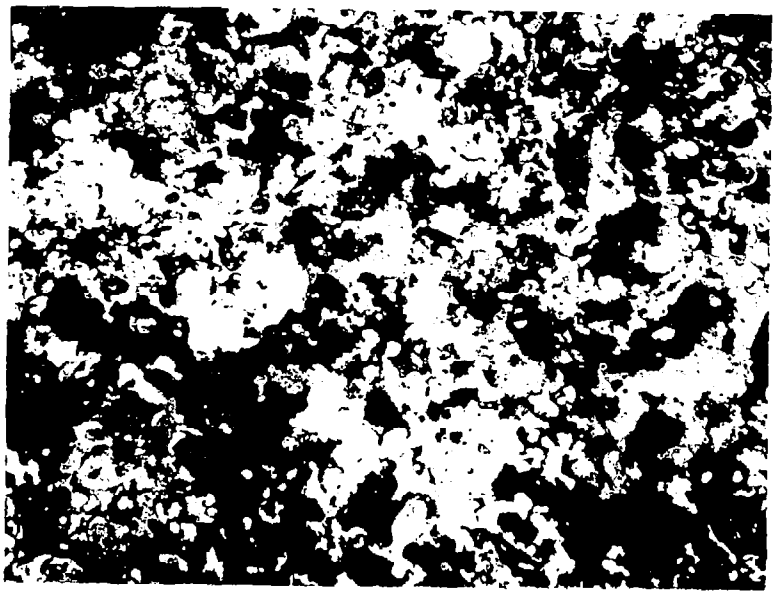
Comparative values of the bond strengths are given in Table 24.

All specimens of Sets 1 and 2 showed clean breaks; there were no adhesive failure with the Armstrong A-12 resin, even for the heat-treated specimens. Two specimens of the set with no bond coat (Nos. 13 and 18 of Set No. 3 in Table 24) showed partial adhesive failure. The adhesive agent for this Set was Hysol brand, IC White epoxy resin.

The data, coupled with microscopic examination, show the following results:

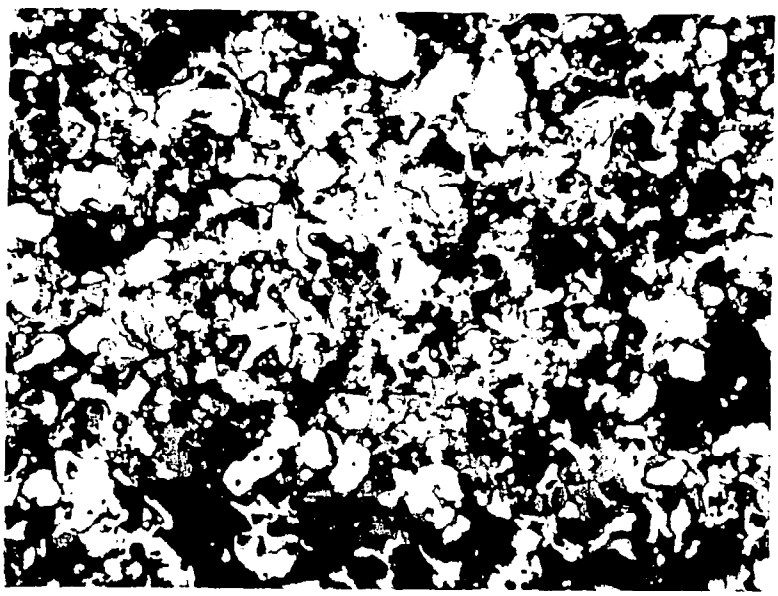
(1) As-sprayed nichrome intermediate bond coat specimens gave strengths consistently higher than that for NiAl bond coat or no bond soat samples.

(2) More material adherence to the substrate of bond-coated specimens indicates more failure in the coat itself whereas the no-bond-coat material showed greater failure at the substrate interface.



80X

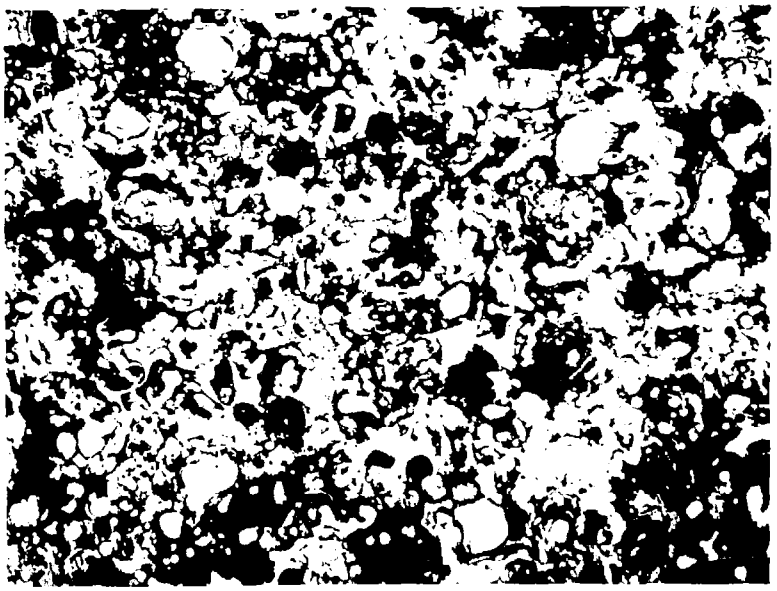
(a)



80X

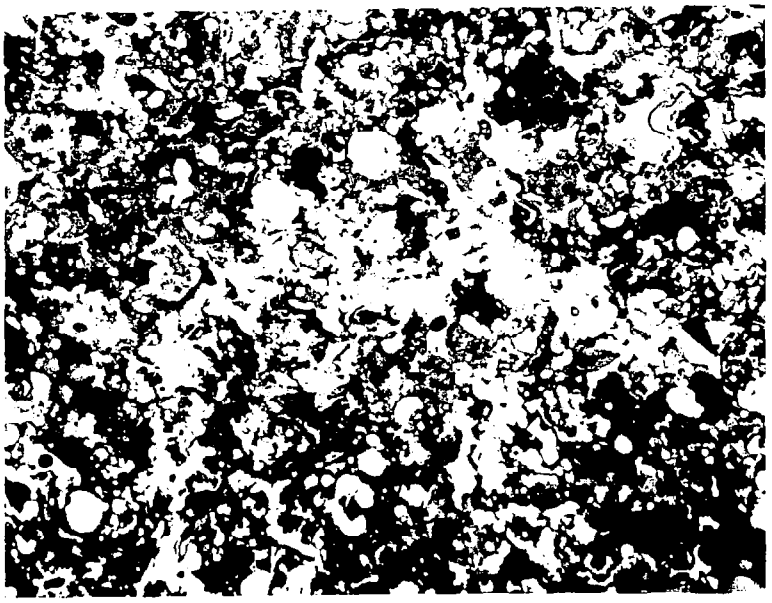
(b)

*Figure 19. Photomicrographs of polished and etched sections of (a) NASA 5141 and (b) IITRI 6-8,9-3.*



80X

(a) Specimen No. 6-8,9-4



80X

(b) Specimen No. 23A2

*Figure 20. Photomicrographs of polished and etched specimens of two specimens obtained from different powder batches.*

(3) For the heat-treated materials, the type of failure was similar for all three Sets. Very little difference could be seen in the amount of material adherence for the three Sets. The data indicate that the difference between Sets are small.

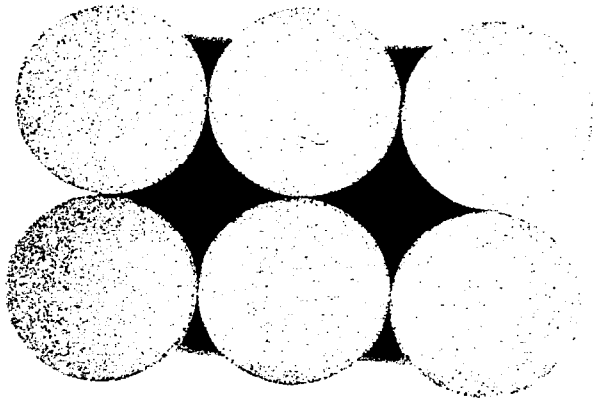
TABLE 24. BOND STRENGTHS OF PS106 COATS

| Sample Description | As-Sprayed Sample No. | As-Sprayed Bond Strength, psi | Heat-Treated[a] Sample No. | Heat-Treated[a] Bond Strength, psi |
|---|---|---|---|---|
| Set No. 1, sandblast, nichrome coat | 18 | 1248 | 13 | 2443 |
| | 17 | 1401 | 3 | 2243 |
| | 1 | 1286 | 16 | 2335 |
| | Avg | 1312 | Avg | 2275 |
| Set No. 2, sandblast, nickel aluminide bond coat | 4 | 1038 | 2 | 2196 |
| | 5 | 1095 | 8 | 2355 |
| | 6 | 968 | 9 | 1948 |
| | Avg | 1034 | Avg | 2166 |
| Set No. 3, sandblast, no bond coat | 14 | 1019 | 13 | 1656[b] |
| | 16 | 1096 | 15 | 2420 |
| | 17 | 1050 | 18 | 2343[b] |
| | Avg | 1055 | Avg | 2140 |

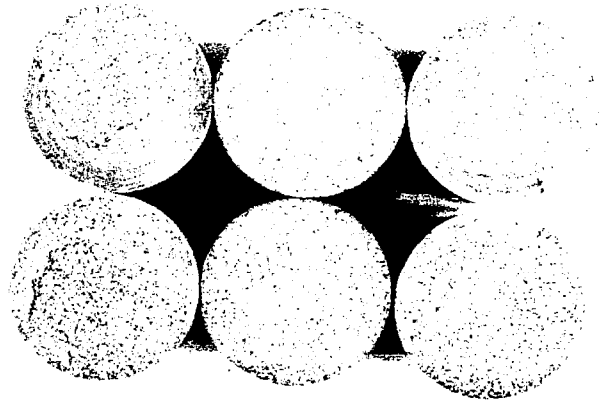
[a]20 hr at 649°C (1200°F); oxidizing heat treatment.

[b]Partial adhesive failure. Calculated effective cross-sectional areas were used.

Microscopic comparison of the failure surfaces of Set No. 3 (as-sprayed strengths compared to the heat-treated strengths) revealed that more particles and larger particles are bonded to the substrates for the heat-treated specimen, indicating that a chemical bonding at the surface may occur on heat treating (Fig. 21). In Fig. 22 a comparison of the failure surface of specimen 16 (as-sprayed) and specimen 15 (heat-treated) is shown under a magnification of 26X with a stereoscopic microscope. The higher density of particles adhering to the substrate of the heat-treated specimen (No. 15) can readily be seen.

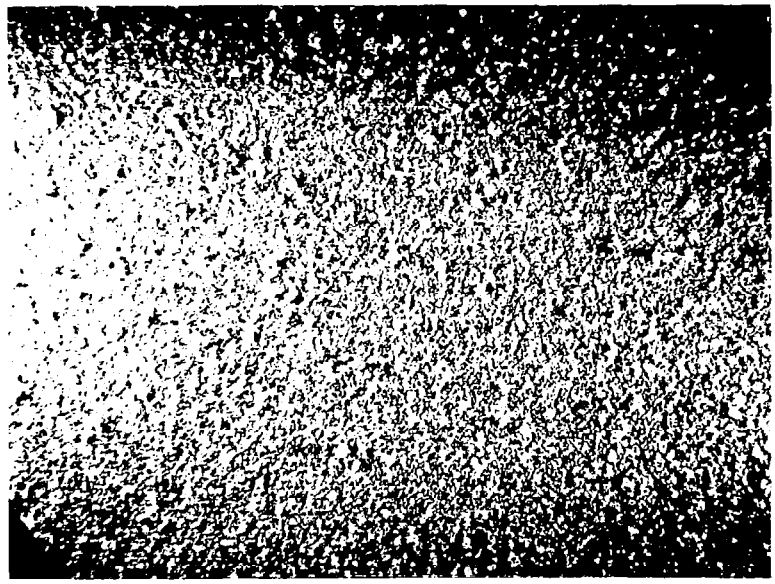



(a) As-sprayed specimens

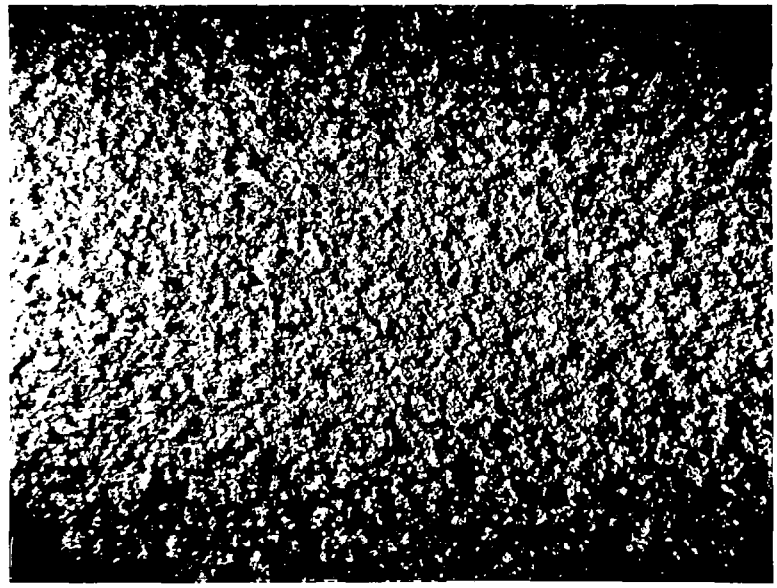



(b) Heat-treated specimens
(20 hr at 1200°F)

*Figure 21. Adhesion of PS106 coatings to Inconel 750 substrates after bond strength tests.*



(a) Specimen 16 (as-sprayed)



(b) Specimen 15 (heat-treated)

*Figure 22. Microscopic comparison of an as-sprayed and a heat-treated substrate.*

Variability of data from one Set to another of plasma-sprayed coats is shown in the comparison of adhesive strengths of PS106 no-bond coat, heat-treated specimens (Table 25). The lower strength specimens of Set No. 1 as compared to Set No. 2 of this table appeared to have slightly larger agglomerated particles in the fracture face (by microscopic examination of the failure surfaces). Set No. 1 still shows values higher than Set No. 3 (previous program strength values). The reason for the lower values of Set No. 1 as compared to Set No. 2 is not known at this time.

Table 26 compares the no-bond coat strength data of the present program (1979) with those of the previous program (1978). The improvements in strength resulting from changes incorporated in the present program can readily be seen.

TABLE 25. COMPARISON OF BOND STRENGTHS OF NO-BOND COAT, HEAT-TREATED SPECIMENS[a] OF PS106

| Set No. 1 | | Set No. 2 | | Set No. 3 |
|---|---|---|---|---|
| No. | Armstrong A-12 Adhesive, psi | No. | Hysol Brand 1C Adhesive, psi | Previous Program, psi[c] |
| 7 | 1580 | 13 | 1656[b] | 1120 |
| 10 | 1554 | 15 | 2420 | 1210 |
| 12 | 1376 | 18 | 2343[b] | 1170 |
| Avg | 1503 | | 2140 | 1167 |

[a]Heat treatment: 20 hr at 649°C.

[b]Partial adhesion, calculated strength on bonded area.

[c]Values fromfinal report IITRI-D6146, December 1978, Contract NAS3-20827.

TABLE 26. ADHESIVE STRENGTH RESULTS OF PS106 NO-BOND COATS

| As-Plasma Sprayed Strength, psi | | Strength after 20 hr, 1200°F (649°C) Heat Treatment in Air, psi | |
|---|---|---|---|
| 1978 | 1979 | 1978 | 1979 |
| 740 | | | 1580 |
| 600 | | | 1554 |
| | | | 1376 |
| 1135 | 1019 | 1120 | 1656 |
| 734 | 1096 | 1210 | 2420 |
| 956 | 1055 | 1170 | 2343 |
| Average: | | | |
| 835 | 1055 | 1167 | 1823 |

### 3.7 INTERMITTENT MODE OXIDATION STUDIES

To determine the actual gain in weight of the coat, a correction factor was used to subtract the substrate oxidation. For the intermittent mode, two blanks were run at each of the required temperatures. For the continuous mode one substrate blank run was made at each of the three temperature ranges.

The following equation was used for both the intermittent and continuous modes to calculate the percent weight gain of the coat, $O_c$, %.

$$O_c, \% = \left[ \frac{(W_t - W_o) - W_s \frac{O_s}{100}}{W_o - W_s} \right] 100 \qquad (1)$$

where $W_t$ = weight of coat + substrate after time t

$W_o$ = initial weight of coat + substrate

$W_s$ = initial weight of substrate

$O_s$ = one-half of the percent substrate oxidation after time t.

In the intermittent mode the coupons were placed on ceramic setter pins, and then inserted directly onto a SiC slab resting in the hot furnace. The time taken to reach temperature was monitored. The specimen held at temperature for a specified time, quickly removed, air cooled for 30 min, then cooled in a dessicator for 30 more min and weighed. Table 27 gives the values

obtained for the substrate oxidation at the three temperature ranges. The weight gain tabulated is 1/2 of the average percent gain in weight of two substrates for 100 hr total exposure at temperature. Only 1/2 of the actual gain in weight is used as a correction factor since the coated specimens have only one bare side of the substrate exposed.

A graphical presentation of the data is given in Fig. 23 where a significantly higher weight gain for the 1650°F (899°C) temperature range is observed; importantly, the rate of weight gain, dw/dt, at 100 hr is much greater for the 1650°F test than for the lower temperatures.

TABLE 27. COMPARISON OF INCONEL 750 SUBSTRATE OXIDATION AT DIFFERENT TEMPERATURES (INTERMITTENT MODE)

| Exposure Period, hr | Total Exposure Time, hr | Percent Weight Gain[a] | | |
|---|---|---|---|---|
| | | 1200°F (649°C) | 1400°F (760°C) | 1650°F (899°C) |
| 1 | 1 | .0019 | .0036 | .0101 |
| 1 | 2 | .0012 | .0029 | .0157 |
| 1 | 3 | .0023 | .0033 | .0186 |
| 3 | 6 | .0031 | .0045 | .0241 |
| 3 | 9 | .0031 | .0050 | .0292 |
| 6 | 15 | .0033 | .0073 | .0337 |
| 18 | 33 | .0033 | .0078 | .0490 |
| 22 | 55 | .0037 | .0091 | .0617 |
| 22 | 77 | .0038 | .0102 | .0713 |
| 23 | 100 | .0043 | .0119 | .0803 |

[a]All values are one-half of the average gain in weight for two samples.

### 3.7.1. The 1200°F and 1400°F Series

The average percent weight gain ($O_c$, %) data are tabulated in Table 28 for the 1200°F range and in Table 29 for the 1400°F range. Data from the two tables are graphically presented in Fig. 24. The 1200°F series shows that PS106 and MPS106 behave somewhat similarly up to 50 hr. From this point the rate of weight change of MPS106 shows a constant gain while PS106 shows a

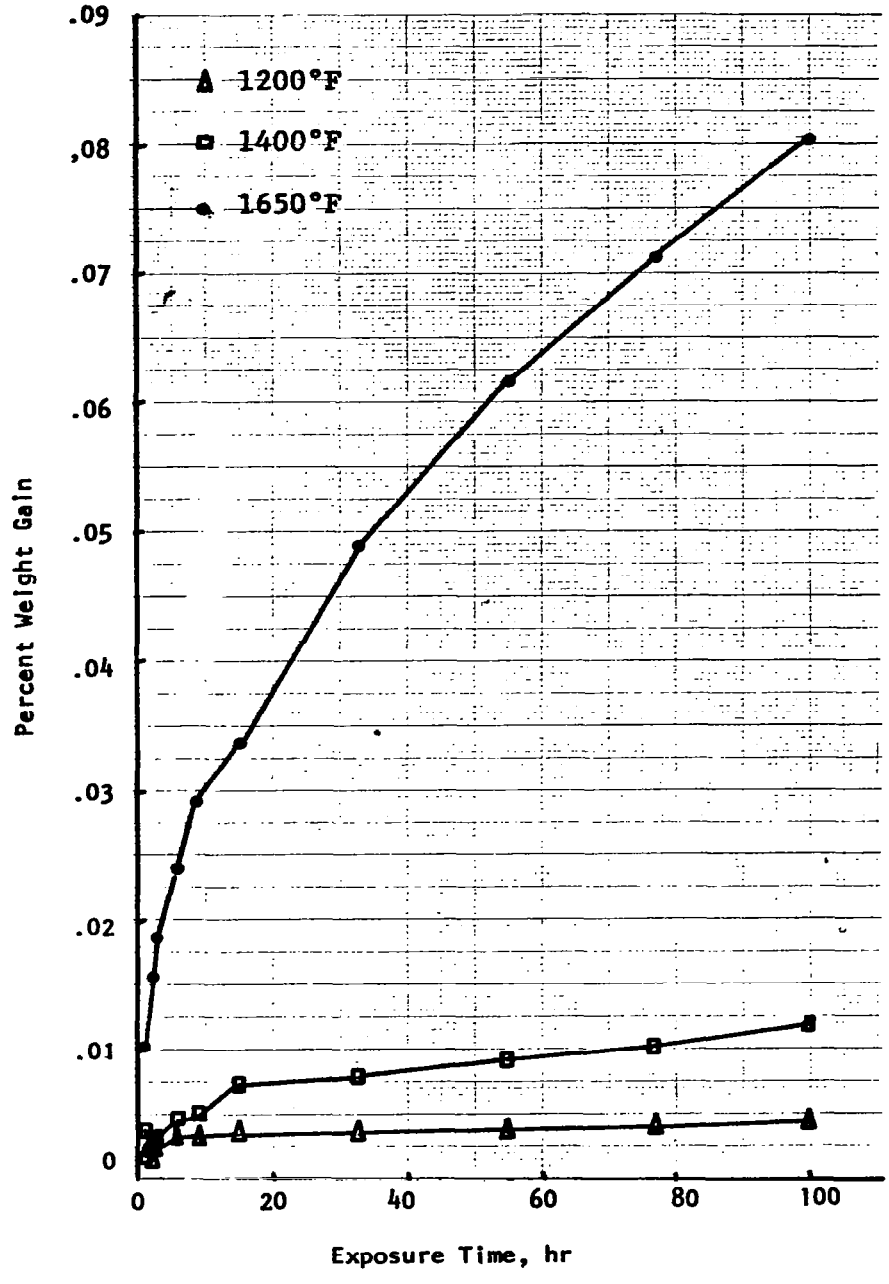



*Figure 23. Oxidation of Inconel 750 substrate blanks exposed for 100 hr at 1200°F, 1400°F, and 1650°F (intermittent mode).*

*Note: All values are one-half of the average percent gain in weight.*

TABLE 28. OXIDATION TEST RESULTS: 100 HOUR EXPOSURE AT 1200°F (649°C)

| Total Exposure Period, hr | Percent Weight Gain[a] | | |
|---|---|---|---|
| | PS106 | MPS106 | PS101 |
| 1 | 0.65 | 0.85 | 0.43 |
| 2 | 0.93 | 1.09 | 0.95 |
| 3 | 1.10 | 1.45 | 1.20 |
| 6 | 1.54 | 1.87 | 1.72 |
| 9 | 1.83 | 2.18 | 2.50 |
| 15 | 2.28 | 2.57 | 3.60 |
| 33 | 2.93 | 3.23 | 4.69 |
| 55 | 3.44 | 3.77 | 5.45 |
| 77 | 3.70 | 4.23 | 6.29 |
| 100 | 3.90 | 4.76 | 7.42 |

[a]Adjusted to account for substrate oxidation.

TABLE 29. OXIDATION TEST RESULTS: 100 HOUR EXPOSURE AT 1400°F (760°C)

| Total Exposure Time, hr | Percent Weight Gain[a] | | | Substrate[b] |
|---|---|---|---|---|
| | PS106 | MPS106 | PS101 | |
| 1.3 | 3.33 | 3.88 | 3.87 | 0.003 |
| 2 | 3.83 | 4.46 | 5.18 | 0.003 |
| 3 | 4.24 | 5.18 | 6.20 | 0.003 |
| 6.3 | 4.90 | 6.59 | 7.03 | 0.005 |
| 9 | 5.36 | 7.59 | 7.42 | 0.005 |
| 15 | 6.09 | 8.72 | 7.88 | 0.007 |
| 33 | 7.52 | 10.43 | 8.74 | 0.008 |
| 55 | 9.13 | 11.59 | 9.11 | 0.009 |
| 77 | 9.84 | 12.26 | 9.39 | 0.010 |
| 100 | 10.43 | 12.7 | 9.53 | 0.012 |

[a]Adjusted to account for substrate oxidation.

[b]One-half of the average percent weight gain of two blanks.

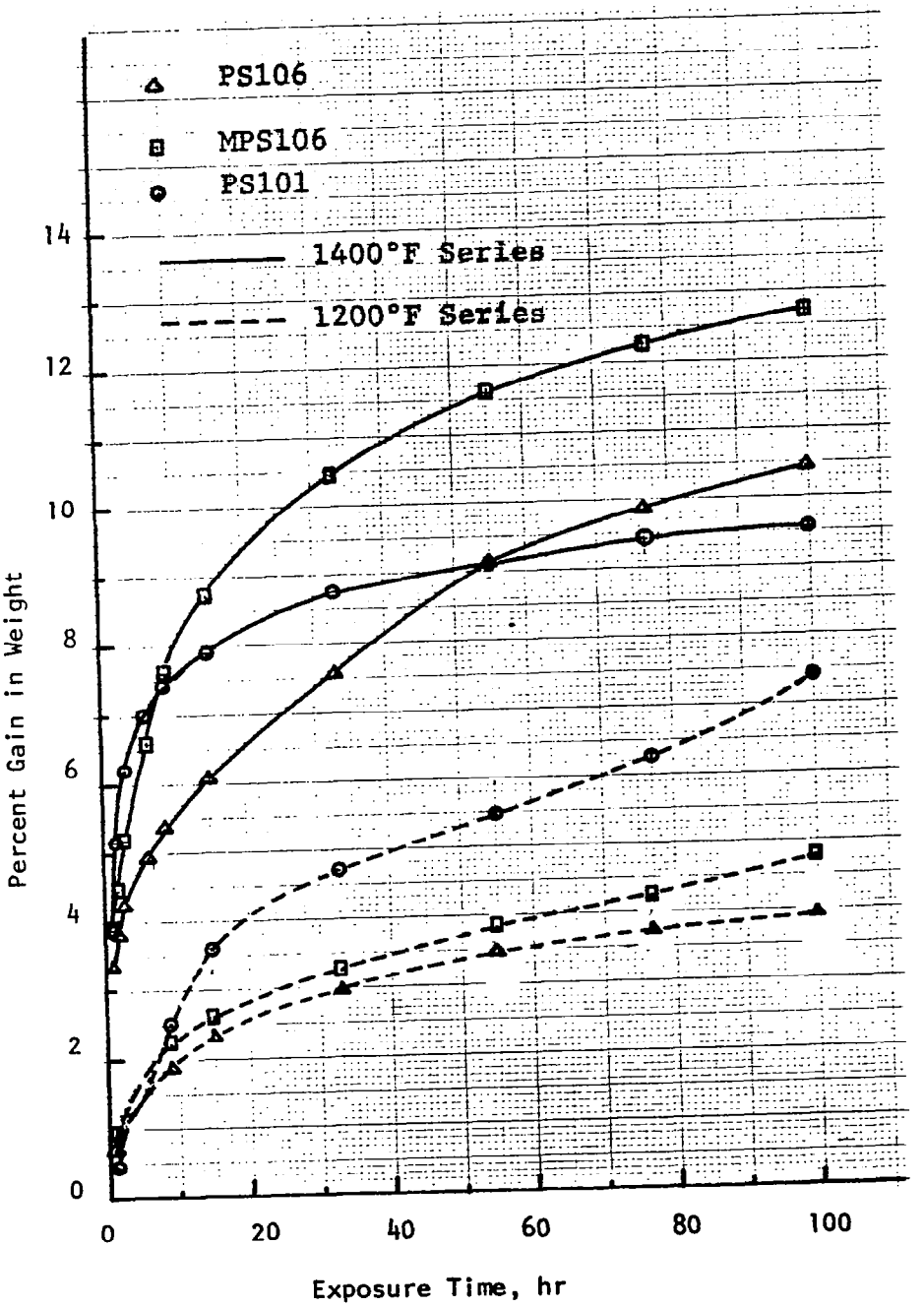



*Figure 24. Oxidation of PS106, MPS106, and PS101 exposed to 1200°F (649°C) and 1400°F (760°C) temperature ranges.*

slight decrease in rate. PS101 showed a high rate of oxidation up to 15 hr, then began an increasing rate of weight gain from 75 to 100 hr.

A different behavior was observed for the different coatings in the 1400°F series, where PS101 showed the highest rate of oxidation in the first 6 hr, but then dramatically decreased its rate of weight gain, dw/dt, to end up with the lowest total weight gain at 100 hr. The PS106 and MPS106 were higher in total weight gain at 1400°F as compared to 1200°F.

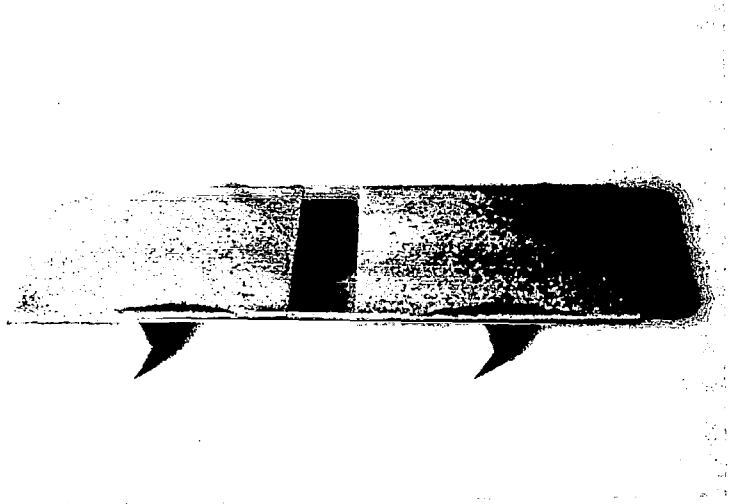
### 3.7.2 The 1650°F (899°C) Series

As was the procedure with the 1200°F (649°C) and 1400°F (760°C) oxidation test series, the 1650°F specimens were placed directly into the furnace which was at the test temperature of 1650°F (899°C). Approximately 3 to 5 min were required for the furnace to reach equilibrium after insertion of the specimens in this "rapid heat-up" method.

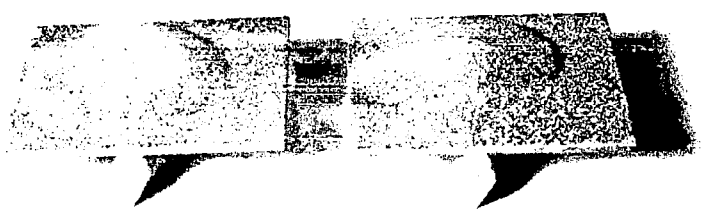
After one hour of exposure, both PS106 specimens exhibited a swelling of an area approximately 1/8 in. diameter in the center of the specimen, while the adhesion at the edges of the sprayed coats was still intact. When the specimens were inserted into the furnace at 1650°F for another hour, the coatings separated from the substrate at the edges as well.

Two other coated specimens, PS106-2 and PS106-4 with coat thickness of 0.0092 and 0.0094 in., were tested but under a slower, more gradual sample introduction into the furnace. Twenty minutes were required to reach equilibrium temperature in this "moderate heat-up" method. After a one-hour exposure at temperature, PS106-2 developed only minor swelling, and PS106-4 showed no apparent swelling. In a second one-hour exposure using the same gradual heating technique, both coats swelled and cracked at the peak of each bubble, indicating formation and escape of gases. Both coats remained intact over a 1/4 in. edge area. Figure 25 shows all four specimens after two hours total exposure time at equilibrium.

In the gradual insertion or "moderate heat-up" method, the furnace power was turned off and the specimens inserted slowly by moving forward at two- to three-minute intervals. The furnace temperature dropped, but not below 1400°F (760°C). Thus, these specimens were exposed to high temperatures an extra 15 min over the "rapid heat-up" set, all at temperatures above 1400°F (760°C).



(a) "Rapid Heat-up" Samples



(b) "Moderate Heat-up" Samples

*Figure 25. Total two-hour exposure of PS106 coated specimens at 1650°F (899°C).*

This is probably why the "moderate heat-up" samples gained more weight for the exposure period designated as one hour at 1650°F (see Table 30). The two hour values show that the final total weight gain was similar for both groups. This was probably due to the separation of the coat from the substrate for the "fast" group (during the second hour), exposing more surface area available for oxidation.

TABLE 30. COMPARISON OF PERCENT GAIN IN WEIGHT OF SPECIMENS OXIDIZED AT 1650°F (899°C)

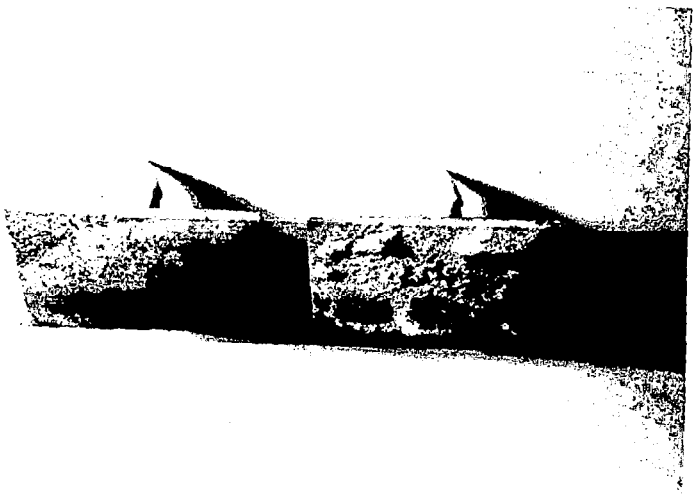
| Specimen No. | Type of Heating | Percent Weight Gain for Total Exposure Periods at 1650°F | |
|---|---|---|---|
| | | One-Hour | Two-Hour |
| PS106-7 | Fast | 4.402[a] | 9.188 |
| PS106-8 | Fast | 4.249 | 8.940 |
| PS106-2 | Slow | 7.55 | 9.086 |
| PS106-4 | Slow | 7.458 | 8.936 |

[a]All values corrected for substrate oxidation.

Two specimens each of MPS106 and PS101 were then tested. It was decided to eliminate one variable, namely, physical water pickup that might influence high-temperature behavior; subsequent specimens were oven dried at 115°-120°C to remove any moisture and then inserted into the 1650°F (899°C) equilibrium atmosphere without allowing the specimens to cool to room-temperature. This elimination had no apparent effect.

Bloating occurred for MPS106-3 and MPS106-9 after one hour exposure at 1650°F (899°C). The bloating was of a blister formation type and appeared to be caused by outgassing. The edges of the coat appeared to be intact. The PS101 coat showed no bloating after one hour.

After 2 hr total exposure, one blister of MPS106-3 showed a crack at its base, and the large blister of MPS106-9 also developed a slight crack at its base. No apparent increase in size of the blisters was noticed. Figure 26 shows the type of blistering that occurred. After 15 hr the crack in MPS106-3 grew considerably, and the blistered portion of MPS106-9 became completely removable.



MPS106-3 MPS106-9

*Figure 26. Specimens MPS106-3 and MPS106-9 after 2-hr exposure at 1650°F (899°C).*

In contrast, PS101-5 and PS101-6 coats remained flat and exhibited good adherence to the substrate through a total of 9 hr. However, after 15 hr both samples began showing separation around the edges. although no blistering had occurred. Figure 27 shows both MPS106 and PS101 compositions after 15 hr exposure. The test was discontinued at this point. Table 31 lists the calculated oxidation data for all three types of coating.

TABLE 31. OXIDATION TEST RESULTS AFTER 15 HOURS INTERMITTENT EXPOSURE AT 1650°F (899°C)

| Total Exposure Time, hr | Percent Weight Gain,[a] $O_c$, % | | | Percent Substrate Oxidation[b], $O_s$ |
|---|---|---|---|---|
| | PS106 | MPS106 | PS101 | |
| 1 | 4.33 | 5.52 | 5.92 | 0.010 |
| 2 | 9.06 | 11.41 | 7.71 | 0.016 |
| 3 | | 13.27 | 9.16 | 0.019 |
| 6 | | 14.34 | 11.28 | 0.024 |
| 9 | | 14.77 | 13.79 | 0.029 |
| 15 | | 14.94 | 14.54 | 0.034 |

[a]All values corrected for substrate oxidation. All values the average of two specimens.

[b]One-half of the average percent weight gain of two blanks.

Examination of the interface between the parted coat and substrate for MPS106-9 revealed that a considerable amount of plasma coat still adhered to the substrate. The underside of the blister showed practically none of the dark green discoloration of the topside of the coat. The separation occurred within the coating itself. It appears that a dense surface layer formed preventing gases from escaping, but the high temperature softened the coat enough to cause separation within the plasma coat, indicating a stronger adhesive bond.

On the other hand, the removable portion of PS101-6 showed a black, thin layer adhering to the underside of the coat, and the exposed blackened substrate appeared to show very few plasma coat particles. The separation is more at the substrate interface. The identity of the dark layer adhering to the underside is not known.

MPS106-3 MPS106-4

PS101-5 PS101-6

*Figure 27. Plasma-sprayed coats of MPS106 and PS101 compositions after 15-hr exposure at 1650°F (899°C).*

### 3.7.3 Oxidation at 1650° (899°C) of Previously Heated Specimens

The oxidation test at 1650° (899°C) has shown that PS106 and MPS106 both bloated within 1 or 2 hr exposure, and that after 15 hr exposure, PS101 had separated from the substrate. Because of these failures, a test was devised to allow such outgassing to occur at a lower temperature (before the surface can be sealed). In the case of PS101 it appears that the glass composition may have a greater chance to react with the substrate (forming a tighter bond) if heat-treated at a lower temperature. By immediately inserting into a high temperature 1650°F, as has been done in test No. 1, the hardened surface has a greater tendency to shrink and curl before adequate bonding to the substrate occurs.

In this series of experiments one sample of each composition that had been exposed at 1200°F (649°C) for 100 hr (PS106, MPS106, and PS101), and another set of these three compositions that had been exposed for 100 hr at 1400°F (760°C) were subjected to testing at 1650°F (899°C).

The same intermittent exposure periods of previous tests were used. Included in the first set tested were: BL-7 (a blank substrate), PS106-1, MPS106-1, and PS101-1. All had been previously exposed at 1200°F for 100 hr, so this test was designated as the 1200W series. The second set was composed of BL-9 (blank substrate), PS106-5, MPS106-4, and PS101-3. These were previously exposed at 1400°F for 100 hr and were designated as the 1400W series.

#### The 1200W Series

Since the total exposure time included the previous 1200°F-100 hr exposure, zero time for this test was indicated as 100 hr and the previous weight results were also listed. Thus, for this series, 1 hr exposure was designated as 101, 2 hr as 102, etc.

After the first hour, PS101 developed a small growth near one corner which appeared to have been due to a defect in the surface. More significantly, several very fine, small (less than 1/16 in. diameter), fragile glass bubbles formed on the edges at the interface between the coat and the substrate. It is suspected that such a bubble may have caused the small rise at a weak point on the surface. These bubbles were extremely fine and could be removed by merely handling the specimen.

After 2 hr, slight cracks had developed on MPS106 on two corners. However, no bloating occurred, and the cracks did not increase in size as exposure was continued. PS106 did not bloat. All specimens remained intact for the entire 100 hr exposure.

Strong color changes occurred for the various samples. PS106 discolored to almost a black color, interspersed with beads of silver; MPS106 showed more of a dark green color with the black, and the surface was not as smooth as PS106; PS101 was a very light gray with some yellow with a more uniform appearance and very fine beads of spherical silver uniformly dispersed on the surface.

The 1400W Series

After the first hour no bloating had occurred in all three specimens. No bubbles formed on PS101. After a total of 6 hr, MPS106-4 developed a blister at one corner. The rest of the surface remained flat but was badly mottled. After 15 hr the coat separated from the substrate at the corner where the blister had previously developed (see Fig. 28) and the test for MPS106-4 was discontinued. The coats of PS106-5 and PS101-3 remained flat and intact.

After 55 hr failure of coat PS106-5 occurred. Figure 29 shows the crack that had developed and the uplifting of the coat at one corner. PS101 remained intact. For the 1400W series PS101 was the only coat to last 100 hr. This coat was flat, even and was slightly more dark yellow-brown than the 1200W PS101.

### 3.7.4 Summary

Intermittent mode oxidation studies at 1650°F (899°C) of plasma-sprayed coating samples on Inconel were completed for all three compositions (PS106, MPS106,and PS101). These were carried either to failure, i.e., significant blistering and/or separation of the coating from the substrate, or to a 100 hr total exposure.

Three different groups of the three compositions tested at 1650°F (899°C) were as follows:

(1) Conventional series; polished, as-sprayed specimens. No prior exposure to high temperature oxidation.

*Figure 28. Plasma-sprayed coat of MPS106-4 (1400W series) after 15-hour exposure at 1650°F (899°C).*

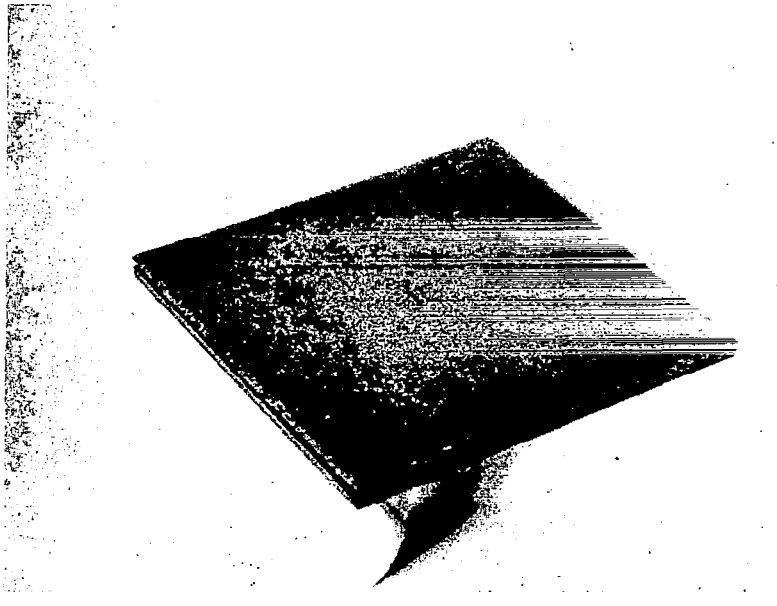


*Figure 29. Failure of PS106-5 (1400W series) after 55 hr at 1650°F (899°C) intermittent-mode.*

(2) The 1200W series; preoxidized at 1200°F (649°C) for 100 hr.

(3) The 1400W series; preoxidized at 1400°F (760°C) for 100 hr.

As tabulated in Table 32, all three compositions of the 1200W series survived the 100 hr exposure; for the 1400W series, only PS101 could be carried to 100 hr; and in the conventional series, all coating separated from the substrates by 15 hr exposure.

TABLE 32. COMPARISON OF THE HOURS-TO-FAILURE FOR THREE COMPOSITIONS WHEN EXPOSED TO 1650°F

| | Hours of Exposure[a] | | |
|---|---|---|---|
| Composition | Conventional Series | 1200W Series | 1400W Series |
| PS106 | 2 | 100 | 55 |
| MPS106 | 2 | 100 | 15 |
| PS101 | 15 | 100 | 100 |

[a]Any value less than 100 hr indicates that coat failure occurred within the designated number of hours.

Oxidation data for the uncoated substrates ($O_s$) in the 1200W and 1400W series, exposed for an additional 100 hr at 1650°F (899°C), are shown in Table 33. The oxidation after the additional 100 hr at 1650°F (899°C) was greater for the 1200W series than for the 1400W series. For the initial 100 hr exposure, 1200W samples showed less oxidation ($O_s$ = 0.0046%, 100 hr/1200°F) as compared to 1400W samples ($O_s$ = 0.0126%, 100 hr/1400°F). It appears that the oxide skin developed on the 1400W substrate during its first 100 hr exposure provided greater oxidation resistance than the oxide skin developed on the 1200W specimen. Consequently, when both were placed in a 1650°F (899°C) atmosphere, the initial oxidation rate was higher for the 1200W specimen. This difference in oxidation rates, as shown in weight gain behavior, may be seen in Fig. 30. Eventually, both oxidation rates became similar.

By use of the substrate oxidation values, $O_s$ (Table 30), the percent weight gain ($O_c$, %) was calculated for the completed exposure tests.

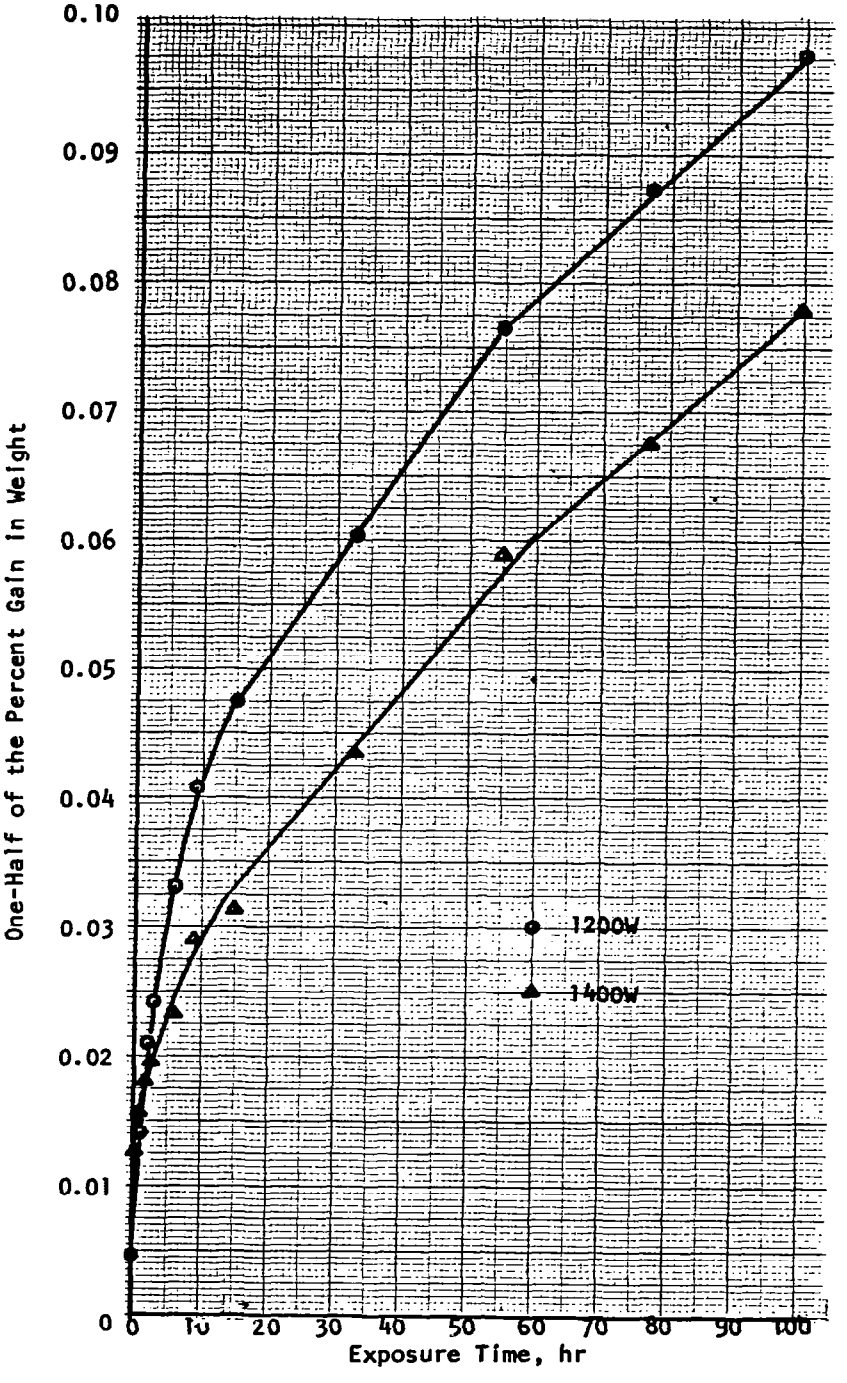



*Figure 30. Substrate oxidation of the 1200W and 1400W series after 100 hours at 1650°F (899°C).*

TABLE 33. SUBSTRATE OXIDATION OF THE 1200W AND 1400W SERIES EXPOSED FOR AN ADDITIONAL 100 HOURS AT 1650°F (899°C)

| Exposure Time, hr | One-Half of the Percent Gain in Weight ($O_s$) | |
|---|---|---|
| | 1200W | 1400W |
| 100[a] | 0.0046 | 0.0126 |
| 101 | 0.0140 | 0.0156 |
| 102 | 0.0211 | 0.0180 |
| 103 | 0.0242 | 0.0194 |
| 106 | 0.0329 | 0.0232 |
| 109 | 0.0407 | 0.0289 |
| 115 | 0.0475 | 0.0313 |
| 133 | 0.0603 | 0.0435 |
| 155 | 0.0766 | 0.0589 |
| 177 | 0.0872 | 0.0675 |
| 200 | 0.0977 | 0.0779 |

[a]100 hr data are the results of previous exposures at 1200°F and 1400°F, respectively; zero time for this exposure.

Calculated percent weight gain ($O_c$, %) results are shown in Tables 34 and 35 for the 1200W and 1400W series, respectively. Graphic presentation of the data is given in Fig. 31.

The curves show that of the four specimens exposed for the full 100 hr at 1650°F, MPS106 (1200W) was the only composition that continued to gain weight up to 100 hr. Sample PS101 (1200W) began losing weight after 3 hr; and PS101 (1400W) and PS106 (1200W) began losing weight after 9 hr, but showed very little loss after 33 hr. Both PS101 specimens continued to lose weight to 100 hr.

Examination of the thermocouple support, made out of insulating brick, showed that the surface adjacent to the specimens (not in contact with the specimens) was coated with a green deposit interspersed with metal. X-ray fluorescence analysis revealed the deposit to be high in Cr, with some Ag and very small amounts of K and Ca. This analysis shows that the weight losses of some of the samples are due to loss by a vaporization process of Ag, NiCr, and

TABLE 34. OXIDATION TEST RESULTS OF 1200W SERIES EXPOSED TO 100 HOURS INTERMITTENT EXPOSURE AT 1650°F (899°C)

| Total Exposure Time, hr | Percent Weight Gain ($O_c$), % | | |
|---|---|---|---|
| | PS106-1 | MPS106-1 | PS101-1 |
| 100[b] | 4.02 | 4.76 | 7.88 |
| 101 | 9.19 | 10.15 | 10.47 |
| 102 | 10.57 | 11.14 | 10.55 |
| 103 | 11.14 | 11.74 | 10.60 |
| 106 | 11.73 | 12.92 | 10.39 |
| 109 | 11.86 | 13.59 | 10.41 |
| 115 | 11.7 | 14.29 | 9.88 |
| 133 | 11.22 | 15.12 | 9.70 |
| 155 | 11.20 | 15.93 | 9.16 |
| 177 | 11.16 | 16.28 | 8.69 |
| 200 | 11.25 | 16.95 | 8.25 |

[a]All values corrected for substrate oxidation.

[b]100 hr data are the results of previous 1200°F exposure; zero time this exposure.

TABLE 35. OXIDATION TEST RESULTS OF 1400W SERIES EXPOSED TO 100 HOURS INTERMITTENT EXPOSURE OR TO FAILURE AT 1650°F (899°C)

| Total Exposure Time, hr | Percent Weight Gain ($O_c$), % | | |
|---|---|---|---|
| | PS106-5 | MPS106-4 | PS101-3 |
| 100[b] | 10.39 | 11.89 | 9.31 |
| 101 | 12.09 | 13.95 | 9.70 |
| 102 | 13.04 | 15.05 | 9.79 |
| 103 | 13.54 | 15.85 | 9.83 |
| 106 | 14.25 | 17.13 | 9.87 |
| 109 | 14.69 | 17.81 | 9.91 |
| 115 | 15.06 | 18.50[c] | 9.81 |
| 133 | 15.43 | | 9.47 |
| 155 | 15.75[c] | | 8.85 |
| 177 | | | 8.26 |
| 200 | | | 7.70 |

[a]All values corrected for substrate oxidation.

[b]100 hr data are the results of previous 1400°F exposure; zero time this exposure.

[c]Coat failure.

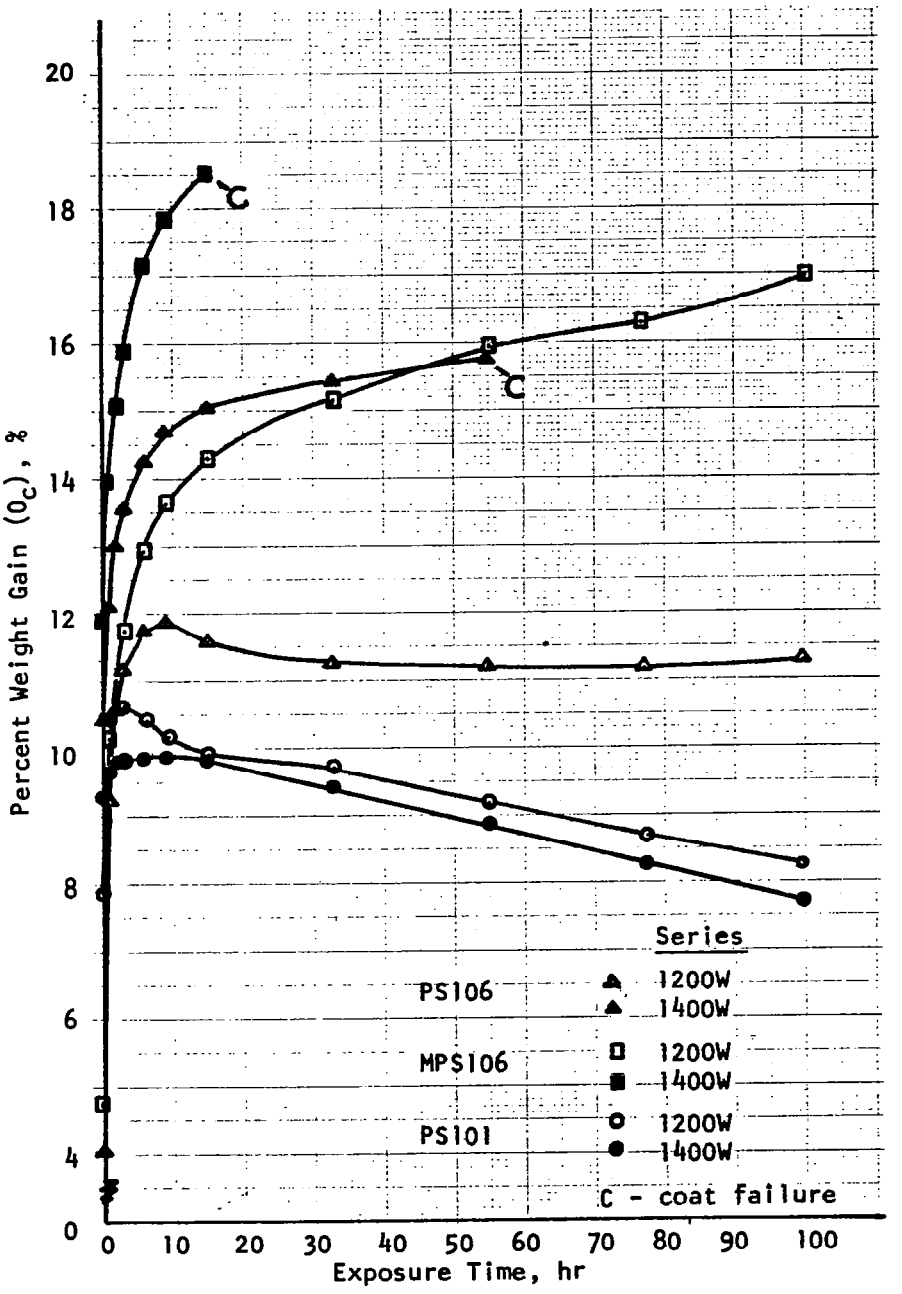



*Figure 31. Comparison of the 1200W and 1400W oxidation series of PS106, MPS106, and PS101 coatings after 1650°F (899°C) exposure. (All values corrected for substrate oxidation)*

probably glass from the self-lubricating coat. The losses in weight for the PS101 composition indicate that this composition deteriorates at the 1650°F (899°C) temperature range. Further work is needed to corroborate these findings.

## 3.8 CONTINUOUS MODE OXIDATION STUDIES

For the continuous mode tests one specimen of each composition (PS106, MPS106, PS101) and a blank substrate coupon were run at each of the specified temperatures: 1200°F (649°C); 1400°F (760°C); and 1650°F (899°C). A malfunction in recording occurred periodically in the use of the Ainsworth balance. However, since the samples were weighed analytically before and after the 100 hr exposures, and a correction factor was used to correlate the recorded test values with the analytical values, meaningful, accurate data were obtained.

The data for the substrate blanks were converted to one-half of the percent weight gain ($0_s$). These values were tabulated and then plotted on an $0_s$ vs. exposure time curve. The $0_s$ values for any exposure time were then obtained and used in equation (1) to determine ($0_c$,%) the percent coat oxidation.

Readings from the recording balance (Table 36) are tabulated from the actual starting time, i.e., when the furnace and specimen are at room temperature. Therefore, in order to obtain values of 100 hr-at-temperature, times to reach specific temperature ranges were included. For the 1200°F (649°C) it took 29 min for the substrate to reach temperature; for 1400°F (760°C) 42 min; and for 1650°F (899°C) 75 min. In Fig. 32 a curve of the intermittent mode is also given for comparison purposes. It shows a lower gain in weight for the continuous mode.

### 3.8.1 The 1200° Series

Weight gains for the three compositions exposed for 100 hr at 1200°F (649°C) are compared with the intermittent mode values (Table 37). In each instance the values for the continuous mode were higher. The table also shows that for both the continuous and intermittent mode increasing oxidation occurred in the order: PS106, MPS106, PS101. The oxidation behavior of each composition throughout the 100 hr is shown graphically and compared with the intermittent mode of each respective compositions in Figs. 33, 34, and 35.

TABLE 36. OXIDATION VALUES, $O_s$, OF BLANK SUBSTRATES FOR 1200°F (649°C), 1400°F (760°C), AND 1650°F (899°C) AFTER 100 HOURS AT TEMPERATURE (CONTINUOUS MODE)

| Time, hr | Weight Gain Values, $O_s$ ($O_s$ = 1/2 of the percent weight gain) | | |
|---|---|---|---|
| | 1200°F | 1400°F | 1650°F |
| 0.0 | -- | -- | -- |
| 0.5 | 0.0034 | 0.0052 | 0.0049 |
| 1.0 | 0.0045 | 0.0085 | 0.0915 |
| 2.0 | 0.0051 | 0.0106 | 0.0174 |
| 3.0 | 0.0055 | 0.0112 | 0.02065 |
| 4.0 | 0.0057 | 0.0118 | 0.0227 |
| 5.0 | 0.0060 | 0.0124 | 0.0245 |
| 10.0 | 0.0061 | 0.0139 | 0.0300 |
| 20.0 | 0.0061 | 0.0159 | 0.0369 |
| 30.0 | 0.0064 | 0.0175 | (0.0420) |
| 40.0 | 0.0066 | 0.0183 | (0.0467) |
| 50.0 | 0.0066 | 0.0188 | 0.0509 |
| 75.0 | 0.0070 | (0.0200)[b] | (0.0595) |
| 100.0 | 0.0073 | 0.0212 | 0.0679 |
| (100 + X)[a] | 0.0073 | 0.0212 | 0.0683 |

[a]This is the total time for 100 hr at the specified range and includes the heat-up time (X) to reach temperature. For 1200°F, X = 0.4 hr; 1400°F, X = 0.7 hr; for 1650°F, X = 1.25 hr.

[b]Interpolated from curves and data.

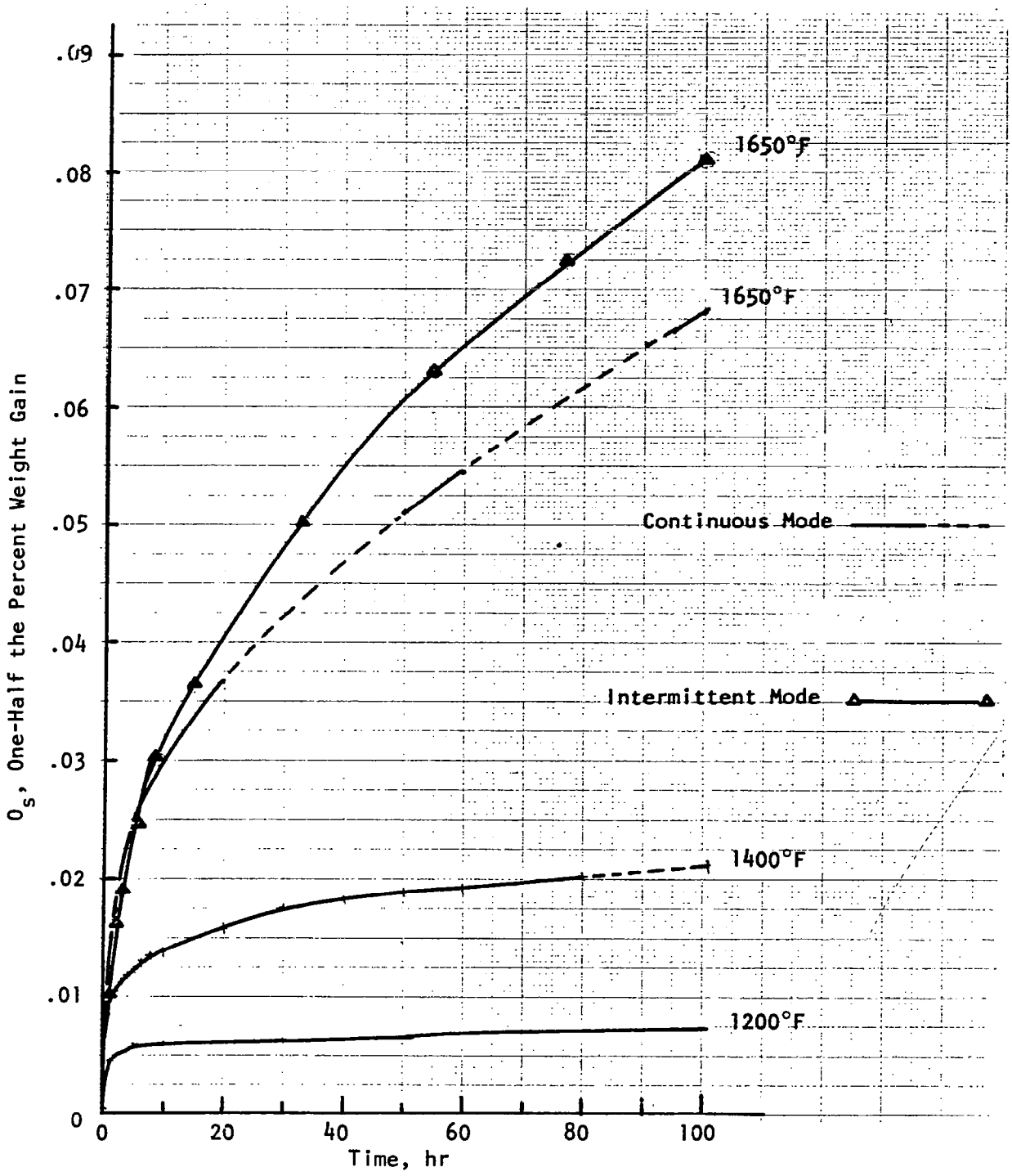



*Figure 32. Comparison of oxidation behavior of blank substrates for 100 hr of exposure.*

TABLE 37. COMPARISONS OF INTERMITTENT MODE AND CONTINUOUS MODE WEIGHT GAINS FOR DIFFERENT COATING COMPOSITIONS AFTER 100 HOURS AT 1200°F (649°C)

| Specimen | Percent Weight Gain | |
|---|---|---|
| | Intermittent Mode | Continuous Mode |
| Blank Substrate | 0.009 | 0.015 |
| PS106-1, PS106-11 | 4.02 | 4.40 |
| MPS106-1, MPS106-12 | 4.76 | 5.47 |
| PS101-1, PS101-9 | 7.88 | 8.95 |

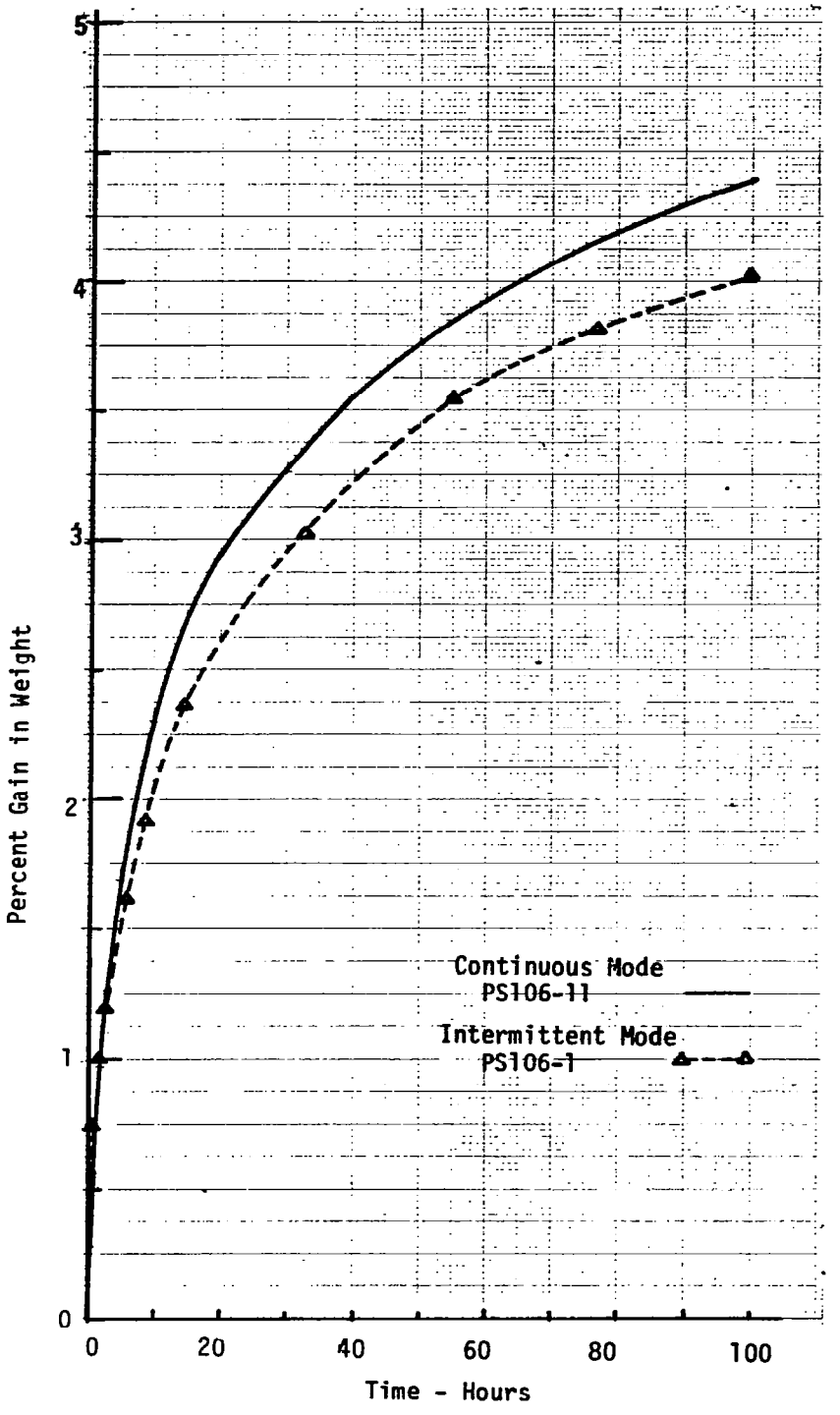



*Figure 33. Comparison of oxidation curves of PS106 plasma-sprayed coats heated at 1200°F (649°C) for 100 hours in the continuous and intermittent modes.*

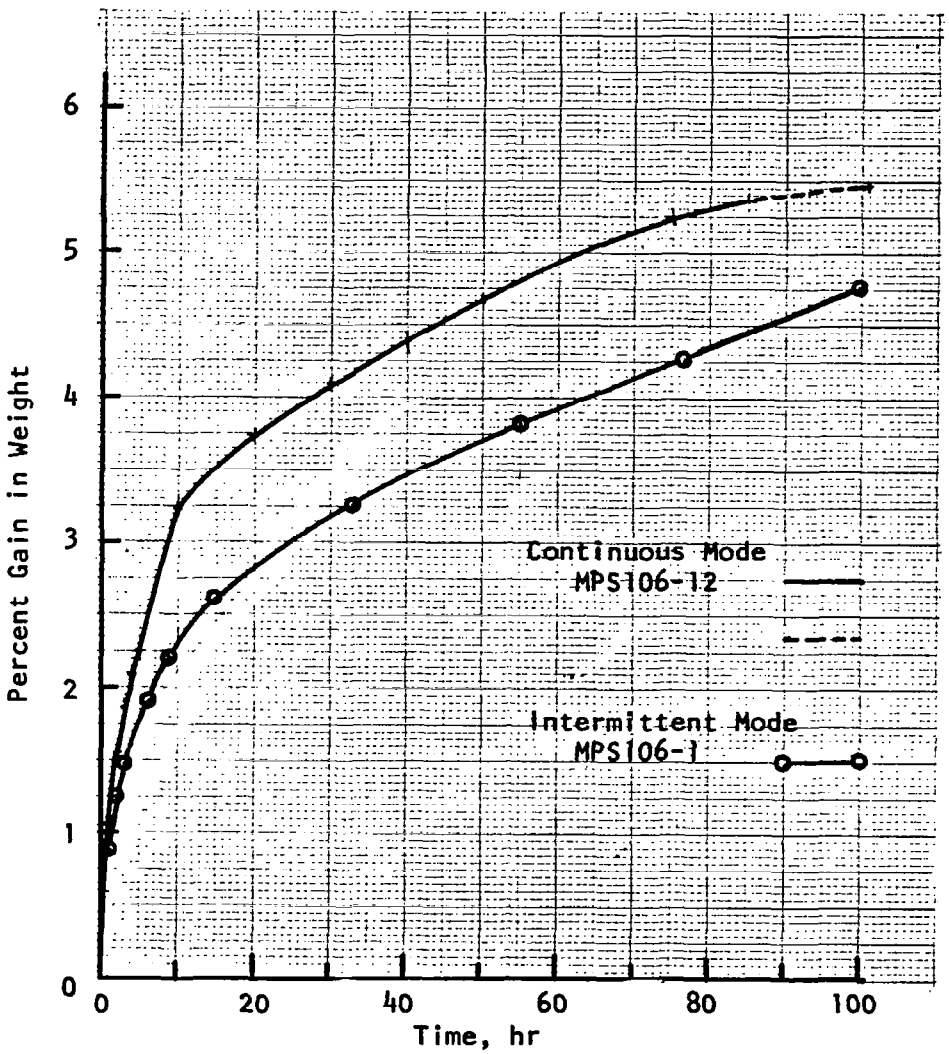



*Figure 34. Comparison of oxidation curves of MPS106 plasma-sprayed coats heated at 1200°F (649°C) for 100 hr in the continuous and intermittent modes.*

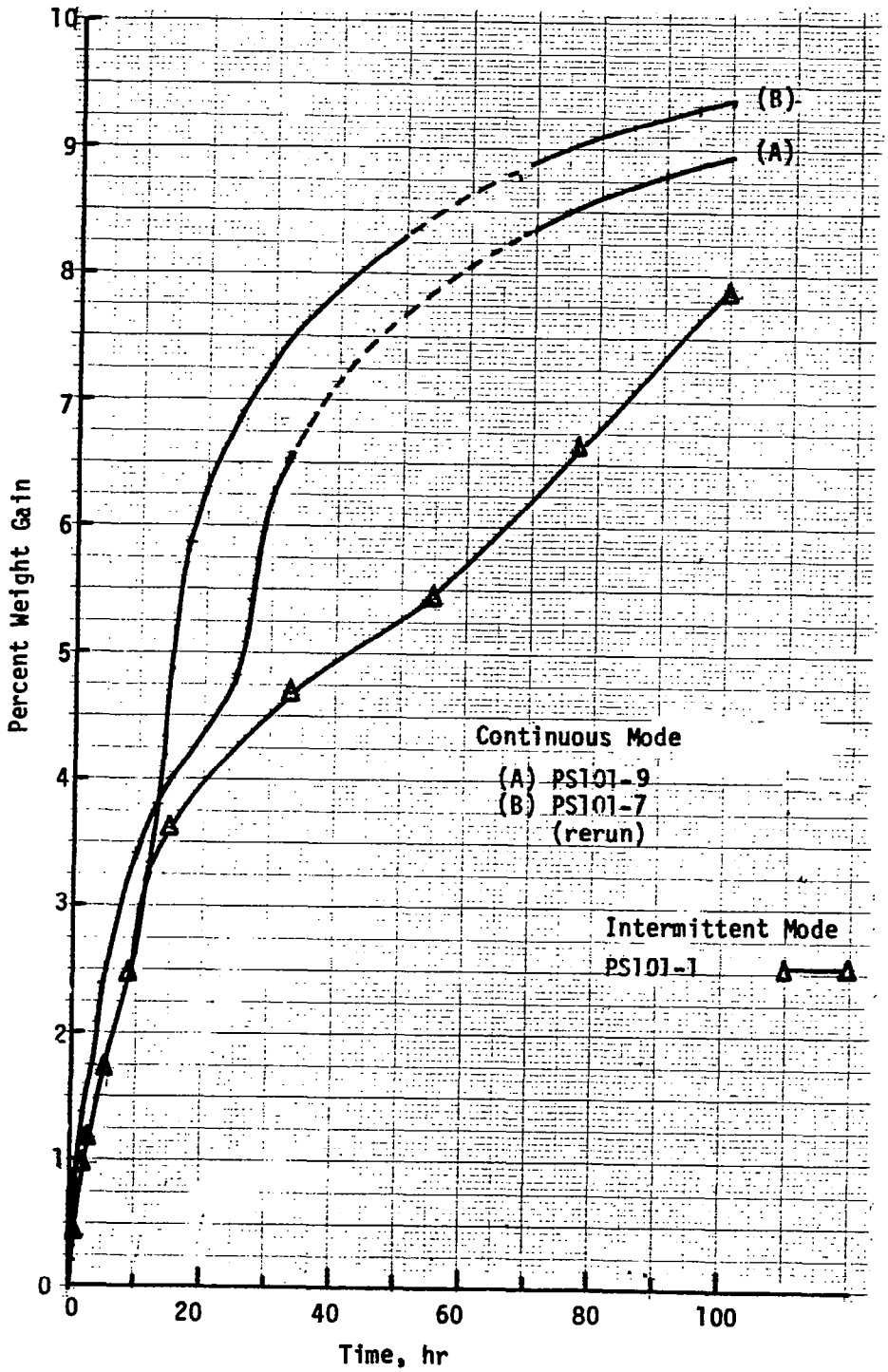



*Figure 35. Comparison of oxidation curves of PS101 plasma-sprayed coats heated at 1200°F (649°C) for 100 hours in the continuous and intermittent modes.*

For PS106-11 it required 24 min to reach 1200°F (649°C). During this heatup time, the approximate percent oxidation of the coat was 0.22%. The percent oxidation of the coat for 100 hr at temperature is calculated to be 4.40-0.22 or 4.18% where 4.40 is "$0_c$, %" for 100.4 hr. Approximately 5% of the total percent weight gain occurs before the equilibrium temperature is reached. A plot of the 100-hr oxidation given in Fig. 33 indicates that the continuous mode revealed a percent weight gain of 4.40% compared to 4.02% for the intermittent mode. The values are reversed during the first hour where the continuous mode has a percent weight gain of 0.57 compared to 0.73 for the intermittent mode. The second hour was 0.97 to 1.00. In the third hour the continuous mode showed a higher gain, and this was a position that it did not relinquish thereafter (1.27% compared to 1.18%).

The curve for MPS106-2 (Fig. 34) shows a sharp decrease in the oxidation rate after about 10 hr of exposure. For the first 10 hr its rate was much faster than in the intermittent mode. After 10 hr the rates for the two modes were quite similar. After 60 hr there was a rate decrease for the continuous mode. The dotted line from 85 hr to 100hr exposure is an interpolated curve where the balancing mechanism failed to record. However, the extension of the curve from the 75 hr to 85 hr values to the analytically weighed 100.4 hr value is a smooth, continuous line, indicating the validity of the curve.

Figure 35 gives the curves of PS101-9 and PS101-7. Both are compared to the intermittent mode. Two samples of PS101 were tested because of its unusual behavior (in comparison with the intermittent mode specimen, PS101-1). The second specimen (PS101-7) showed a similar type of oxidation behavior as the first continuous mode specimen (PS101-9), thus confirming the fact that an interim rapid weight gain occurs in the course of a 100-hr test.

PS101-9 had shown a higher oxidation rate in the first 5 hours, and then a very similar rate up to 20 hours (in comparision with the intermittent mode specimen). For example at 15 to 20 hours, the rate of weight increase was approximately 0.08 mg/hr for both the intermittent and continuous mode. This rate remained the same for the intermittent mode sample to approximately 55 hr; however, the continuous mode sample departed from this rate by a rapid rise in the 25 to 30 hr period, reaching a maximum dw/dt of 0.33 mg/hr between 26 and 28 hr.

The second specimen (PS101-7) was very similar in behavior to the intermittent mode sample during the first 10 hr. Its rapid oxidation behavior occurred earlier than that for PS101-9 reaching a maximum rate, dw/dt, of 0.54 mg/hr between 13 to 15 hr. The two continuous mode samples showed similar oxidation rates to 100 hr after the initial rapid oxidation rates.

The dotted portion of the continuous mode curves are periods where the balance did not record. The specimens were weighed before and upon the completion of each test. These weight values were checked with the results of the Ainsworth balance to confirm the validity of the interpolation. The total weight percent gain after 100 hr at temprautre was 9.40% for the rerun specimen (PS101-7) compared to 8.95% for PS101-9.

3.8.2. The 1400°F (760°C) Series

The continuous mode oxidation values for 100 hr exposure at 1400°F (760°C) are compared with those tested by intermittent mode (Table 38). The continuous mode gave slightly higher weight gain values for all specimens except the PS106 composition. A graphic presentation of the comparative weight gain patterns for the continuous and intermittent modes are given in Figs. 36, 37, and 38. The oxidation rates for both modes are quite similar.

TABLE 38. COMPARISON OF INTERMITTENT AND CONTINUOUS MODE WEIGHT GAIN VALUES FOR 100 HOURS AT 1400°F (760°C)

| Specimen | Percent Weight Gain, mode | |
|---|---|---|
| | Intermittent | Continuous |
| Blank Substrate | | |
| BL-9, BL-10 | 0.0119[a] | 0.0212[a] |
| Coated Composition | | |
| 1. PS106-5, PS106-8A | 10.39 | 9.97 |
| 2. MPS106-10, MPS106-9 | 13.51 | 13.56 |
| 3. PS101-4, PS101-8 | 9.75 | 10.72 |

[a] $0_s$ values, 1/2 of the percent gain in weight.

The PS106 curves (Fig. 36) show that the intermittent mode specimen had somewhat higher weight gains from the start. These higher weight gain values

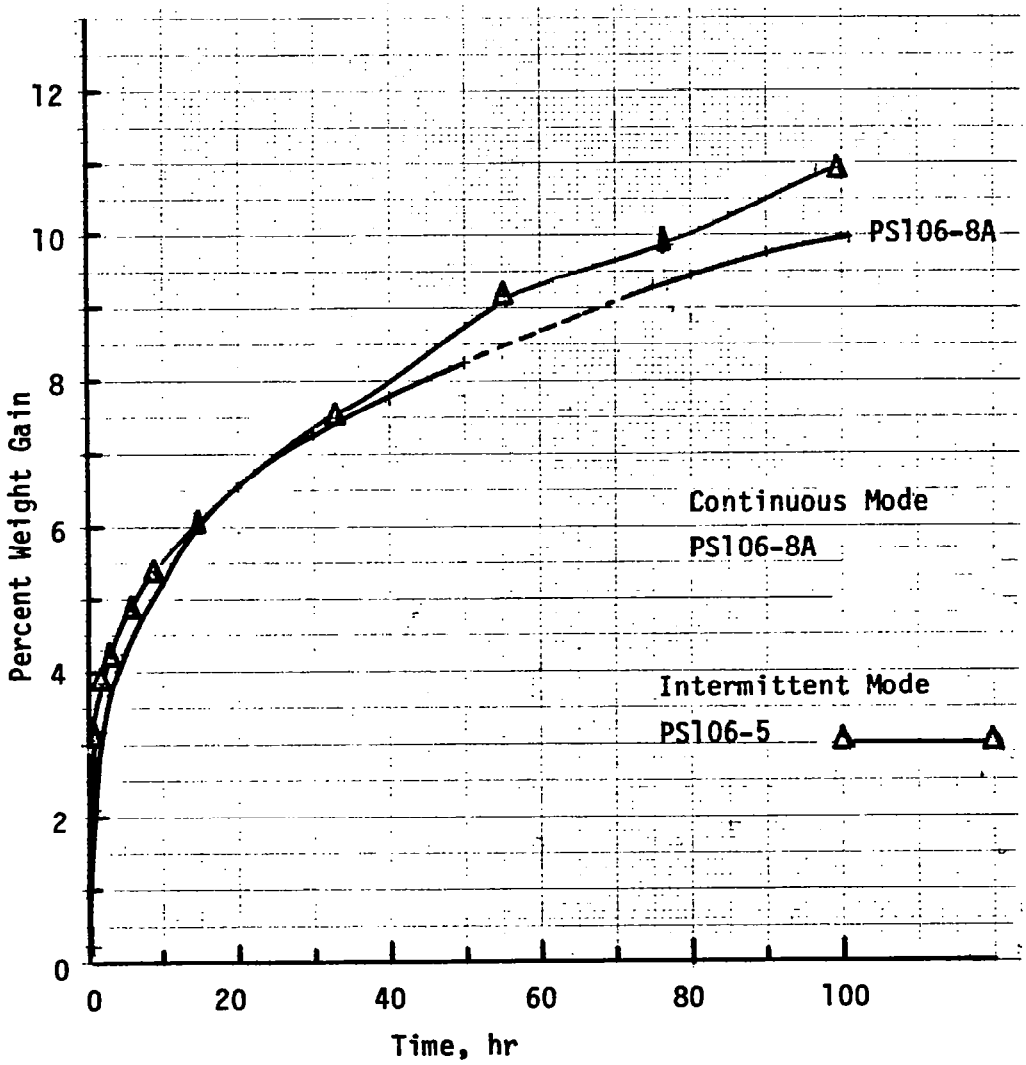



*Figure 36. Comparison of oxidation curves of PS106 plasma-sprayed coats heated at 1400°F (760°C) for 100 hours in the continuous and intermittent modes.*

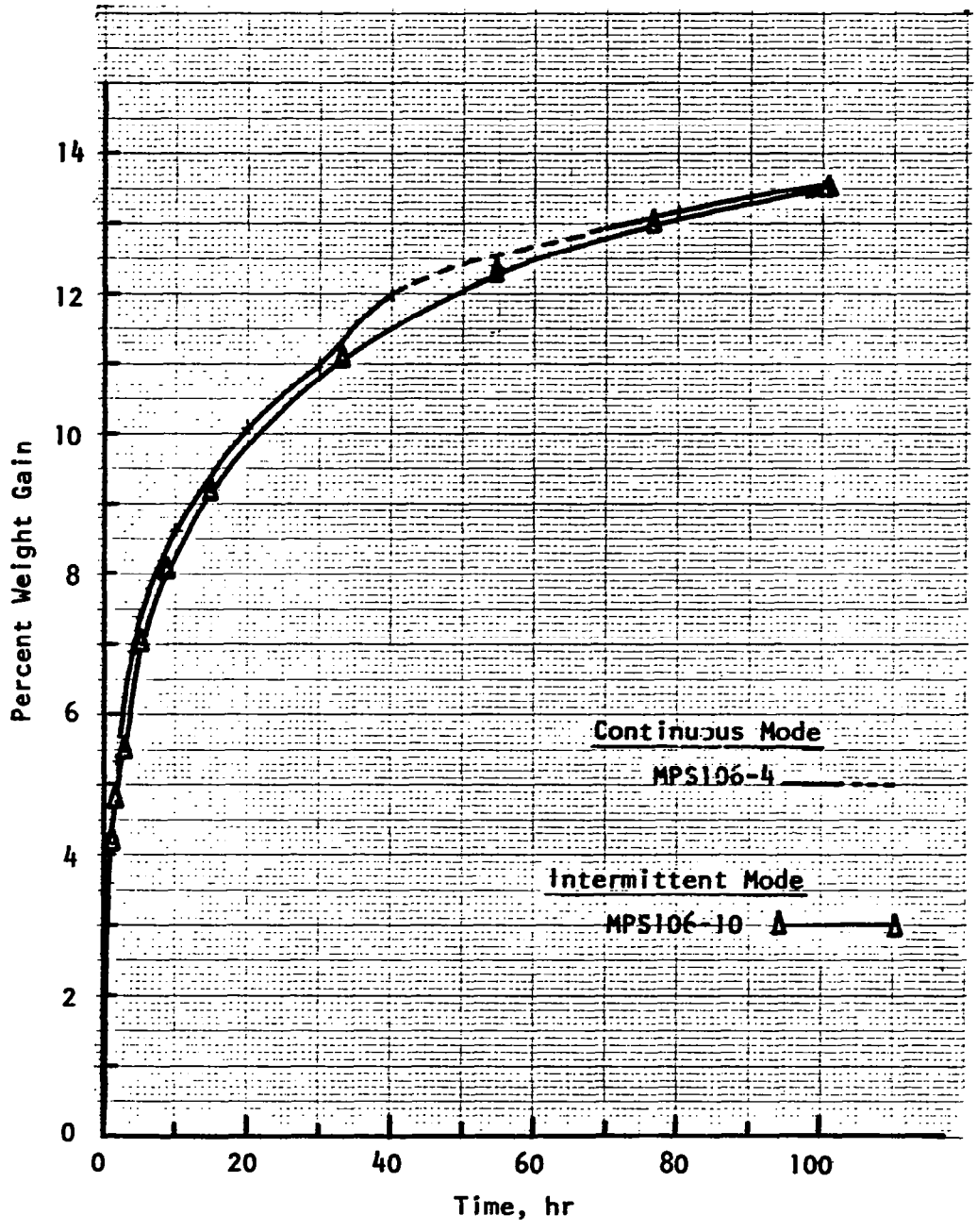



*Figure 37. Comparison of oxidation curves of MPS106 plasma-sprayed coats heated at 1400°F (760°C) for 100 hr in the continuous and intermittent modes.*

were especially noticeable after 30 hr of exposure. The MPS106 compositions (Fig. 37), with the exception of a short term rate increase for the continuous mode during the interval from 30 to 40 hr, gave similar weight gain values. For the PS101 compositions (Fig. 38), the values of weight gain, dw/dt (in mg/hr), were very similar up to 5 hr; at this point the intermittent mode sample rate decreased whereas the continuous mode sample continued at a considerably higher rate to 25 hr. Rates of both modes were similar after 25 hr.

### 3.8.3 The 1650°F (899°C) Series: PS106

Single oxidation tests of a blank substrate, coat compositions PS106, MPS106, and PS101, were made in the continuous mode. A comparison of the weight gains for a blank substrate of this mode with the intermittent mode is given in Table 39. This comparison was graphically presented as curves in Fig. 32. The oxidation data show that this is the first temperature range at which the intermittent mode substrate blank had a higher weight gain. Comparison of PS106 in continuous mode with the intermittent mode could not be made because of the failure of the coat in the intermittent mode within 2 hr by blistering and separation from the substrate.

TABLE 39. COMPARISON OF INTERMITTENT AND CONTINUOUS MODE WEIGHT GAIN VALUES FOR 100 HOURS AT 1650°F (899°C)

| Specimen | Percent Weight Gain, mode | |
|---|---|---|
| | Intermittent | Continuous |
| Blank Substrates | | |
| BL-11, BL-5 | 0.0810 | 0.0682 |
| Coat Specimens | | |
| PS106-7, PS106-9A | --[a] | 14.872[b] |

[a]Failed by blistering and separation after 2 hr exposure.

[b]Suspending wire broke after 33 hr, but analytical weight gain was obtained.

A recording of the weight gain of PS106-9A in the continuous mode was obtained for 32 hr at which time the suspending wire broke. The percent weight gain at this point was 14.84%. The specimen fell in such a manner that it was leaning against the furnace wall at an approximate 60° angle with the

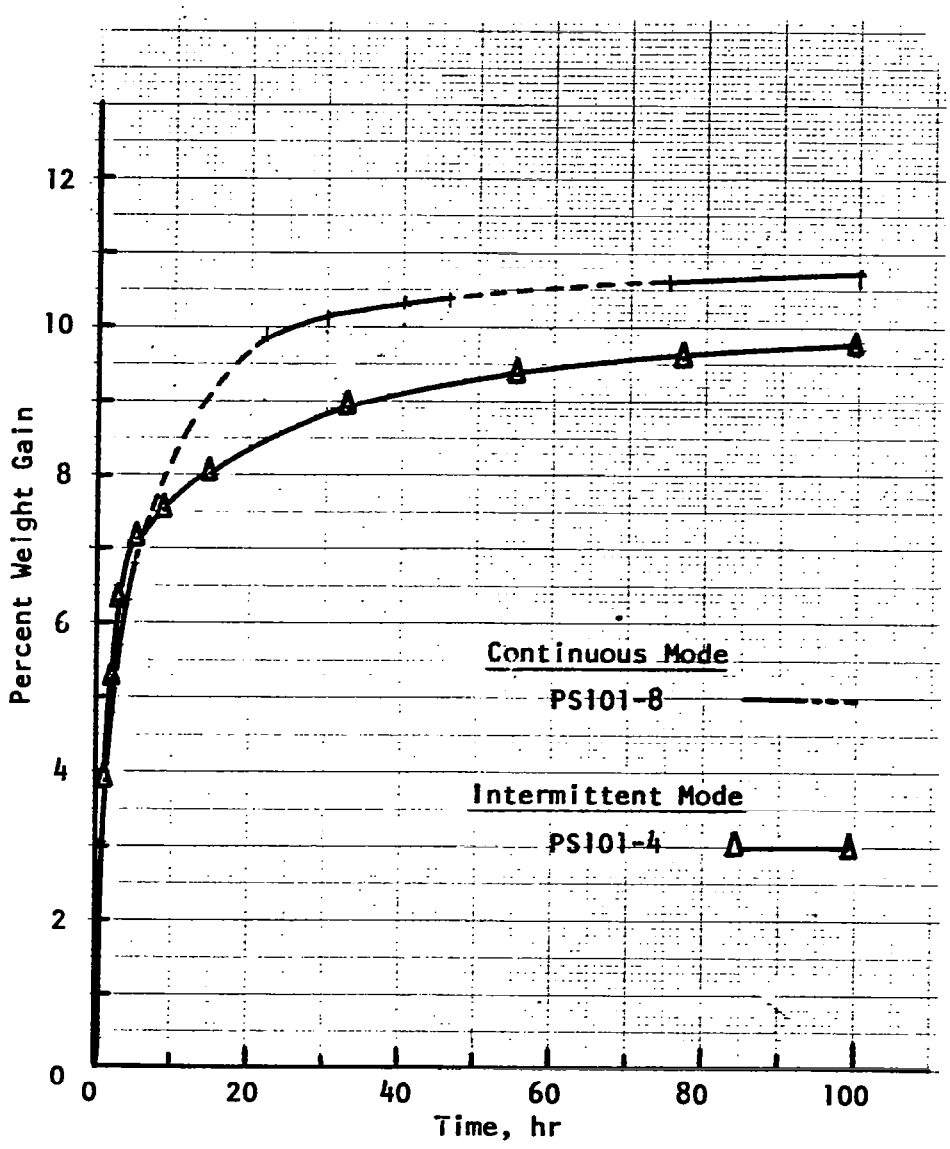



*Figure 38. Comparison of oxidation curves of PS101 plasma-sprayed coats heated at 1400°F (760°C) for 100 hr in the continuous and intermittent modes.*

coated face less than 1 in. from the heating elements. This would suggest that the coat was at a higher, if not equivalent, temperature than the required temperature. However, since one edge of the specimen was on the bottom of the furnace and the control temperature remained constant, the possibility of excessive temperature was slight. The specimen was left in the furnace for the full 100 hr and then weighed analytically. The final calculated oxidation weight gain was 14.87%.

Although a blister about the size of a quarter and approximately 3/16 in. in height had formed during the test, the coat remained intact. The surface of the coat was a mottled dark green and black, mixed with white precipitates. During the course of oxidation, the coat softened enough to permit this section to lift up and harden. It would appear that an irreversible chemical reaction had taken place,allowing the blister to harden under the constant 1650°F temperature. Figure 39 shows the specimen after 100 hr despite bloating that had occurred. The bubble is known to have formed before 32 hr exposure.

X-ray examination of the surface particles would be necessary to help determine the cause of blistering. Changes in chemical composition due to oxidation, or reaction between ingredients may change the coat density. If such a change is deleterious, an increase in volume change may cause blistering. If reaction has caused a gas to form, a blister may develop.

Figure 40 compares graphically the oxidation of PS106 at the three temperatures. The weight gain to 33 hr and the final weighed analytical value at 100 hr is shown in the 1650°F oxidation. Practically all of the weight gain had occurred by 11 hr. The extension of the curve from 32 hr to the 100 hr weighed value indicates that the temperature of the coat did not reach an excessively high temperature so as to cause an increased oxidation of the coat.

The recording chart of weight gain from zero time to 10 hr showed very clearly increasing and decreasing rates of weight gain. This behavior is detailed in Table 40 (giving the calculated rates of weight increase, dw/dt in mg/hr) and the specific periods in which they occurred. Figure 41 shows the section of this portion of the weight gain.

*Figure 39. PS106 continuous mode specimen after 100 hr exposure at 1650°F (899°C).*

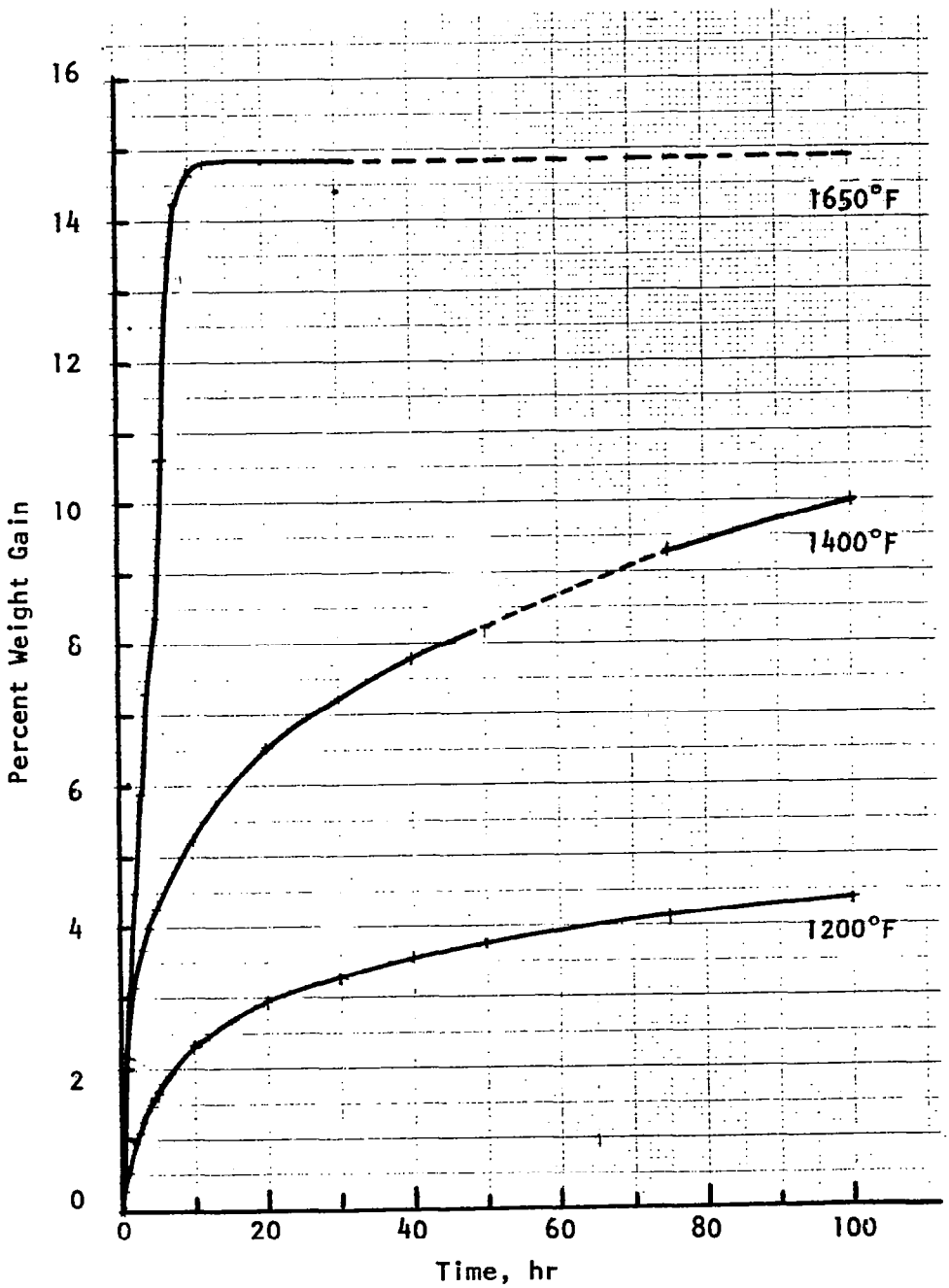



*Figure 40. Comparison of oxidation curves of PS106 for 100 hr exposure at 1200°F, 1400°F, and 1650°F in the continuous mode.*

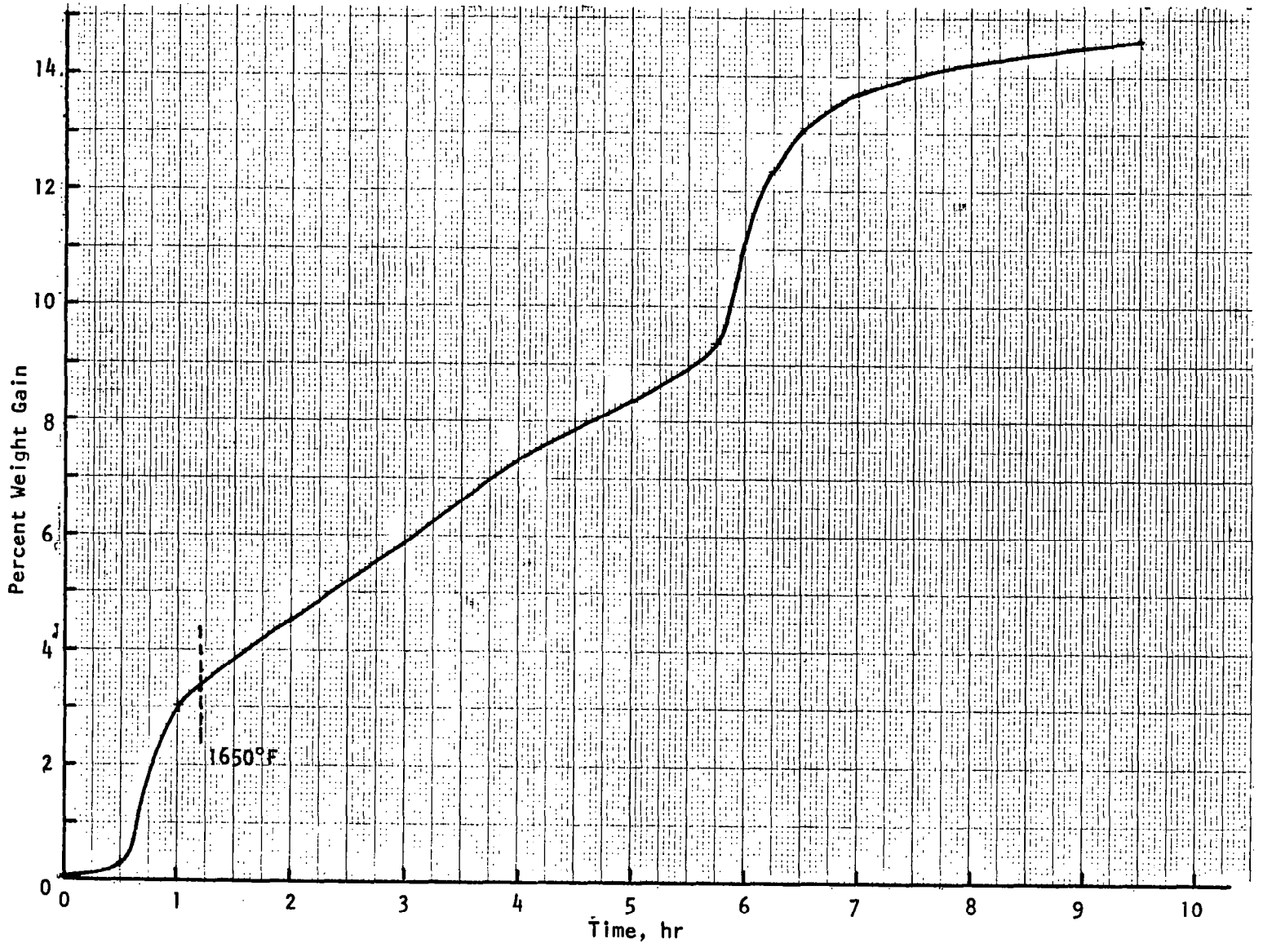



*Figure 41. Expanded oxidation curve of PS106-9A plasma-sprayed coa heated at 1650°F (899°C) in the continuous mode.*

TABLE 40. RATE OF WEIGHT GAIN OF PS106-9A DURING THE OXIDATION PERIOD OF 0.5 TO 10 HOURS IN THE COURSE OF A 100-HOUR TEST AT 1650°F (899°C)

| Weight Gain Period, hr[a] | Rate of Weight Gain dw/dt, mg/hr[b] |
|---|---|
| 0.75-1 | 5.81 |
| 1-4 | 1.43 |
| 4-5.75 | 1.07 |
| 5.75-6.0 | 6.84 |
| 6.0 -6.25 | 5.09 |
| 6.25-7 | 1.32 |
| 7-10 | 0.97 |

[a]Time based on recorder readings where zero time equals room temperature.

[b]dw/dt, in mg/hr, is based on 100 mg of coat material.

As in all previous oxidation series the specimen was placed in the furnace at room temperature. Time was recorded when the furnace was turned on. In the case of the 1650°F (899°C) series it took approximately 1.2 hr to reach temperature. This point is shown in Fig. 41 and indicates that 3.2% weight gain had occurred by the time the specimen had reached temperature (approximately 21.5% of the maximum oxidation).

It is interesting to note that a high rate of weight gain occurred in the 0.5 to 1 hr period with dw/dt of 5.5 mg/hr where the test temperature of 1650°F (899°C) had not been reached. The approximate temperature range was 1285°F (696°C) to 1650°F (899°C). This suggests that a low-temperature pre-oxidation treatment may give a more stable coat for high-temperature performance. A previously run intermittent mode test of PS106 (No. 1200 → 1650°F, IITRI Report No. 21) had shown that this reaction may be completed at a lower temperature (1200°F). No bloating occurred in a subsequent 100 hr exposure test at 1650°F for a sample which had previously been subjected to a 1200°F/100 hr test (the 1200W series).

The highest oxidation rate occurred at 5.75-6.0 hr or approximately 4.5 hr after reaching the equilibrium temperature of 1650°F (899°C). Whether the blister had formed during this period is not known.

In Table 41 a comparison of the data for coat PS106 is made for the three temperature ranges, including the time to reach each temperature and the amount of oxidation (by analytically weighing) after 100 hr of exposure.

TABLE 41. COMPARISON OF DATA FOR PS106 COATS AT 1200°F (649°C), 1400°F (760°C), AND 1650°F (899°C) FOR 100 HOURS AT TEMPERATURE

| | PS106-11 (1200°F) | PS106-8A (1400°F) | PS106-9A (1650°F) |
|---|---|---|---|
| Time to Reach Temperature, min | 24 | 41 | 72 |
| 100 hr Oxidation wt% Gain | 4.40 | 9.97 | 14.87[a] |

[a]Analytical value, fell in 33 hr, but test was able to be continued to 100 hr.

### 3.8.4 The 1650°F (899°C) Series: MPS106

MPS106 data for 1650°F (899°C) in the continuous mode could not be compared with its intermittent mode counterpart since the intermittent mode at this temperature failed in 2 hr. Although a blister formed in the continuous mode (all before 3.5 hr time) and the suspension wire broke after 3.5 hr, the experiment was restarted and continued for 100 hr. The coating remained intact for 100 hr despite this early formation of a blister. Figure 42 shows the blistered specimen.

Table 42 compares the gain in weight for the three temperature ranges of 1200°F, 1400°, and 1650°F. The curves for the three temperature ranges in Fig. 43 show that the 1400°F specimen is approaching the 1650°F weight gain at the 100 hr exposure time. The 1650°F sample appears to have practically reached its maximum oxidation after 10 hr. There seems to be a slight weight gain between 20 to 60 hr.

Table 43 details the rate of oxidation, dw/dt, for the first 10 hr period based on a 100 mg coat. Figure 44 gives an expanded view of the first 10 hr

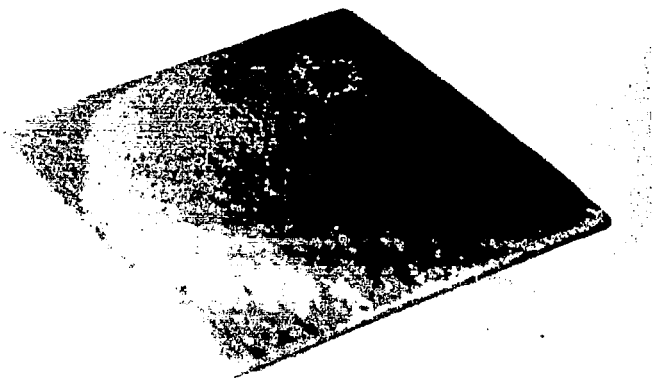


*Figure 42. Intact specimen of MPS106 continuous mode after 100 hr exposure at 1650°F (899°C) despite early formation of a blister.*

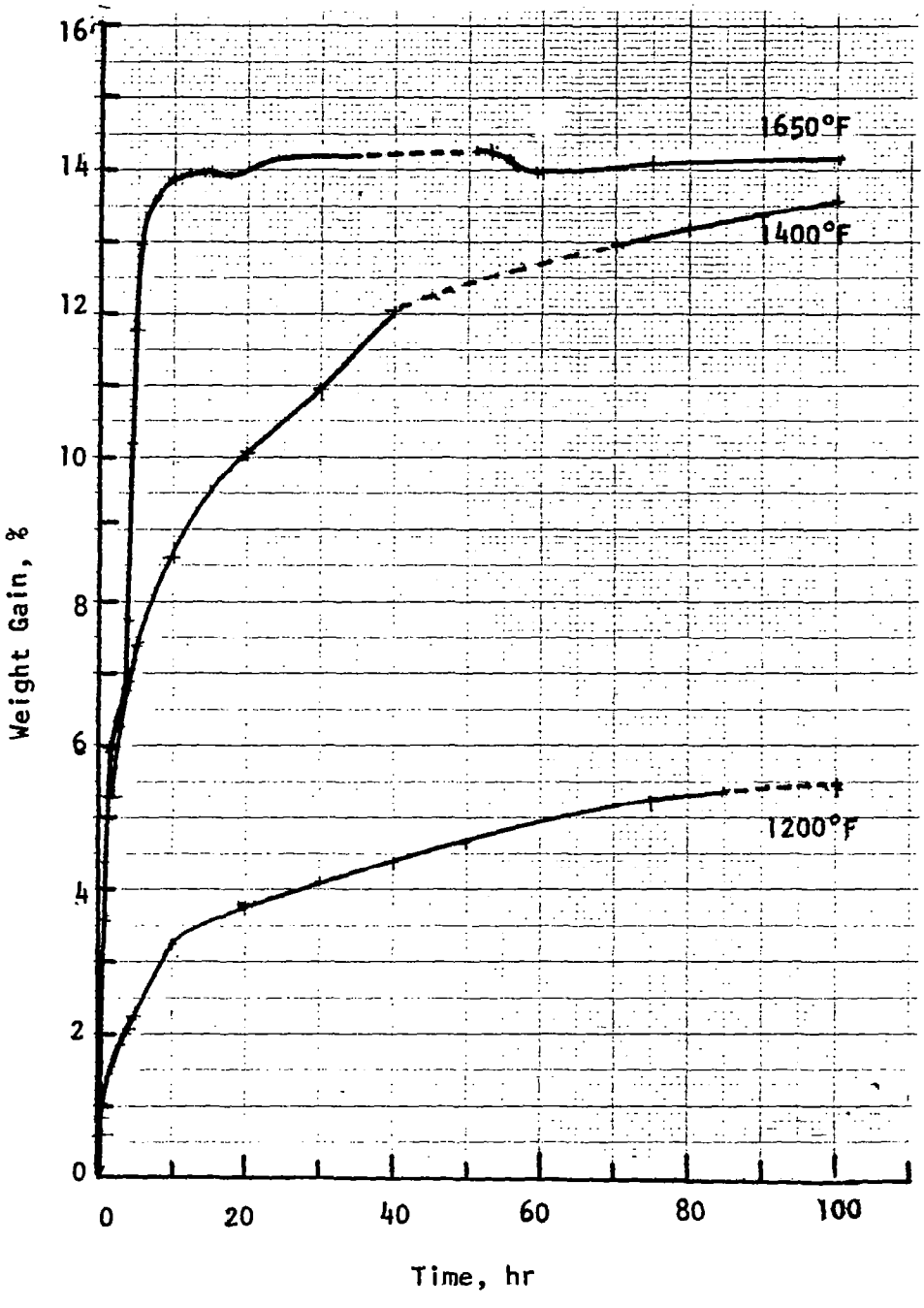



*Figure 43. Comparison of oxidation curves of MPS106 for 100 hr exposure at 1200°F, 1400°F, and 1650°F in the continuous mode.*

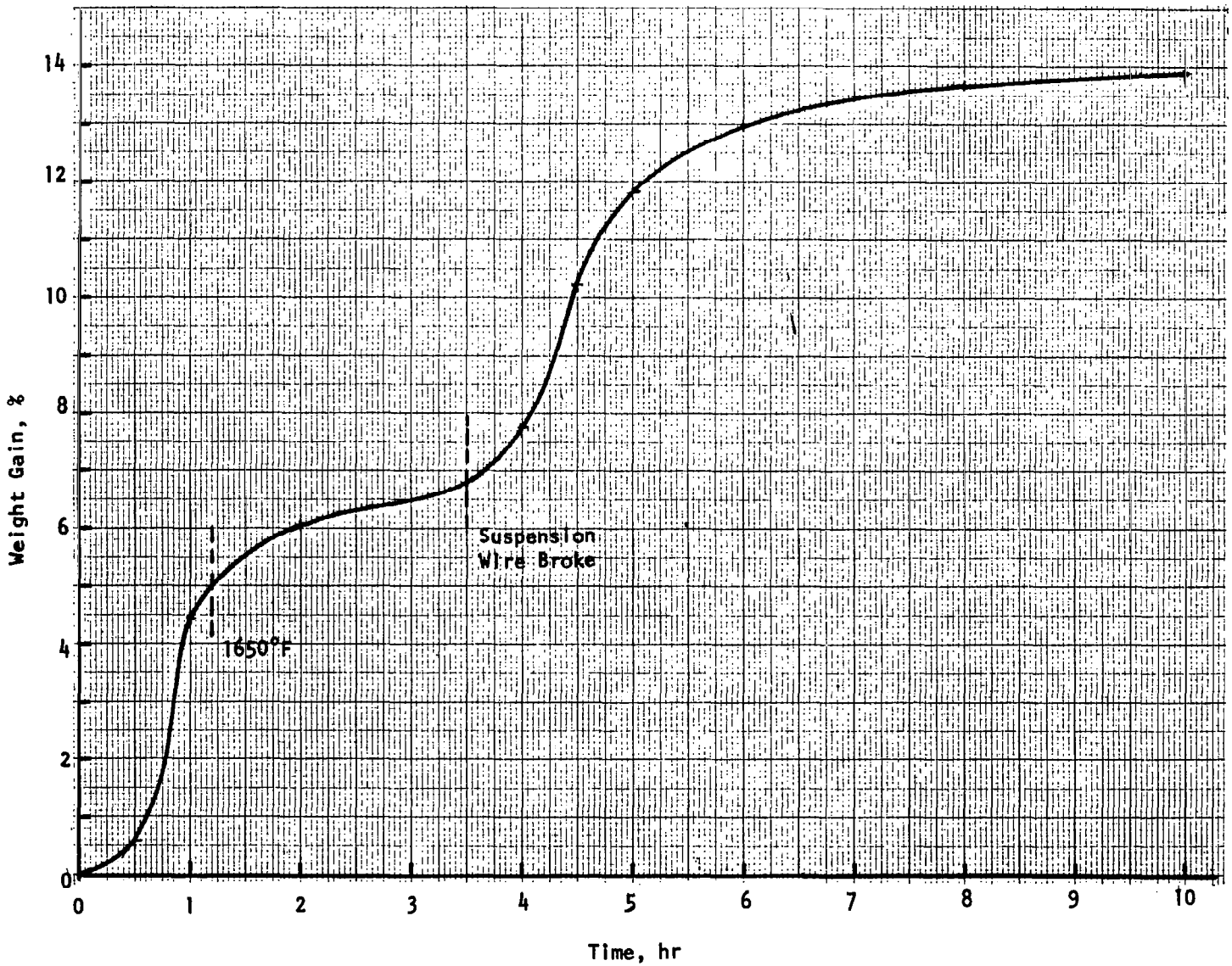



*Figure 44. Expanded oxidation curve for MPS106 plasma-sprayed coat heated at 1650°F (899°C) in the continuous mode.*

TABLE 42. COMPARISON OF DATA FOR MPS106 COATS AT 1200°F (649°C), 1400°F (760°C), AND 1650°F (899°C) FOR 100 HOURS AT TEMPERATURE

| | MPS106-12 (1200°F) | MPS106-9 (1400°F) | MPS106-14 (1650°F) |
|---|---|---|---|
| Time to Reach Temperature, min | 24 | 41 | 72 |
| 100 hr Oxidation, wt% gain | 5.37 | 13.56 | 14.15 |

TABLE 43. RATE OF WEIGHT GAIN FOR MPS106 DURING THE OXIDATION PERIOD OF 0.5 HOURS TO 10 HOURS IN THE COURSE OF A 100-HOUR TEST AT 1650°F (899°C) (CONTINUOUS MODE)

| Weight Gain Period, hr[a] | Rate of Weight Gain, dw/dt, mg/hr[b] |
|---|---|
| 0.5-1.0 | 7.78 |
| 1.0-2.0 | 1.58 |
| 2.0-3.5 | 0.51 |
| 3.5-4.0 | 1.92 |
| 4.0-4.5 | 4.9 |
| 4.5-5.0 | 3.2 |
| 5.0-6.0 | 1.16 |
| 6.0-8.0 | 0.33 |
| 8.0-10.0 | 0.12 |

[a]Time based on recorder readings where zero time equals room temperature.

[b]dw/dt, in mg/hr, is based on 100 mg of coat material.

showing the oxidation rates encountered in this period. The curve is marked at the point where the specimen reached temprature (1650°F) in 1.2 hr and the point where the wire broke (3.5 hr) and the test restarted. The continuity did not seem to be affected by restarting. The greatest rate of oxidation occurred between 0.5 to 1.0 hr, which is the time period just prior to the 1650°F temperature and indicates that approximately 35% of the maximum oxidation has occurred. The next fastest rate occurred at 4.0 to 4.5 hr. The

shape of this curve with its cyclic behavior in the first 10 hr is very similar to the curve for PS106 (see Fig. 41).

3.8.5 The 1650°F (899°C) Series: PS101

The PS101 specimen oxidation test at 1650°F (899°) for the continuous mode was conducted in the same manner as for PS106 and MPS106. The specimen was suspended in the furnace chamber at room temperature, and weight changes were recorded as soon as the furnace was turned on. For this composition, 1 hr and 9 min were required to reach 1650°F (899°C). Therefore, to obtain an exposure of 100 hr at temperature, the total recorded time was 101 hr 9 min. The specimens were weighed analytically before and after exposure, and the recorded values were correlated with these weighings.

The weight gain after 100 hr at 1650°F was determined to be 6.42%. Table 44 compares these data with those of the two previous temperature series; 1200°F (649°C) and 1400° (760°C). Figure 45 shows the effect of the three temperatures on the oxidation behavior of PS101 in the continuous mode. The percent weight gain values used for these curves were calculated using equation (1) for coat oxidation ($O_c$, %).

TABLE 44. COMPARISON OF DATA FOR PS101 COATS EXPOSED TO CONTINUOUS MODE OXIDATION AT 1200°F (649°C), 1400°F (760°C), AND 1650°F (899°C) FOR 100 HOURS

| | PS101-7 1200°F | PS101-8 1400°F | PS101-10 1650° |
|---|---|---|---|
| Time to Reach Temperature, min | 24 | 39 | 69 |
| 100 hr Oxidation, | 9.40 | 10.72 | 6.42 |

The pronounced effect of the 1650°F (899°C) temperature on initial weight gain is quite apparent in the data presented in the graph with the curve comparisons of Fig. 45. A rapid weight gain to a maximum of 10.81% was reached in 2 hr 6 min from time zero. This peak was very sharply defined on the recorder chart. Figure 46 is an expanded weight change-time curve, detailing the oxidation behavior from 0.5 to 9 hr exposure. The rate of weight change, dw/dt in mg/hr, is given in Table 45 for this range; plus (+) denoting an

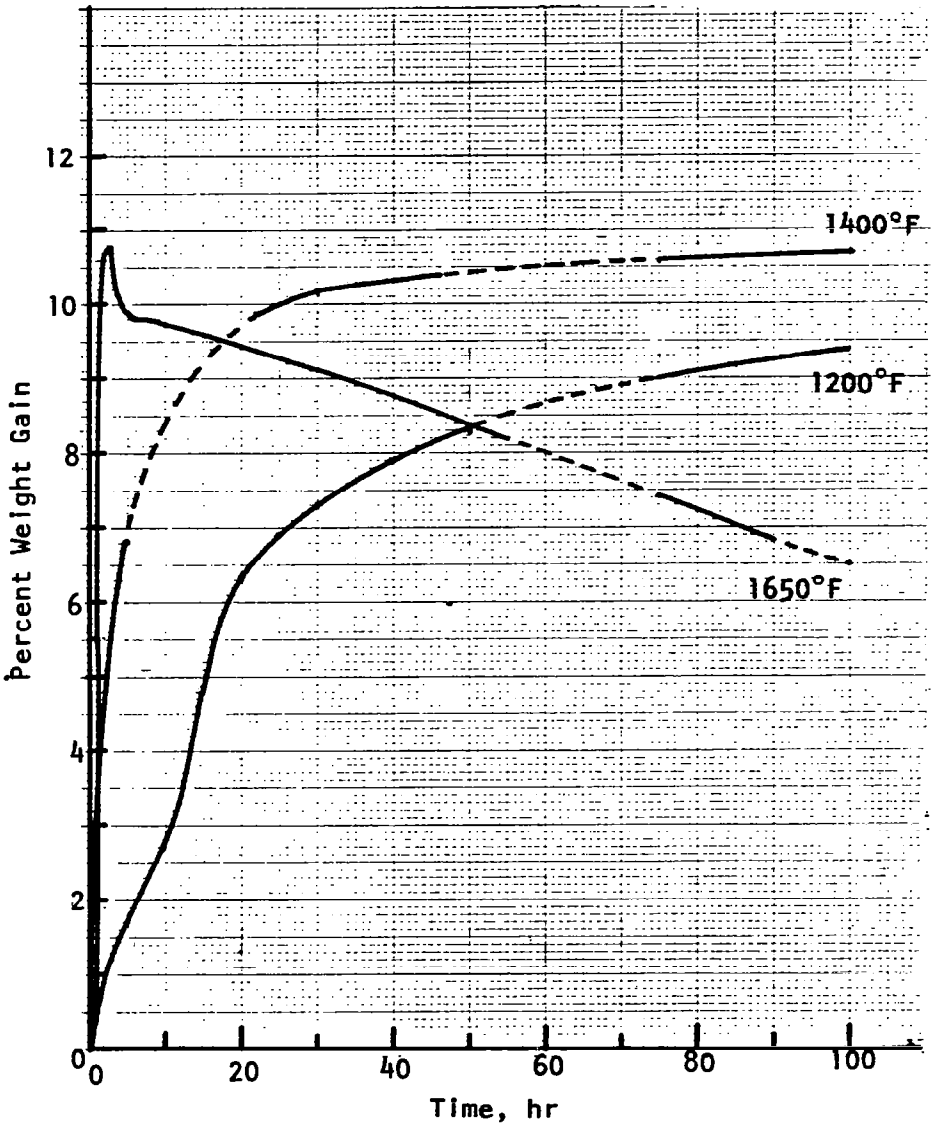



*Figure 45. Comparison of continuous mode oxidation behavior of PS101 coat composition for 100 hours of exposure.*

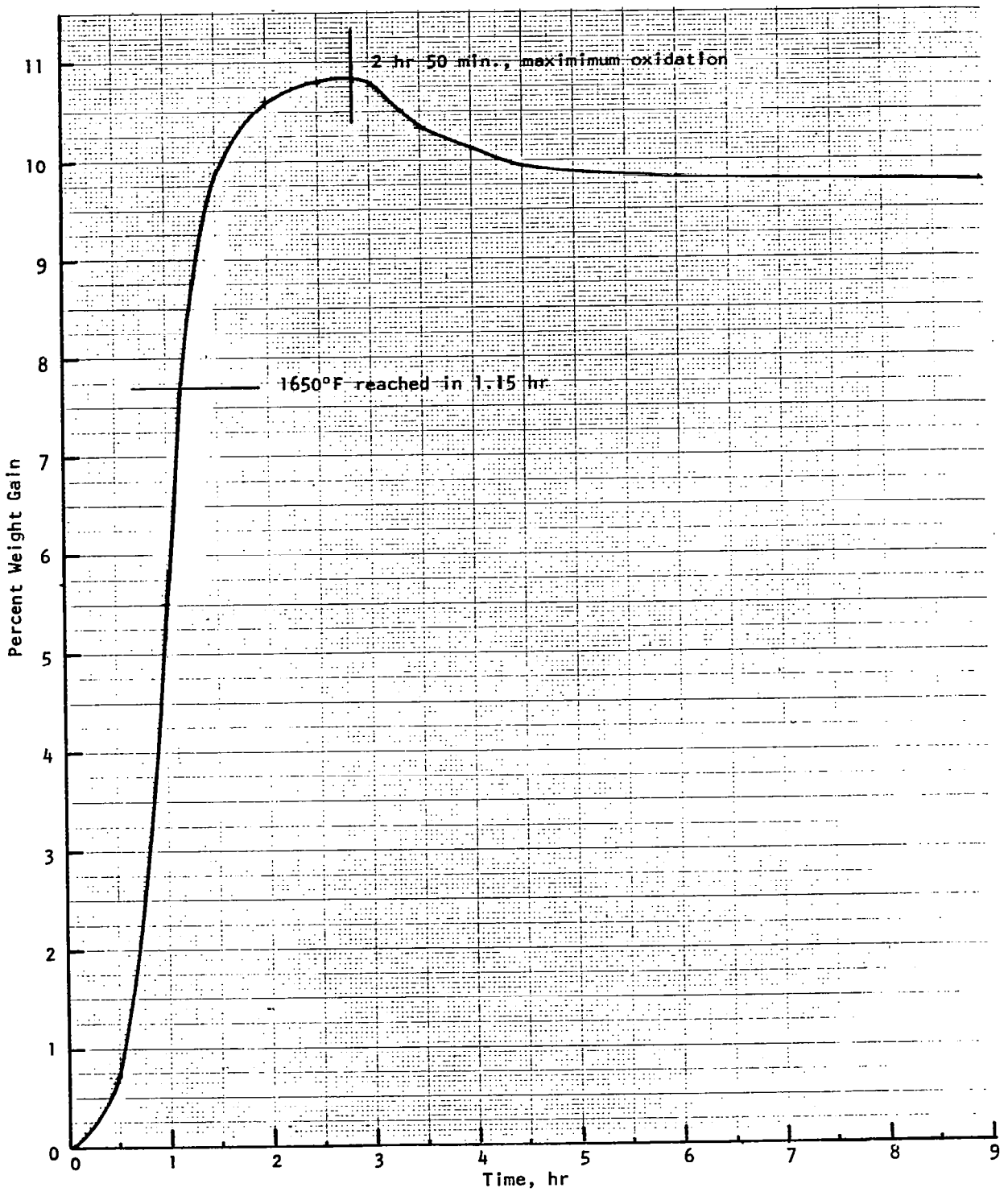



*Figure 46. Expanded oxidation curve of PS101-10 plasma-sprayed coat heated at 1650°F (899°C) in the continuous mode.*

increasing (weight gain) rate and minus (-) denoting a decreasing (weight loss) rate. In Fig. 46 the time of 1.15 hr is marked to indicate that the specimen had reached the oxidation temperature of 1650°F (899°C). The weight gain is also shown to reach a peak of 10.81% at 2 hr 50 min (2.83 hr).

In Table 45 it can be seen that the greatest rate of weight change occurred within two time intervals--the period from 0.5 to 1.0 hr (dw/dt = +9.61) and from 1 to 1.15 hr (dw/dt = +14.5 hr). The temperatures at these intervals were approximated to be as follows:

| Test Duration | Temperature | Wt Gain, % |
|---|---|---|
| 30 min | 700°C (1292°F) | 0.71 |
| 1 hr | 875°C (1607°F) | 5.52 |
| 1 hr 9 min | 899°C (1650°F) | 7.69 |

TABLE 45. RATE OF WEIGHT CHANGE OF PS101-10 DURING THE OXIDATION PERIOD OF 0.5 TO 9 HOURS IN THE COURSE OF A 100-HOUR TEST AT 1650°C (899°C)

| Weight Change Period, hr[a] | Rate of Weight Change, (dw/dt), mg/hr[b] |
|---|---|
| 0.5 - 1 | +9.61 |
| 1 - 1.15 | +14.5 |
| 1.15 - 1.5 | +6.28 |
| 1.5 - 2 | +1.44 |
| 2.83 | 0[c] |
| 3 - 3.5 | -0.97 |
| 3.5 - 4.5 | -0.36 |
| 4.5 - 5.0 | -0.18 |
| 5 - 6 | -0.06 |
| 6 - 9 | -0.02 |
| 10 - 100 | -0.04 |

[a]Time based on recorder readings where zero time equals room temperature.

[b]dw/dt in mg/hr is based on 100 mg of coat material.

[c]Point of maximum weight gain, 10.81%.

By the time the temperature of 1650° (899°C) had been reached (1.15 hr), 70% of the maximum weight gain had already been attained. After the maximum weight gain of 10.81% had been reached (2 hr 50 min), a fairly rapid weight loss occurred from 3 to 3.5 (-0.97 mg/hr). This gradually decreased to a rate of -0.2 mg/hr between 6 to 9 hr. Then from 10 hr to 100 hr, an almost constant rate of weight loss was observed (Fig. 45) of -0.04 mg/hr.

Examination of the interior of the furnace base after completion of the test showed the presence of a green material with small crystals of silver. This had also occurred in the intermittent mode test at 1650°F (899°C) for the same composition, PS101. At that time, X-ray fluorescence analysis revealed high chromium with some silver and small amounts of potassium and calcium. These observations and the data results indicate that a vapor-condensation reaction occurred involving a breakdown of NiCr, vaporization of silver, and a loss of some glass. The curves for the 1650°F (899°C) specimen in Figs. 45 and 46 show that the loss began 1 hr 38 min after having reached temperature (2 hr 50 min from time zero). Further studies are needed to corroborate these indicated findings.

### 3.9 COMPARISON OF OXIDATION DATA

A comparison of the weight gain of coats ($O_c$, %) for all the compositions at all ranges is given in Table 46. The weight gains for the intermittent and continuous modes are quite similar for the 1200°F (649°C) and 1400°F (760°C) series. At 1650°F (899°C) all samples for the regular intermittent mode had failed by blistering and separation of the coat from the substrate; therefore, the oxidation values for these aborted specimens are probably inordinately high due to oxidation of the substrate interface area and coat interface area.

Specimens that were previously heat treated at 1200°F for 100 hr all remained intact when tested at 1650°F for 100 hr in the intermittent mode (1200W series). For samples heat treated at 1400°F for 100 hr (1400W series), only the PS101 sample remained intact on testing at 1650°F.

All of the continuous mode specimens for the 1650°F exposure remained intact although PS106 and MPS106 formed a blister during the early stages of the test. The PS101 remained flat and intact.

TABLE 46. OXIDATION STUDIES

| Temperature Range, Mode | PS106 | MPS106 | PS101 | Substrate |
|---|---|---|---|---|
| 1200°F (649°C) | | | | |
| Intermittent | 3.90 | 4.76 | 7.42 | 0.004 |
| Continuous | 4.40 | 5.47 | 8.95 | 0.015 |
| 1400°F (760°C) | | | | |
| Intermittent | 10.43 | 12.71 | 9.53 | 0.0119 |
| Continuous | 9.97 | 13.56 | 10.72 | 0.0212 |
| 1650°F (899°C) | | | | |
| Intermittent | | | | |
| 1. no preheat | (9.06)[a] | (14.94)[b] | (14.54)[b] | 0.080 |
| 2. preheat, 1200W | 11.25 | 16.95 | 8.25 | 0.097 |
| 3. preheat, 1400W | (15.75)[c] | (18.50)[b] | 7.70 | 0.078 |
| Continuous | 14.87 | 13.56 | 6.42 | 0.068 |

Percent Weight Gain of Coats ($O_c$, %)
Percent Weight Gain of Substrate ($O_s$ = 1/2 of % Gain)
( ) failed, removed: [a]Failed in 2 hr.
[b]Failed after 15 hr.
[c]Failed after 55 hr.

## 3.10 THERMAL EXPANSION

Thermal expansion measurements were made on two free-standing PS106 cylinders approximately 1 in. in length with a diameter of 1/4 in. The first specimen was measured as-sprayed. Figure 47 shows thermal expansion curve. At about 1100°F the amount of expansion was 0.96%. At higher temperatures, the rate became much higher, and expansion of the specimen exceeded the capacity of the dilatometer. At 1364°F the dilatometer was turned off with a 4.62% expansion. The cooled specimen showed a permanent expansion of 4.72%.

The second specimen received a 20 hr heat treatment at 1200°F (649°C) prior to thermal expansion measurement. This specimen was heated to 1650°F. Figure 48 shows the thermal expansion curve. A relatively linear thermal

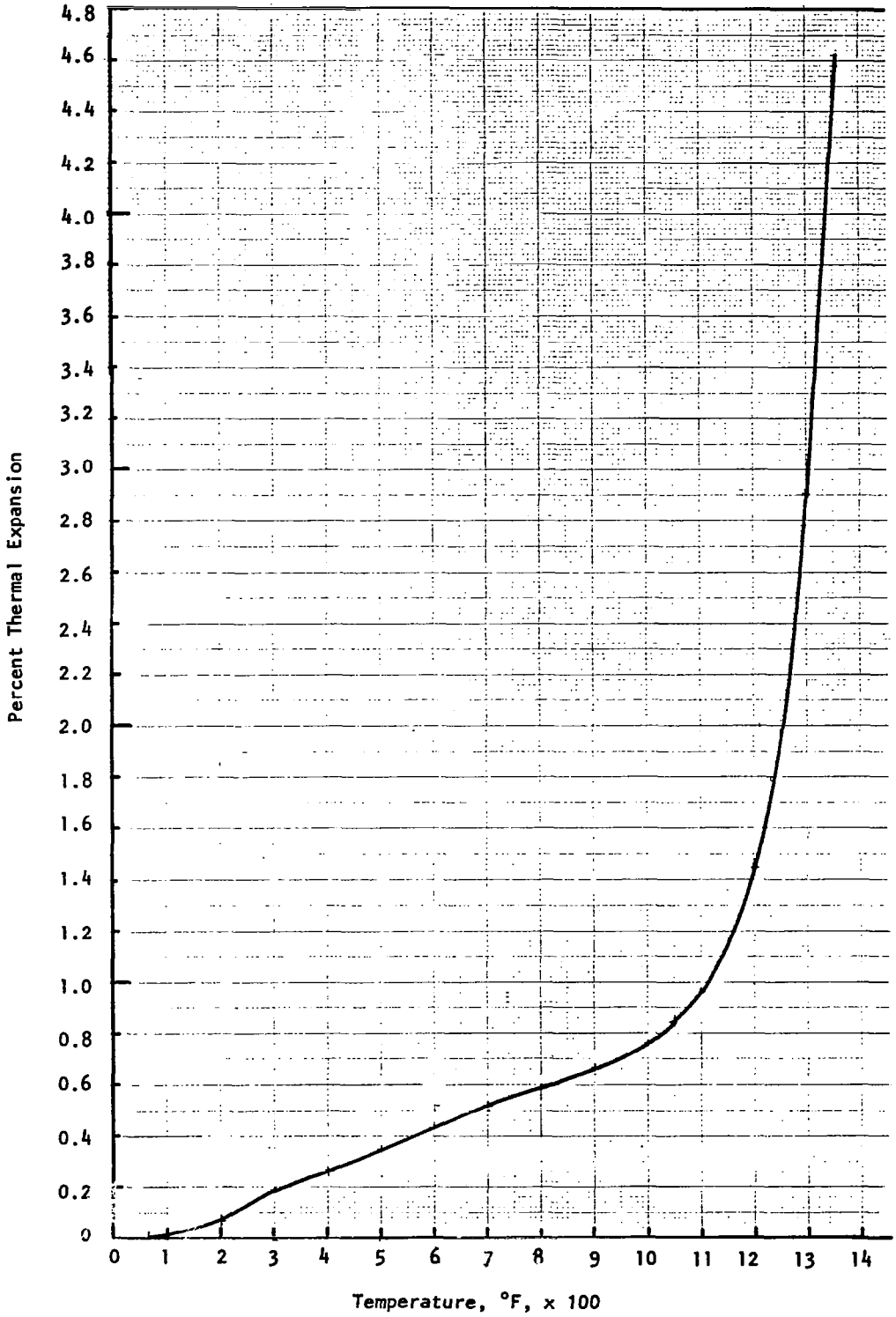



*Figure 47. Linear thermal expansion of a free-standing cylinder of PS106 coat, as-sprayed.*

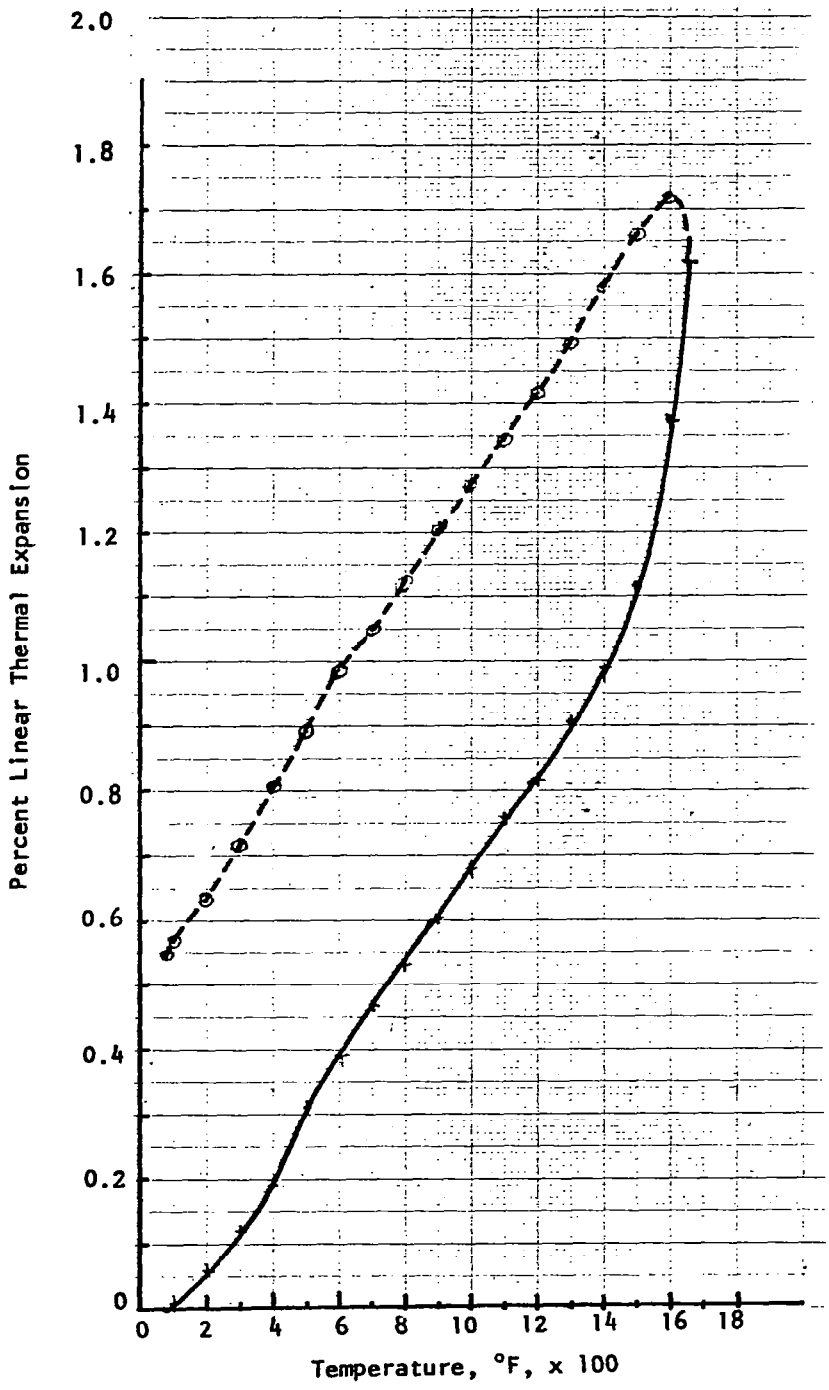



*Figure 48. Linear thermal expansion of a free-standing cylinder of PS106 coat, heat treated at 1200°F for 20 hr before testing.*

expansion is shown to 1400°F where an expansion value of 0.988% was obtained. The curve then shows a sharp rise from 1400° to 1650°F. The percent expansion at 1650°F was 1.62%.

On termination of the test, the sample continued to expand, reaching a maximum expansion of 1.72% at 1600°F on the cooling cycle. This suggests a continuing chemical reaction with a phase change. After 1600°F on the cooling cycle a straight-line relationship is shown. This specimen showed a permanent expansion of 0.55% by the dilatometer or 0.78% by measurement with a micrometer. Table 47 shows the amount of weight gain for the two specimens as well as permanent expansion values.

TABLE 47. THERMAL EXPANSION OF PS106 FREE-STANDING BODY SPECIMENS

| Specimens | Final Temp., °F | Permanent Expansion % | Weight Change, % |
|---|---|---|---|
| As-sprayed | 1364[a] | +4.72 | +3.79 |
| Heat-treated to 1200°F for 20 hr before testing | 1650 | +0.78 | +2.70 |

[a]Dilatometer turned off; expansion beyonf the maximum scale range.

### 3.11 DENSITY/POROSITY

The density/porosity of two free-standing cylinders of PS106 coat composition were measured by the liquid immersion method. The data are presented in Table 48. Specimen No. 3 in the table is the resulting measurements after heat treating specimen No. 1 at 1200°F for 20 hr. It was found that by heat treating the PS106, the water solubility increased; therefore, density measurement of No. 3 was made in kerosene. A drop of water on the heat-treated body became yellow in color. This indicates that the oxidation at this temperature produced a state of oxidation to form a water soluble chrome ion (which is yellow in color). Further testing is needed to confirm this conclusion.

Heat treating resulted in a gain in weight (8.73%), permanent expansion (5.25%), increased porosity (20.6%), and decreased bulk density (-12.5%).

TABLE 48. PHYSICAL PROPERTIES OF PS106 FREE-STANDING CYLINDRICAL SPECIMENS

| Specimen No. | Weight (D), g | Length, in. | Diameters, in. | | Porosity, % | Bulk Density, g/cc |
|---|---|---|---|---|---|---|
| | | | OD[a] | ID[b] | | |
| 1 | 1.2505 | 1.0110 | 0.2928 | 0.2518 | 14.53 | 4.95 |
| 2 | 1.3899 | 1.0285 | 0.2950 | 0.2519 | 13.33 | 5.05 |
| 3[c] | 1.3578 | 1.0641 | 0.3091 | 0.2639 | 17.53 | 4.33 |

[a]Outside dimensions - average of 6 readings: left, center, right, then rotate 90°.

[b]Inside dimensions - average of 4 readings: both ends, then rotate 90°.

[c]This specimen is specimen No. 1 heat-treated at 1200°F (749°C) for 20 hr.
Gain in weight - 8.73%
Permanent expansion - 5.25%

## 4. CONCLUSIONS AND RECOMMENDATIONS

Improved reproducibility and uniformity in the plasma sprayed Ag-NiCr-$CaF_2$ system was obtained by refinements in powder processing procedures. Such improvement was corroborated by the results of material balances, chemical analyses, quantitative analyses, and adhesive strength measurements.

In the coating examination procedures the etching scheme with thioacetamide allowed both image analysis and quantitative microscopic analysis to be obtained. It is recommended that image analysis be used as a confirmatory index in a vendor's shop. It is more accurate and less time-consuming, and is available at a reasonable cost. Quantitative microscopy is very tedious, not as objective, and also very time-consuming (e.g., a count of 960 points over a 0.2 x 2 in. specimen, which was the number of points to give reliable data, took 2 to 3 hr).

The oxidation results, with corroborating data from thermal expansion, show that chemical changes in the coat occur at temperatures above 1200°F. Blistering and deterioration of the coat results (with evidence showing that vaporization had occurred) in the 1400° to 1650°F range. The data indicate that this vaporization reaction above 1400°F is increased for the glass-containing PS101 composition.

The 1650°F oxidation tests show that the cyclic heating/cooling of the intermittent mode caused failure of PS106 and MPS106 (complete separation from the substrate besides blistering) but not of PS101. The continuous mode at 1650°F showed blistering of PS106 and MPS106 but no failure. PS101 did not blister and remained intact but showed a continuing loss of weight after an initial oxidation.

It is recommended that studies of sprayed PS106 and PS101 coatings be made by differential thermal analysis (DTA). DTA studies of the prepared powder mixes should also be conducted. Six sets of the prepared mixes and sprayed coats that should be investigated are (1) a mixture of NiCr, Ag and $CaF_2$; (2) a mixture of NiCr, Ag, $CaF_2$ and glass; (3) mixture No. 1 with MAP; (4) mixture No. 2 with MAP; (5) mixture No. 1 with another inorganic binder, potassium silicate; (6) mixture No. 2 with potassium silicate. DTA studies should be made in air to 1650°F.

Considerations should then be given to changes in the glass composition to reduce the reactivity and the apparent volatility of the present multi-phase coat at the higher temperatures.

The use of microscopically polished specimens for oxidation testing should be considered so that surface analysis before and after oxidation can be made. To obtain a microscopically polished surface, however, would require a thicker substrate than the present one.

Bond strength measurements of several batches of the same composition should be made with closer examination of the powder and the sprayed surface before adhesive strength measurements; the effect of particle size or small changes in the ingredients could be studied.

There have been indications that the oxidation of the coats changes the chemistry of the phases enough to increase the coat solubility in water. This observation has not been fully established, but should be examined in any future work.

## REFERENCES


1. H. E. Sliney, "Preliminary Evaluation of Greases to 600° and Solid Lubricants to 1500°F in Ball Bearings," A.S.L.E. Trans., 11, pp. 330-337 (1968).

2. H. E. Sliney, "An Investigation of Oxidation-Resistant Solid Lubricant Materials," Ibid., 15, pp. 177-183 (1972).

3. H. E. Sliney, "Plasma-Sprayed Metal-Glass and Metal-Glass Fluoride Coatings for Lubrication to 900°C," Ibid., 17, pp. 182-189 (1974).

4. H. E. Sliney, "Bearing Materials," U.S. Patent No. 3,953,343 granted April 27, 1976.

5. R. A. Swenson, J. Roger Attle, "Counting Measuring and Classifying with Image Analysis," American Laboratory, April, 1979, p. 52.

6. W. D. Kingery, "II, Cold Setting Proeprties," J. Amer. Cer. Soc., Vol. 33, No. 8, Aug. 1, 1950, pp. 242-250.

7. M. J. O'Hara, J. J. Dugo, and H. D. Sheets, Jr., "Studies in Phosphate Bonding," Ceramic Bulletin, Vol. 51, No. 7 (1972), pp. 590-595.

## APPENDIX 1

## EXAMPLES OF CHEMICAL ANALYSES RECEIVED FROM COORS/SPECTRO-CHEMICAL AND DATA TRANSFORMATION

| Analyte | Powder Batch PS106-8 | PS106-9 |
|---|---|---|
| Silver | 36.0 ± 0.2 | 34.6 ± 0.2 |
| Nickel | 26.4 ± 0.2 | 26.5 ± 0.2 |
| Chromium | 6.7 ± 0.2 | 6.6 ± 0.2 |
| Calcium | 14.8 ± 0.2 | 15.5 ± 0.2 |
| Fluorine | 14.1 ± 0.2 | 14.8 ± 0.2 |
| Phosphorus | 0.29 ± 0.02 | 0.24 ± 0.02 |
| Aluminum | 0.21 ± 0.02 | 0.18 ± 0.02 |

From the above analyses the weight percentages of the major ingredients were obtained as follows:

| Component | Powder Batch, wt% PS106-8 | PS106-9 | PS106 Specified wt% |
|---|---|---|---|
| Ag | 36.0 | 34.6 | 35 |
| NiCr | 33.1 | 33.1 | 35 |
| $CaF_2$ | 28.9 | 30.3 | 30 |
| $Al(PO_3)_3$ | 2.05* | 1.76* | |

*These values were calculated on the Al content. The phosphorus content was quite low. Coors reports that, in general, the value for aluminum is more reliable than phosphorus for this type of analysis.

To obtain percentages of the major ingredients, the additive method was used for the element analyses because discrepancies appeared to be small. As an example of the discrepancy, the following is presented.

Based on the more reliable calcium value, the weight percent of $CaF_2$ is calculated as:

29.0 instead of 28.9

30.4 instead of 30.3

and NiCr, based on the more reliable Cr value, gives the values

33.5 instead of 33.1

33.0 instead of 33.1

Thus, it appears that the additive method gives results that are valid.

| | Sample | | |
|---|---|---|---|
| Material | MPS106, wt% | NiCrAl, wt% | PS101, wt% |
| Silver | 36.0 ± 0.2 | | 29.9 ± 0.2 |
| Nickel | 27.4 ± 0.2 | 70.3 ± 0.2 | 23.5 ± 0.2 |
| Chromium | 6.5 ± 0.2 | 17.4 ± 0.2 | 6.0 ± 0.2 |
| Calcium | 14.3 ± 0.2 | | 13.1 ± 0.2 |
| Fluorine | 13.6 ± 0.2 | | 13.0 ± 0.2 |
| Phosphorus | 0.51 ± 0.02 | | 0.74 ± 0.02 |
| Aluminum | 1.5 ± 0.1 | 4.0 ± 0.1 | 0.14 ± 0.02 |
| Barium | | | 2.7 ± 0.1 |

Based on these analyses the following weight percentages of major ingredients were calculated:

| | MPS106 | | PS101 | |
|---|---|---|---|---|
| Component | Calculated, wt% | Specified, wt% | Calculated, wt% | Specified wt% |
| Ag | 36.3 | 35 | 30.1 | 30 |
| NiCrAl | 35.6 | 35 | -- | -- |
| NiCr | -- | -- | 29.7 | 30 |
| $CaF_2$ | 28.1 | 30 | 26.3 | 25 |
| Glass | | | 13.9 | 15 |
| $Al(PO_3)_3$ | 1.46 | | 1.38 | |

In MPS106 the binder was calculated to contribute an added wt% of 1.46 to the major ingredients and in PS101, 1.38%. These added weight percents were determined on the basis that monoaluminum phosphate, $Al(H_2PO_4)_3$, dehydrated to form aluminum metaphosphate, $Al(PO_3)_3$, when cured to 400°-450°C. This assumption was based on literature information of Kingery[6] and O'Hara.[7]

Discrepancies in the analyses of the major elements were small enough so that the additive method appears valid. For instance, basing the calculations on the more reliable calcium and chromium data, the changes in percentages were as follows:

For MPS106

| | |
|---|---|
| Ag | 36.7 instead of 36.3 |
| NiCrAl | 34.8 instead of 35.6 |
| $CaF_2$ | 28.5 instead of 28.1 |

For PS101

| | |
|---|---|
| Ag | No change |
| NiCr | 30.2 instead of 29.7 |
| $CaF_2$ | 25.8 instead of 25.6 |
| Glass | No change |

| 1. Report No. | 2. Government Accession No. | 3. Recipient's Catalog No. |
|---|---|---|
| NASA CR-3680 | | |

| 4. Title and Subtitle | 5. Report Date |
|---|---|
| PLASMA-SPRAYED SELF-LUBRICATING COATINGS | July 1983 |
| | 6. Performing Organization Code |
| 7. Author(s) | 8. Performing Organization Report No. |
| H. H. Nakamura, W. R. Logan, and Y. Harada | IITRI-M06051-33 |
| | 10. Work Unit No. |
| 9. Performing Organization Name and Address | 11. Contract or Grant No. |
| IIT Research Institute<br>10 West 35 Street<br>Chicago, Illinois 60616 | NAS3-21979 |
| | 13. Type of Report and Period Covered |
| 12. Sponsoring Agency Name and Address | Contractor Report |
| National Aeronautics and Space Administration<br>Washington, D.C. 20546 | 14. Sponsoring Agency Code<br>505-33-1B (E-1613) |

15. Supplementary Notes

Final report. Project Manager, Thomas P. Jacobson, Structures and Mechanical Technologies Division, NASA Lewis Research Center, Cleveland, Ohio 44135.

16. Abstract

Plasma-sprayed coatings which are self-lubricating from cryogenic temperatures to 840°C (1600°F) have been developed at NASA/Lewis. The composition of the plasma-sprayed coat is described in U.S. Patent 3,953,343, "Bearing Materials," assigned to H.E. Sliney, NASA/Lewis, U.S. Government: it contains three components: silver, nichrome, and calcium fluoride. The objectives of these studies involved the improvement of uniformity and reproducibility of the coats, examination of the oxidation behavior at three temperature ranges, the effect of bond coat and the effect of preheat treatment as measured by adhesive strength tests, investigation of coating examination procedures, and physical property measurements. The following modifications improved the uniformity and reproducibility: 1. Changes and closer control in the particle size range of the raw materials used. 2. Increasing the binder content from 3.2% to 4.1% (dried weight). 3. Analytical processing procedures using step-by-step checking to assure consistency. Other significant results developed during the course of these studies are as follows: 1. The development of an etching technique resulted in obtaining excellent results by image analysis and quantitative microscopy of sprayed coats. 2. Coating bond strength measurements showed that the application of a preheat treatment and/or bond coats of NiCr improved the adhesive strengths of the final coat. Greater strength and uniformity were also obtained as a result of the improved processing procedures.

| 17. Key Words (Suggested by Author(s)) | 18. Distribution Statement |
|---|---|
| Plasma-sprayed composite; Self-lubricating coatings; Silver; Nichrome; $CaF_2$; Glass powder processing; Adhesive bond strength; Oxidation behavior; Thermal expansion | Unclassified - unlimited<br>STAR Category 27 |

| 19. Security Classif. (of this report) | 20. Security Classif. (of this page) | 21. No. of pages | 22. Price* |
|---|---|---|---|
| Unclassified | Unclassified | 124 | A07 |

*For sale by the National Technical Information Service, Springfield, Virginia 22161

NASA-Langley, 1983