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ADVANCED DEVELOPMENT OF PFR-6

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AIR FORCE MATERIALS LABORATORY
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AIR FORCE SYSTEMS COMMAND
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Project No. 7381, Task No. 738102

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Pfaudler Co., a division of Pfaudler Permutit Inc., Rochester, New York,
P. J. Chao, G. J. Dormer, and B. S. Payne, Jr., authors.)

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FOREWORD

This report was prepared by The Pfaudler Co., a division of Pfaudler Permutit Inc., Rochester, New York under USAF Contract AF 33(616)-8125. This contract was initiated under Project No. 1(8-7381). "Materials Application", Task No. 738102, "Materials Pre-Production Processes." The work was administered under the direction of the AF Materials Laboratory, Research and Technology Division, Wright-Patterson AFB , with Mr. L. N. Hjelm acting as project engineer.

This investigation was a continuation of the work initiated under USAF Contract AF 33(616)-7192 on 1 April 1960. The first year's work has been reported in ASD Technical Report 61-241. This report covers the work performed during the period 1 March 1961 to 30 April 1962.

Mr. P. J. Chao was Principal Investigator on the project. He was assisted by Associate Investigators G. J. Dormer and B. S. Payne, Jr. Dr. D. K. Priest was Project Administrator.

This research was performed by The Pfaudler Co. as Project G761-9103. The Pfaudler designation of this report is PF 62-8.

ABSTRACT

The PFR-6 alloy silicide coating, initially developed in the laboratory to protect molybdenum alloys against high-temperature oxidation, has been scaled up and optimized for use at an intermediate level. Pure molybdenum, Mo-0.5 Ti, and TZM have been successfully coated with this pack cementation process. Substrate preparation, pack composition, heat transfer in the retort, and the process cycle were studied extensively to establish desired conditions for applying PFR-6 to components up to 1.5 ft long. Assemblies must be coated before and after riveting to obtain adequate protection. Two non-destructive measurements were found that will indicate within statistical limits expected coating life. The scale up of PFR-6 was accomplished with essentially no change in its previously established, statistically-proven lifetime and reliability. Average life remains approximately 1.4 hr in an oxyacetylene torch test exceeding 3000°F. Recommendations are made for further scale-up of PFR-6 process to attain a capability for coating full-size re-entry vehicle components.

This technical documentary report has been reviewed and is approved.

W. P. Conrardy

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Materials Applications Division
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1. INTRODUCTION

Aerospace vehicles are currently being designed and developed for future Air Force programs involving controlled re-entry from orbital or interplanetary missions. Because of the high temperature generated at the vehicle's leading edges and heat shields by aerodynamic heating on re-entry, these components of the vehicle must be constructed of a material that possesses adequate strength at the maximum temperature it will encounter, and will still retain its structural integrity. Of prime interest for this purpose are some of the refractory metals, in particular molybdenum and its alloys.

Molybdenum and its alloys have many desirable characteristics, particularly strength at high temperature. However, the resistance of molybdenum to oxidation at temperatures above 1500°F is so poor that it cannot be used in contact with oxygen in the temperature range where its high-temperature capabilities establish its usefulness. Protection of the base metal against oxidation is therefore essential.

Substrate protection can be achieved either by alloying or coating. Alloying has not been particularly successful because properties such as weldability, workability, and strength are greatly affected by the large additions of alloying materials. Coating as a means of protection has therefore taken on great importance. The pack cementation method of coating is capable of producing an impervious, oxidation-resistant coating on oddly-shaped structures in a reproducible manner. The pack cementation coating designated as PFR-6, developed on a laboratory scale by Pfaudler under ASD Contract AF 33(616)-7192, successfully protects certain molybdenum alloys for 1.4 hr against oxidation at temperatures in excess of 3000°F.

The initial year's study was designed to develop an oxidation-resistant coating for the protection of molybdenum alloys; to determine the performance and reliability of this coating; and to describe and demonstrate the important variables in the coating process. Three coating concepts and 41 coatings were studied and carefully evaluated before PFR-6 was selected for optimization. The experiments were planned and performed on a statistically valid basis in order to provide results in which confidence could be placed. The effects of pertinent variables were determined and the coating was optimized on a laboratory scale. Adaptation of the experimental results to the more practical application of the optimized and statistically reliable PFR-6 coating was initiated but not completely attained. A detailed report of the first year's work was made in ASD TR 61-241, to which the reader is referred for a more complete discussion of apparatus, procedures, and statistical treatment of the experimental data.

The objective of the second year's work was to transfer the knowledge gained under the earlier contract to an intermediate-size or pilot plant operation. Implicit in this objective was further study and determination of the important process variables. An attempt was made to establish dimensional relationships with process time and temperature, batch composition,

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and growth rate of coating. This report includes the experimental work performed in the investigation of these relationships.

The ultimate objective in the development of PFR-6 is to obtain a statistically proved coating for one or more molybdenum alloys which will be employed in the construction of components for re-entry-type aerospace vehicles. The coating must have a demonstrated reliability and lifetime, while still capable of application by a practical and economical process. The phase of the work reported here was intermediate between the first year's laboratory research to find a potentially useful coating and a subsequent phase involving scale-up to an industrial capability for coating full-size prototype re-entry vehicle components.

2. EXPERIMENTAL WORK

2.1 EQUIPMENT

2.1.1 Furnaces

Two electrically heated furnaces, constructed for the first year's work, were used in all coating operations. Both furnaces employ Globar (silicon carbide) heating elements and are capable of temperatures of 2400°F for long periods and 2600°F for shorter periods of service. One furnace draws 75 kva and has a usable retort volume of 20 by 20 by 20 in. The second furnace requires 12.5 kva and has a usable retort volume of 17 by 7 by 7 in. The samples were coated in small retorts to save expensive packing materials. It was not practical to coat several hundred samples together, since each batch was varied experimentally in most cases.

A 7.5 kva electric furnace similar in construction to the above two furnaces was used for both still and slow-moving air oxidation testing of coated samples. This unit provides a 7.5 by 9 by 19 in. hot zone. Two additional furnaces (Fig. 1) have been constructed for dynamic oxidation testing. One is a 5 kva furnace equipped with Kanthal heating elements and provides a maximum temperature of 2300°F. The other is a 15 kva furnace equipped with Globar elements and provides for a maximum temperature of 3000°F. These multitube furnaces are instrumented for precise control of the mass flow of air (or other gases) to the individual tubes. Since insufficient time was available for their calibration, these two furnaces were not employed in the investigation.

2.1.2 Oxyacetylene Torch Test Facility

One of the techniques for evaluating the coatings employed an instrumented and precisely controlled facility comprising three oxyacetylene torches (Fig. 2) which was developed and calibrated in the first year's work. Transite compartments, 18 by 14 by 18 in., enclose the torch and specimen to avoid disturbing the flame with air flow in the test area. In addition, this shielding serves to keep constant the amount of air aspirated into the flame. The gas composition was generally regulated at 22 cfh oxygen and 8 cfh acetylene, the most oxidizing flame that will not blow out.

Temperatures were measured for the most part with a narrow wave-length (single-color) brightness optical pyrometer manufactured by the Pyrometer Instrument Co., Bergenfield, New Jersey. This instrument was supplemented with a two-color, automatic reading pyrometer, Pryo-Eye Model No. F3L200, manufactured by Instrument Development Laboratories, Inc., Attleboro, Massachusetts. The pyrometers indicate apparent temperature only; true temperature can be calculated if the emittance of the coating is known.

2.1.3 Bend Test Apparatus

The minimum-bend test apparatus employed in the first year's work (Fig. 3) was used to evaluate the ductility or formability of the coated composite at room temperature. In this test, sheet samples are bent around a series of dies of successively smaller nose radius varying from 1.5 in. on the largest to a knife edge on the smallest. Bending is done by means of a hydraulic jack and a female die which has an included angle of 105 degrees. A pressure gauge on the jack permits reproducible operation.

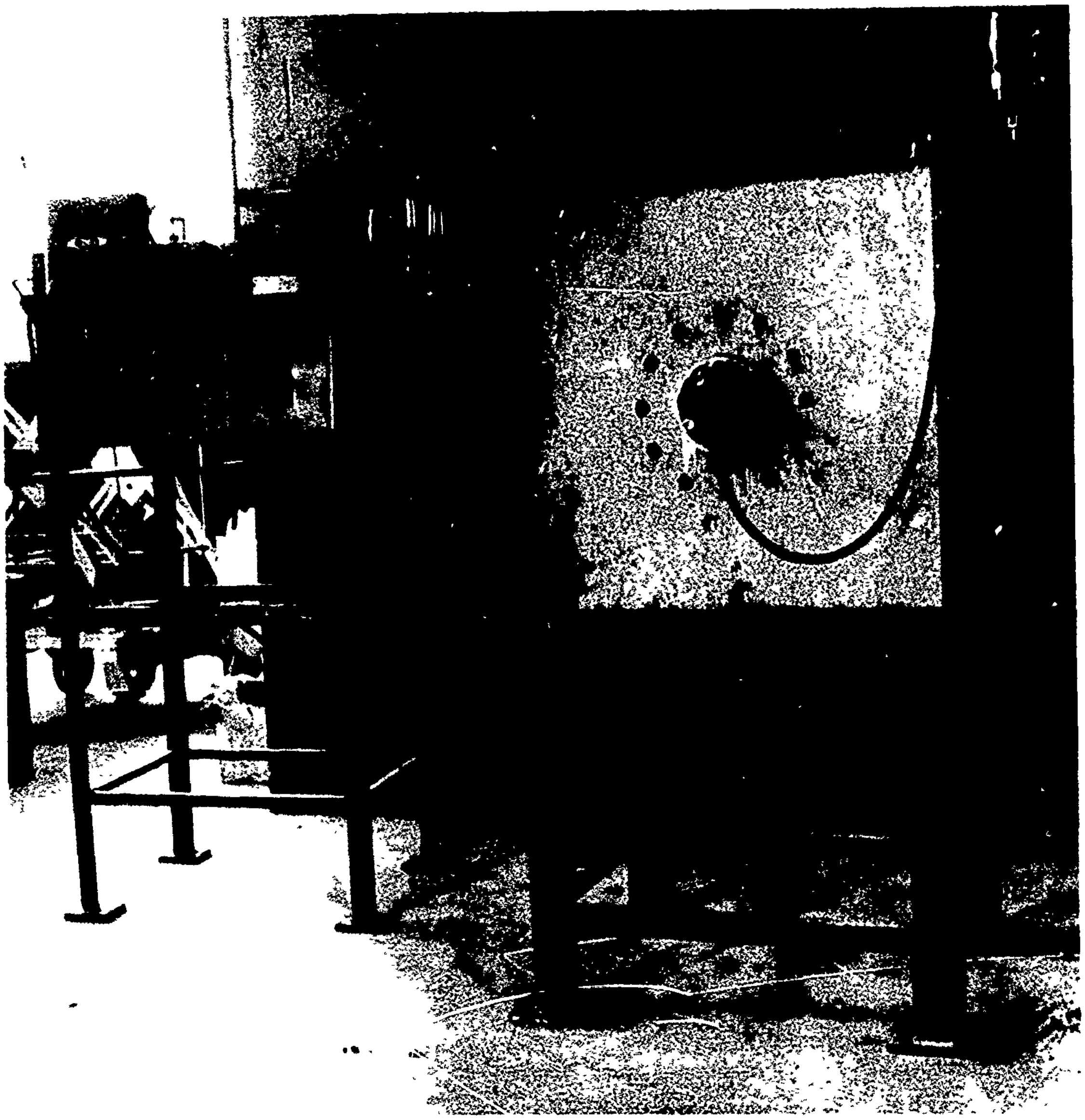


Fig. 1 Multitube Electric Furnaces for Dynamic Oxidation Testing

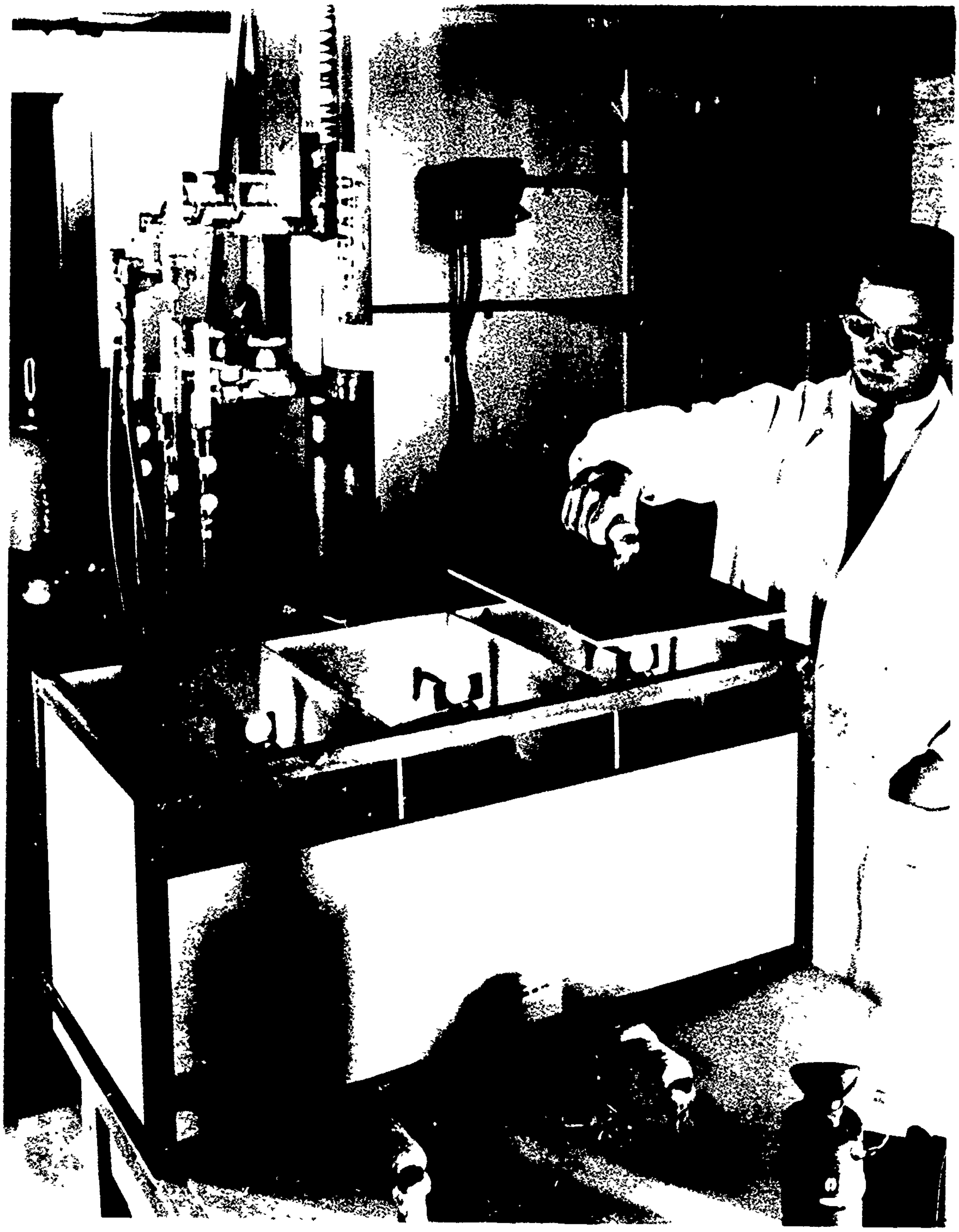


Fig. 2 Oxyacetylene Torch Test Facility

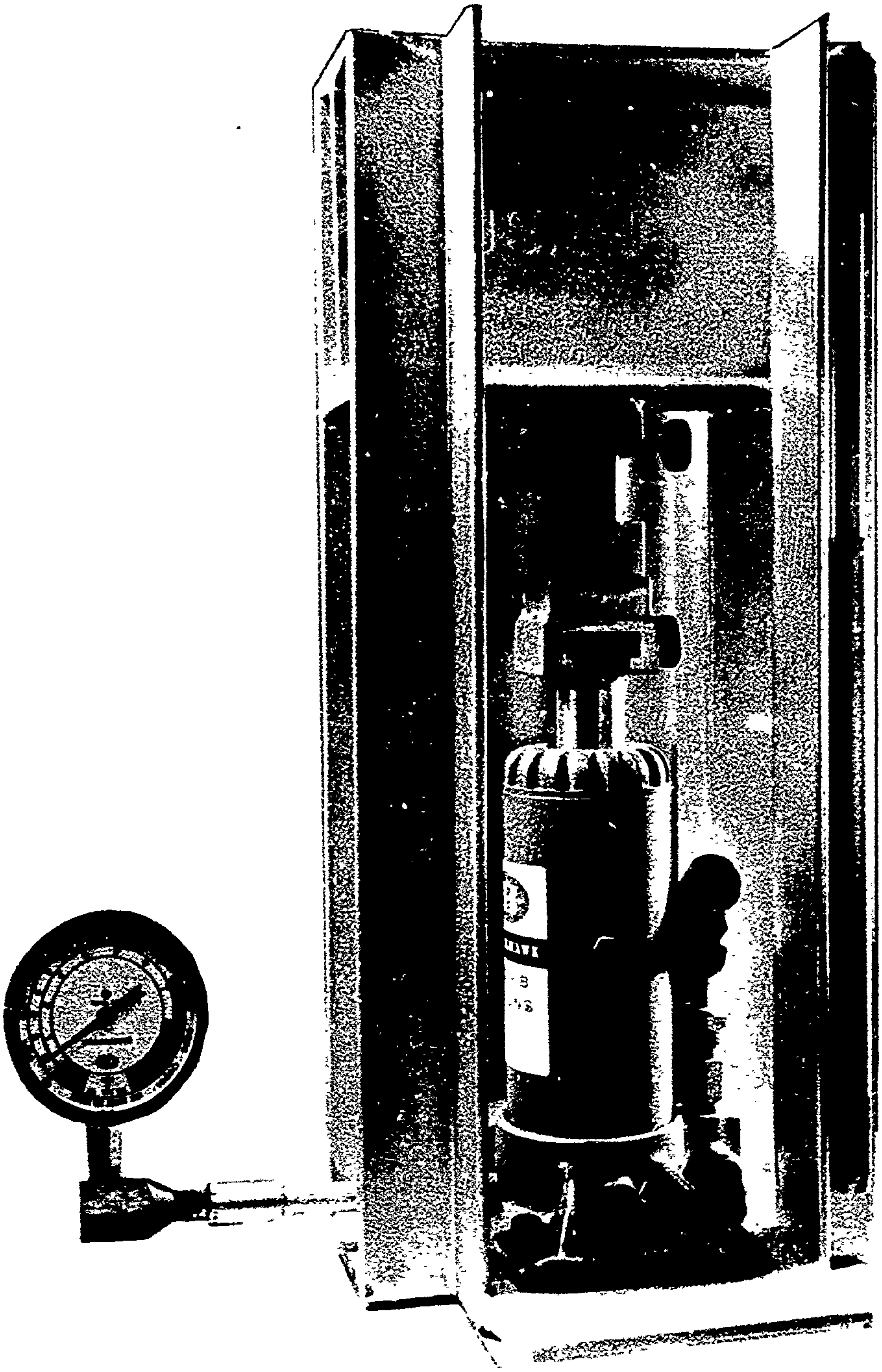


Fig. 3 Bend Test Apparatus

2.1.4 Metallographic Equipment

Preparation of metallographic samples and the metallographic investigation and evaluation of the coating were carried out in a manner slightly modified from that conventionally used. In addition to standard metallographic equipment, solid polyethylene polishing wheels were employed. Photomicrographs were obtained and processed using standard photographic equipment.

2.2 MATERIAL

In this project, PFR-6 coatings were applied to two molybdenum alloys and to pure molybdenum. The two alloys, Mo-0.5% Ti and TZM, were purchased from Universal Cyclops Steel Corp., Refractomet Division, in 10- and 30-mil sheets. This material is consolidated by the vacuum arc method and is subsequently rolled to the desired final thickness with intermediate anneals, as necessary. Base metal quality was good. No laminations, surface imperfections, or other defects which can detrimentally affect the coating and its integrity were found. Commercially pure molybdenum produced by the sinter powder process was purchased from Metallwerke Plansee in 30-mil sheets. This material was also of good quality with no flaws or imperfections.

2.3 PREPARATION OF SAMPLES

Standard samples were cut from large sheets of material into 1.5 by 3.0 in. pieces using a water-flooded shellac wheel saw. Special care was taken to avoid overheating of the samples. Specimen edges and corners were manually ground and radiused on a wet belt sander. The corner radius was 0.125 in. minimum, the edge radius 0.005 in. (t/2 minimum desired). The samples were next scrubbed with a warm detergent solution, thoroughly rinsed, and dried between paper towels. They were then soaked in acetone for 20 min and dried just prior to packing into the retort. Besides this standard means of sample preparation (polish-plus-wash), developed in the first year's work, several other methods including ultrasonic cleaning, vibratory finishing, liquid honing, abrasive blasting, and etching were investigated. These techniques and their influence on coating quality are discussed in detail in section 3.2.5. In all cases, following the final step in preparation, tweezers or clean plastic gloves were used to handle the samples.

2.4 PACK PROCESS

PFR-6 is an alloy silicide coating. It is applied by the pack cementation process on molybdenum substrates to provide protection to the base-metal against oxidation at elevated temperatures. This thin coating (0.001-0.002 in. thick) is composed of a molybdenum-rich diffusion layer (approximately one quarter of the total coating thickness) and a silicon-rich diffusion layer. The coating is primarily molybdenum disilicide formed as a result of the deposition of silicon in the cementation process and the subsequent interdiffusion of the molybdenum and silicon. The very small amount of columbium believed to be present (hence, "alloy silicide"), results in an improvement in the properties of PFR-6 over a pure molybdenum disilicide coating.

The pack constituents (Appendix I) are powders that are weighed separately on a laboratory balance and then blended immediately. A thorough mixing is provided to insure homogeneity of the pack. Part of the mixed pack material is placed in a freshly sandblasted retort. Samples are placed in the pack material and are properly aligned. The remaining pack material is then poured over and around the samples, insuring good contact at every point. The retort cover is put in place, the retort is inverted, and the ceramic sealing compound is packed around the cover to a predetermined height.

The entire pack system is heated to temperatures in the range of 1750°F to 2250°F for 4 to 8 hr depending upon the desired composition and structure of coatings. When, during the heating cycle, the temperature reaches 270°F, the atmosphere-control compound (urea) melts and on further heating vaporizes and decomposes to form biuret and ammonia. These gases expel air from the retort chamber and fill it with a reducing atmosphere which prevents oxidation from taking place. Excess gases can escape through the sealing material, both when the seal is unmelted and after it becomes molten at higher temperatures. At reaction temperatures (approximately 2000°F), the evolved gaseous reactants are held under pressure greater than atmospheric by the molten seal, but some excess gas can escape. When the reaction is complete and the retort is cooled, the seal solidifies and prevents the entrance of air. Thus, the use of this kind of seal prevents oxidation within the retort during the entire process cycle.

At the completion of the heating cycle, which is programmed and controlled automatically, the retort is air-cooled. After the ceramic seal is chipped away, the samples are removed from the spent pack and are cleaned of adherent pack material. The spent pack compound is saved for possible reclamation.

2.5 TESTING

The oxyacetylene torch facility described earlier was used for the primary testing technique. A sample was mounted in the test apparatus and the torch-to-sample distance adjusted until the desired test temperature was obtained. The temperature for most of the evaluation work was 3000°F as measured by the single-color optical pyrometer (based on an emittance of 1.0). This corresponds to a true temperature of 3125°F if an emittance of 0.8 is assumed.

The sample was removed from the flame every 0.5 hr and immediately quenched with a 30 psi air blast from a nozzle held 3 in. away, cooling it to room temperature in a few seconds. This constituted a thermal shock test. The samples were examined carefully without removing them from the holder and were then returned to the flame position. Particular care was taken to insure that the flame tip was on the same spot previously heated. When there was sudden rise of sample temperature and white fumes (the vapor of molybdenum trioxide) and a visible hole in the coating were detected, the test was stopped and the lifetime recorded. This was in all cases an end point that was readily detected.

The bend test samples were bent over a series of dies of decreasing radius until the coating failed. The next largest radius was then recorded as the minimum radius prior to failure. Each sample was bent in a female die with an included angle of 105 deg at a uniform maximum hydraulic jack pressure. A thin rubber sheet was placed on each side of the test sample to minimize abrasion damage. The sample was inspected visually after each bend. Samples and dies were heated in water to about 140°F before bending to insure that the testing temperature was above the transition temperature of the substrate.

Another series of tests, termed the bend-torch test, involved an initial bending of the sample over a 1.5 in. radius die. The sample was then tested to failure in the oxyacetylene torch test unit described earlier.

2.6 METALLOGRAPHIC EXAMINATION

Selected experimental samples were mounted for metallographic examination. This required special care because conventional mounting techniques caused coatings to be cracked or partially pulled off the substrate. The iron plating previously used prior to cutting and mounting was eliminated. After cutting, the coated pieces were mounted without pressure in an epoxy resin which sets at room temperature. All rough polishing was done manually on 600-grit wet silicon carbide paper. Final etch-polishing was done manually on microcloth-covered solid polyethylene polishing wheels using levigated alumina as the abrasive and 10 percent chromic acid as a combination wetting-etching agent. Coating thickness measurements were made by using a filar eyepiece on the Bausch and Lomb Research Metallograph.

3. TECHNICAL DISCUSSION

3.1 HEAT TRANSFER STUDIES

When planning heat transfer studies and calibration runs for retorts, consideration must be given to the size of the retort, the selection of the packing material, and the positioning of the thermocouples. In the PFR-6 coating of large specimens, large retorts and hence an increased volume of pack material are required. As the retort cross section increases, more time is required for the center of the retort to reach coating temperature, since the mass to be heated and the resistance to heat transfer are greater and the retort surface area to volume ratio is usually smaller. Any increase in the heating rate with constant heat input must come from one of the following:

- Increasing the thermal conductivity of the pack material without significantly changing pack weight.
- Decreasing the pack weight while keeping the thermal conductivity relatively constant.
- Increasing thermal conductivity of the pack material while decreasing the weight of the pack.
- Using shaped retorts.

Only alumina (or magnesia) was used in the retorts in the calibration runs. This choice was based on both economy and ease of operation and on the nature of the required data. A substantial cost saving was realized by omitting the reactants and seal materials. In large retorts, the cost of the columbium powder alone would have been substantial, and the other reactants and seal materials would have further increased the cost.

Furthermore, since only a measure of the unaffected heat transfer characteristics was desired, it was deemed unwise to include reactants whose heat input is unknown. Undoubtedly, the absence of the coating process reactants has had an effect on these studies, for gas permeation and exothermic reactions resulting from the presence of such materials would have a beneficial effect in increasing the heating rate at the center of the retort. The exact result of these effects is not known, nor may it be calculated at this time due to the lack of thermodynamic data. It must therefore be studied experimentally.

An economical method of investigation is to compare heat flux studies performed for smaller retorts filled with 100% inert materials and with actual PFR-6 coating mixtures. Then only one or two runs in a large retort will be required for confirmation of data extrapolated from the results obtained with the smaller ones.

Omission of the usual reactants in these studies permitted the use of an open retort, since no reacting gases had to be contained. This, in turn, simplified the positioning of the thermocouples and their recorder leads. In addition, the inevitable effect of the high temperature gaseous reactants on the thermocouples was avoided. Their location in the pack was guided by the desire to obtain as much data from the number of thermocouples used. At first, a large number were used to provide the time-temperature information. It was found, however, that fewer thermocouples would provide satisfactory data and, in addition, would improve the legibility of the recorder chart. Subsequent studies were conducted in such manner.

3.1.1 Heat Flux in a Small Retort

Two retorts measuring 4 by 4.75 by 6 in. inside were filled with minus 20 mesh alumina grit. Ten thermocouples were placed to record a time-temperature history for multiple locations within the retort (Fig. 4), and were connected to a multipoint recorder. Selection of thermocouple locations was governed by the position of the sample, the geometric center of the retort, and the anticipated area of slowest heating.

The heating rates at specific locations are plotted in Fig. 5 and 6. These diagrams show the time-temperature relationship within the retort and present two areas of specific interest. The first is the temperature differential or gradient between the outer layer and the retort center. Although a temperature difference as great as 720°F occurred between these areas initially, this gradient was quickly reduced as the over-all temperature increased. Among the thermocouples positioned within the retort, a temperature differential of approximately 85°F persisted even during a prolonged holding time at a specific temperature. Before further runs were made, the thermocouples were calibrated in relation to each other and to a known temperature. This calibration revealed that a temperature differential of 68°F existed among the thermocouples at 2050°F.

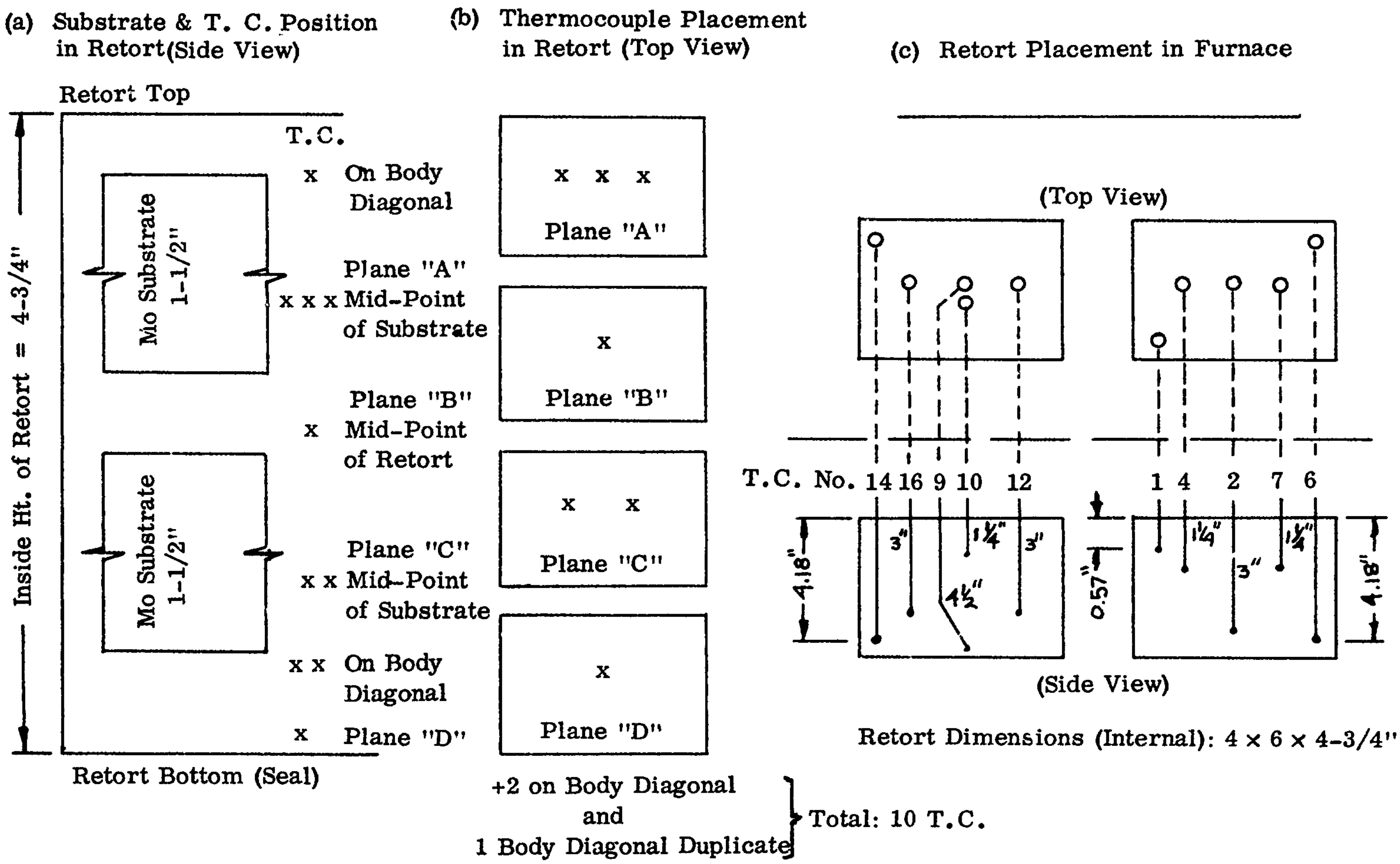
3.1.2 Heat Flux Variation Among Various Particle Size Combinations

A new attempt to increase the heat transfer within the process retort was made by replacing some or all of the 20 mesh alumina with minus 240 mesh alumina. A small beaker containing a measured amount of water was surrounded by mixtures containing 0%, 20%, 40%, and 100% minus 240 mesh alumina, the balance being 20 mesh. The beaker of water was surrounded by the alumina in the center of a larger beaker which was then placed on a laboratory hot plate adjusted to provide a temperature of 550°F. In each case, the heat flux characteristics were determined by measuring the amount of water evaporated from the small beaker at several time intervals.

The data produced in these simple exploratory experiments has been plotted in Fig. 7 and shows an apparent difference in overall heat transfer of the various alumina mixtures. This may be explained by the fact that the thermal conductivity of alumina is much greater than that of vapors present within the mixture. Introducing small particles of alumina among the larger particles eliminated some of the air gaps, resulting in a higher over-all thermal conductivity and a decreased temperature gradient. The amount of fine alumina added to the PFR-6 pack composition must be limited, however, since the amount of vapor retained and the rate of permeation of reactive gases within the retort are markedly influenced by the size, volume, and distribution of air spaces. This, in turn, influences the coating characteristics.

3.1.3 Alumina and Magnesia Combinations

The bulk of the PFR-6 coating pack mixture is inert filler material. In an attempt to improve heat transfer within the retort, magnesia was substituted for alumina. Comparable runs were made simultaneously with alumina-filled and magnesia-filled retorts in order to compare data. Two thermocouples were embedded in a 4 by 5 by 6 in. retort filled with the test mixture and heat was supplied to the 4 by 5 in. sides (Fig. 8). The following four test mixture compositions were studied in duplicate.

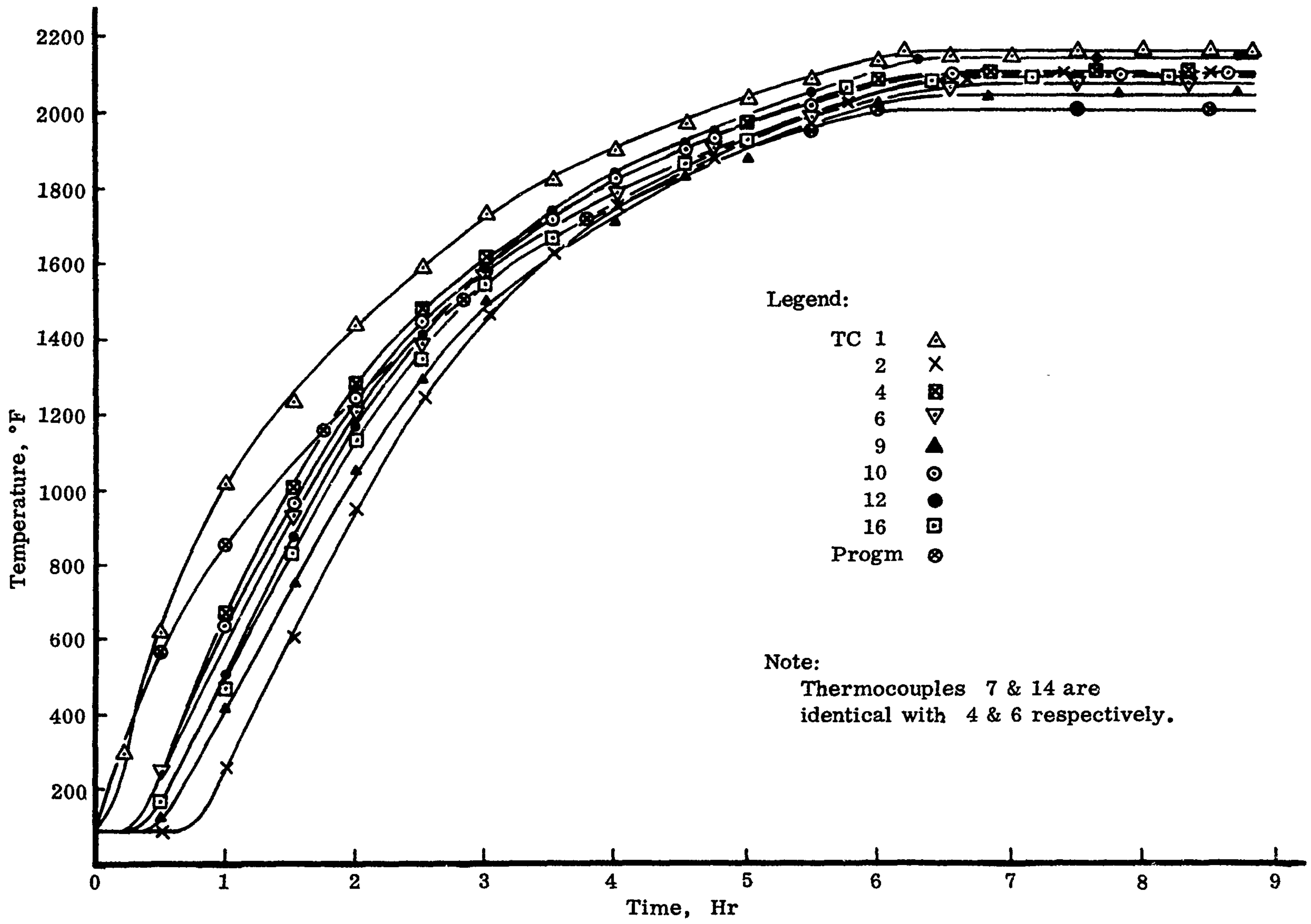


(a) Substrate & T. C. Position in Retort(Side View)

(b) Thermocouple Placement in Retort (Top View)

(c) Retort Placement in Furnace

Fig. 4 Time-Temperature Calibration



Note:
Thermocouples 7 & 14 are identical with 4 & 6 respectively.

Fig. 5 Heat Transfer to Small Retort

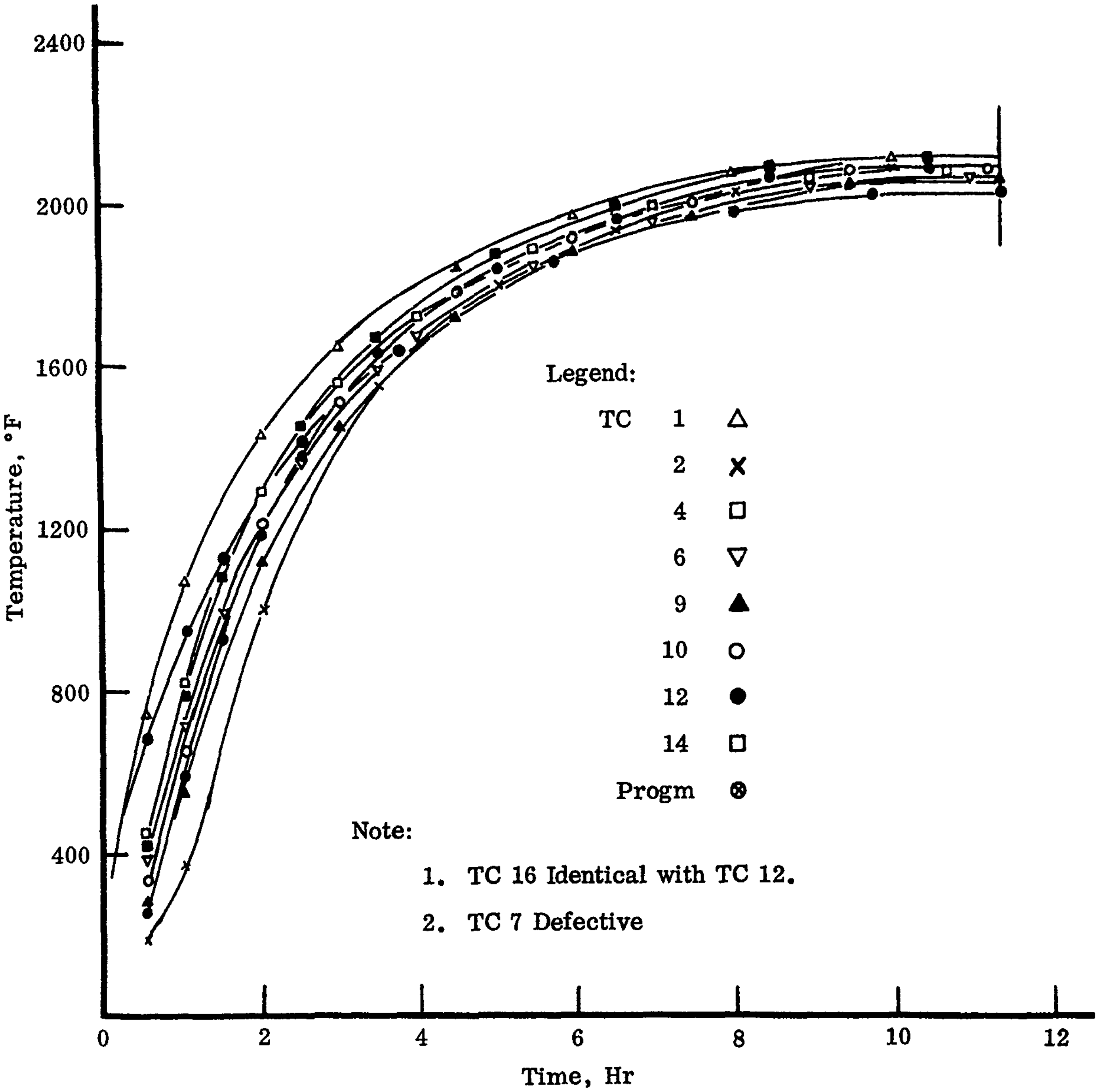


Fig. 6 Calibration Run No. 2 for Furnace No. 13.

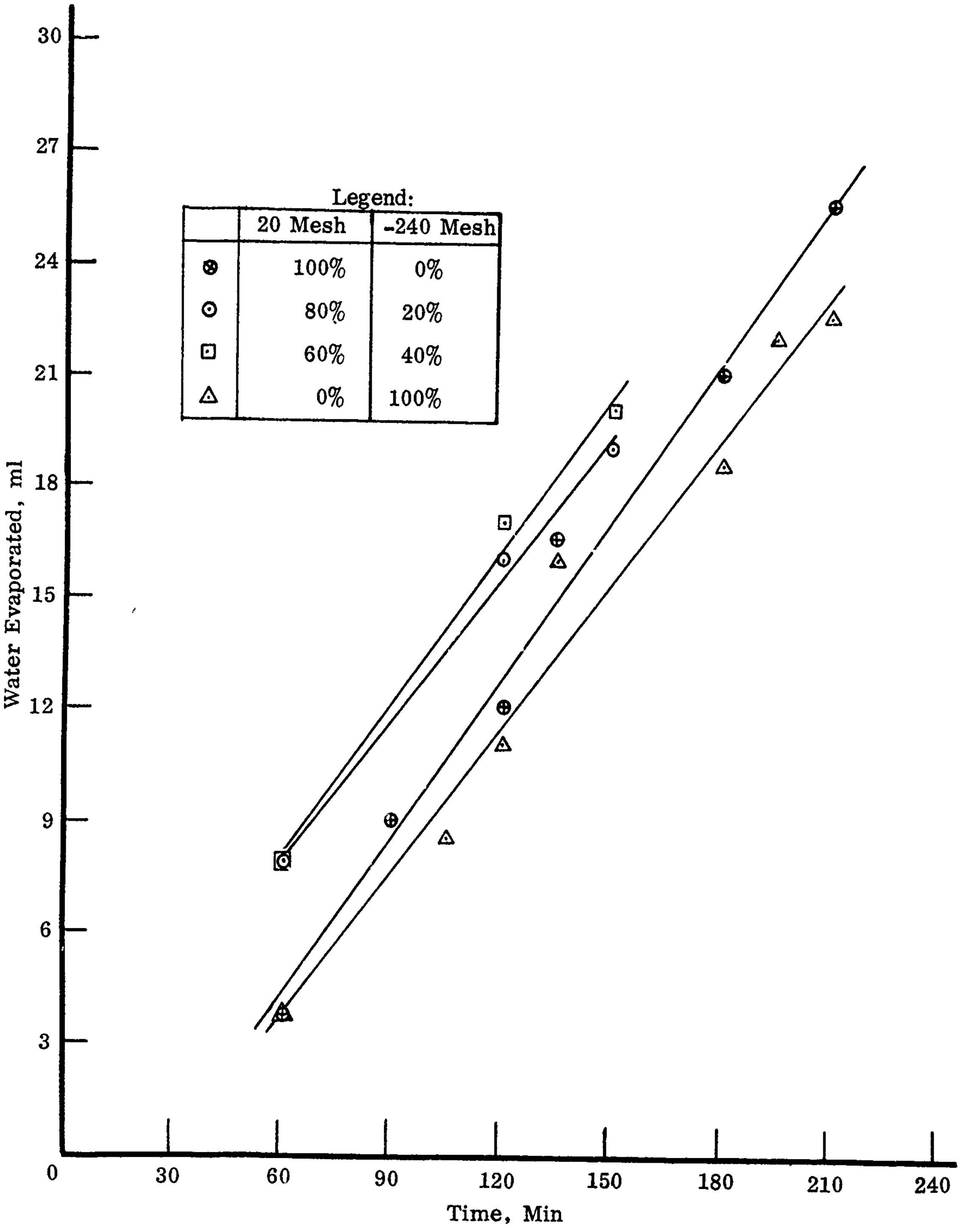


Fig. 7 Heat Transfer Through Mixture of Alumina Particle Sizes

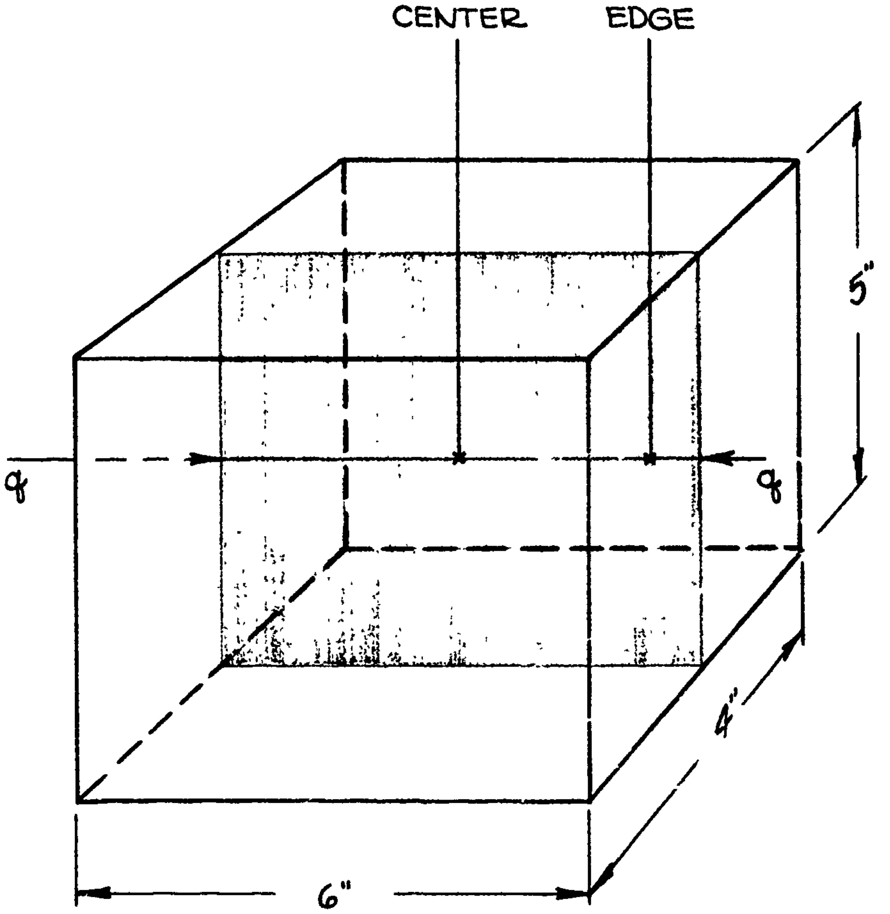


Fig. 8 Thermocouple Hot Junction Location in 4 x 5 x 6 in. Retort

Number	Composition
1	80% 20 mesh alumina, 20% 240 mesh alumina
2	100% 20 mesh alumina
3	80% 20 mesh magnesia, 20% 220 mesh magnesia
4	100% 20 mesh magnesia

The time-temperature data for each run (Tables 1, 2, 3, and 4) are plotted in Fig. 9, 10, 11. For clarity, only the results of the center-located thermocouple are plotted. Both the magnesia and alumina runs show similar results. In each case, the retorts packed entirely with 20 mesh material (compositions 2 and 4) reached temperature somewhat faster than the retorts containing fine-coarse mixtures (compositions 1 and 3). Apparently, the improvement in over-all heat transfer resulting from filling the voids was not enough to overcome the increase in heat input required for the greater mass of filler. Another possibility is that heat transfer by radiation at high temperature is better in the case of 100% 20 mesh than the 80/20 mixture of inert filler because of larger voids characteristic in packing the former.

Again considering Fig. 9 and 10, it is significant to compare the time required to reach a given temperature for 20 mesh and mixed fine-coarse pack material. For alumina, the fine-coarse mixture lags slightly at first, increasing to a lag of 30 minutes as processing temperature is reached. The relationship for the magnesia mixtures is the same, with the fine-coarse mixture lagging by 15 minutes at processing temperature.

According to values reported in the literature, the thermal conductivity of magnesia is somewhat greater than that of alumina at low temperatures, but as the temperature reaches 2000°F, the difference between the two becomes small. As a result, the temperature in the magnesia-filled retort increases more rapidly than that in the alumina-filled retort. However, by the time the temperature reaches 1500°F, the difference in conductivities is less than one-third of that observed initially.

A comparison of results of the prior time-temperature study of 20 mesh alumina in a similar retort (Fig. 5 and 6) with the data from this study (Fig. 9 and 10) shows good correlation.

3.1.4 Heat Transfer in a Large Retort

Time-temperature studies were conducted using a relatively large retort (18.5 in. long by 18.75 in. wide by 22.25 in. high) packed with 20 mesh alumina. The retort was heated in the 75 kva furnace. By placing the retort equidistant from all heating elements, accurate heating rates could be obtained.

In order to measure the temperature at various points in the retort, six chromel-alumel thermocouples 6 ft long were positioned along the body diagonal of the retort (Fig. 12) and were connected to a multipoint recorder. The results of three runs are shown in Fig. 13, 14, and 15. Time-temperature relationship for the furnace controller (programmer) is also included on these graphs.

The selection of the body diagonal for the thermocouple placement has provided a built-in system of data corroboration as well as the necessary time-temperature gradient information. Both horizontal and vertical gradients have been investigated by this positioning of thermocouples. In addition, thermocouples 1 and 12 yield results which may be compared since the retort varies only slightly from a cube. The same is true of thermocouples 4 and 9 and thermocouples 5 and 8.

The variation among the same thermocouple plots in the three runs may be explained by noting the differences in the over-all rates of heat input. This is indicated by the furnace programmer plot on Fig. 13, 14, and 15. It should be further noted that Run No. 2 was only one-half as long as Runs 1 and 3. The difference between corresponding thermocouple time-temperature plots is governed by the variation of the retort from a perfect cube and the precise location of the thermocouple hot junction.

Carrying this investigation somewhat further, the heat transfer characteristics were calculated for a 24 by 24 by 42 in. retort completely filled with alumina and were compared with data obtained experimentally (Fig. 16).

By standardizing the furnace heat input rate in actual PFR-6 runs, the variation among different runs will be eliminated. The gas permeation and exothermic reactions involved in the coating operation will minimize the variation between corresponding thermocouple time-temperature plots in a single run. Moreover, the time to reach temperature at the retort center will be reduced.

The heat flux data (Fig. 13, 14, 15, and 16) represent the worst possible condition for heat transfer in the PFR-6 process since the inert filler material has the lowest thermal conductivity of any of the materials normally employed. It is apparent that in one case, actual heat transfer slightly exceeds that expected from calculations. As previously discussed, it is believed that the addition of reactants to the inert filler material would result in higher heating rates throughout the retort because of gas permeation and exothermic reactions. These factors become increasingly important as the retort size increases, as is apparent from the time-temperature plot for the center thermocouple (Fig. 16).

3.2 OPTIMIZATION STUDIES

The scale-up of a laboratory-scale operation to one of intermediate scope and eventually to one of production capabilities requires an intimate knowledge of several aspects of the coating process. Control of reaction rates, influence of heating schedules, effect of pressure within the retort, placement of parts to be coated, coating process time, and preparation of surfaces to be coated are only a few of the important variables. Ideally, each variable should be thoroughly studied theoretically and the propositions resulting from this study subsequently proved experimentally. In the case of PFR-6 this sequence is not entirely possible since important information such as high temperature thermodynamic data are not available. As a result, sometimes only intuitive reasoning based upon general principles can precede experimental analysis. Also, the close interrelation of many factors in the cementation process often makes it impossible to isolate and evaluate a single variable. These studies, then, were conducted in order to provide guide-lines for coating larger parts with PFR-6.

3.2.1 Effects of Columbium Particle Size

The addition of columbium to the pack material as a reactant produces an "alloy silicide" diffusion coating on the molybdenum substrate. The amount of columbium entering the coating reaction is proportional to the surface area of the columbium present in the pack mixture. If the percentage of columbium in the pack mixture is constant, the surface area varies

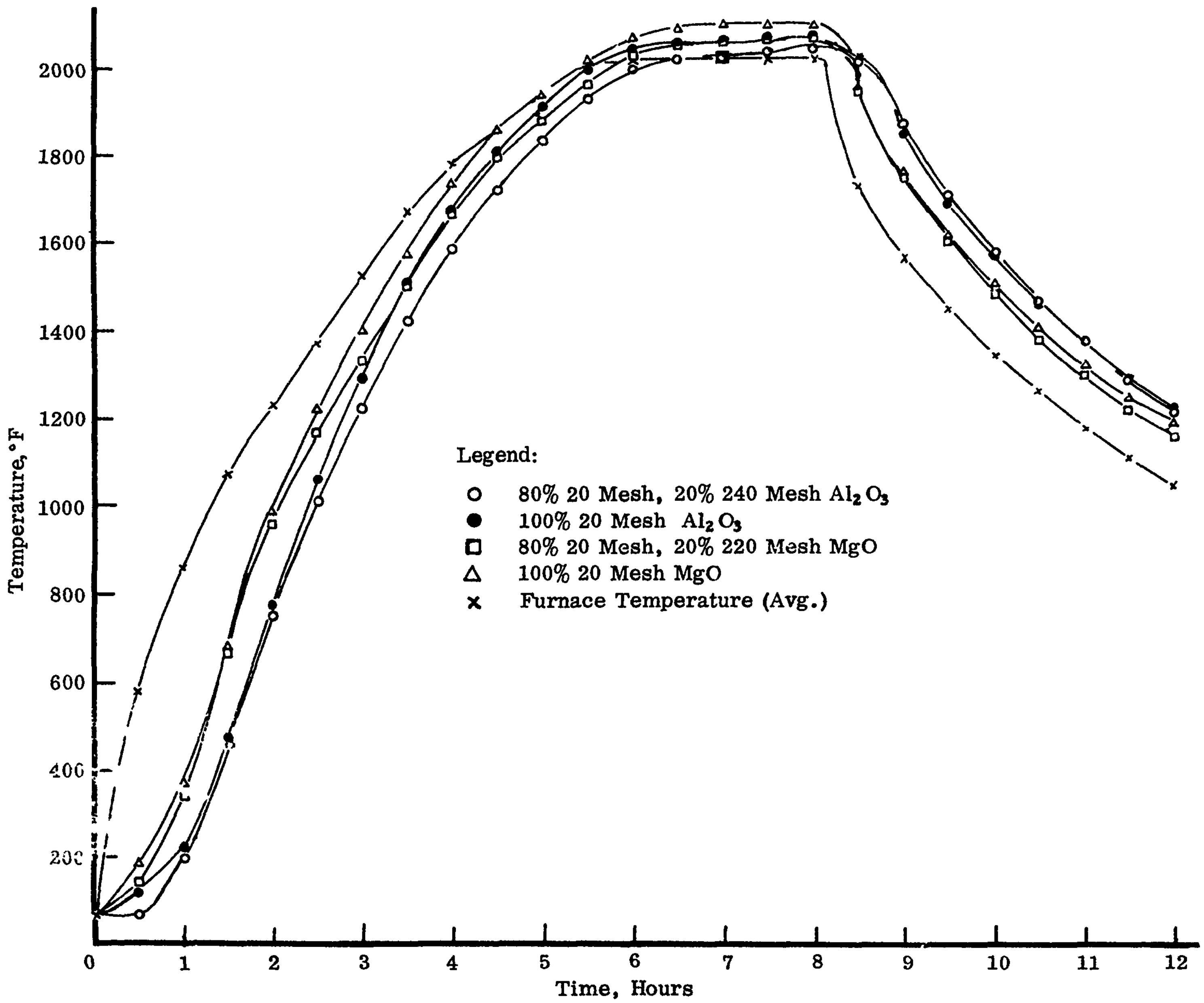


Fig. 9 Retort Temperature as a Function of Time, Run 1.

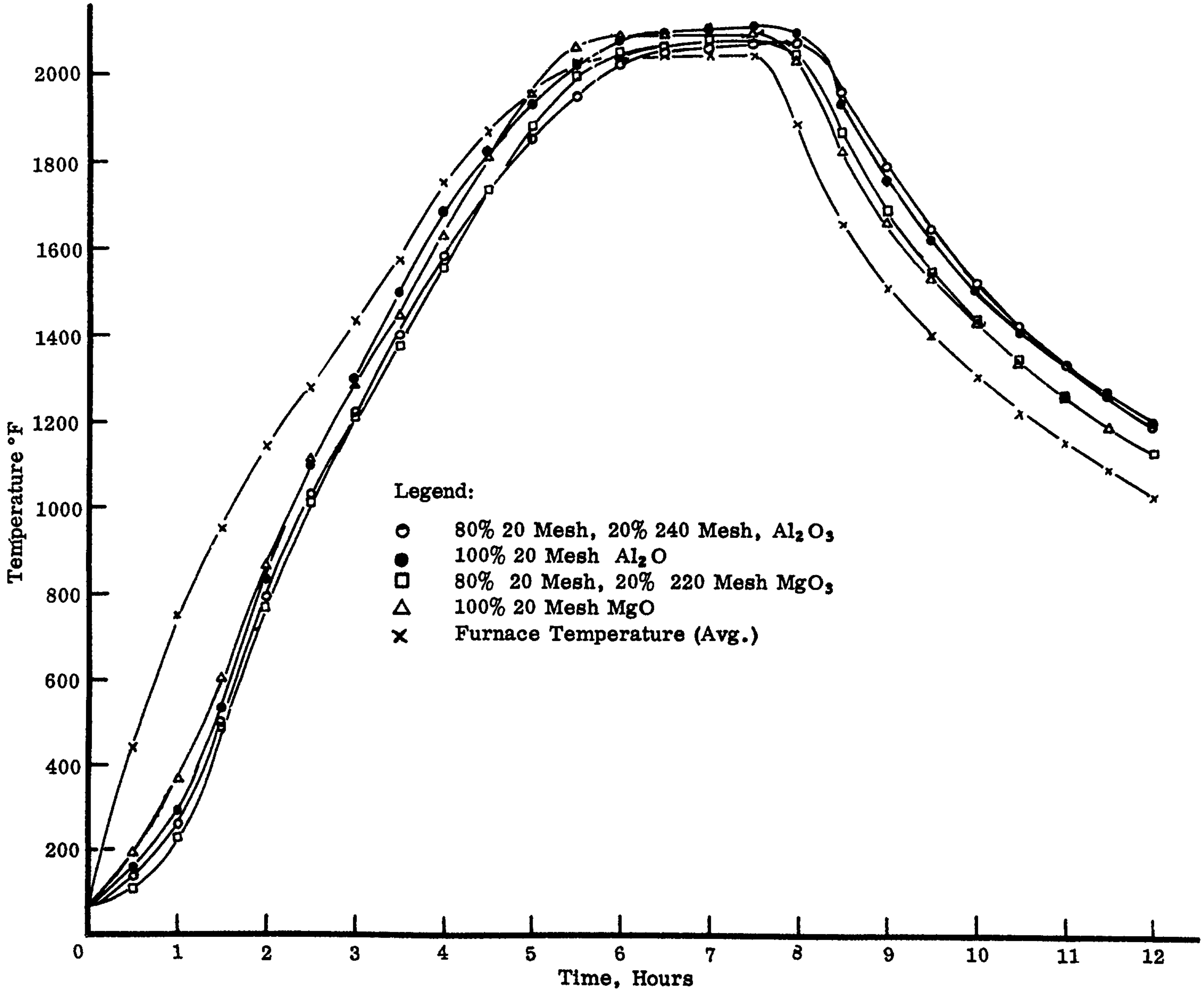


Fig. 10 Retort Temperature as a Function of Time, Run 2.

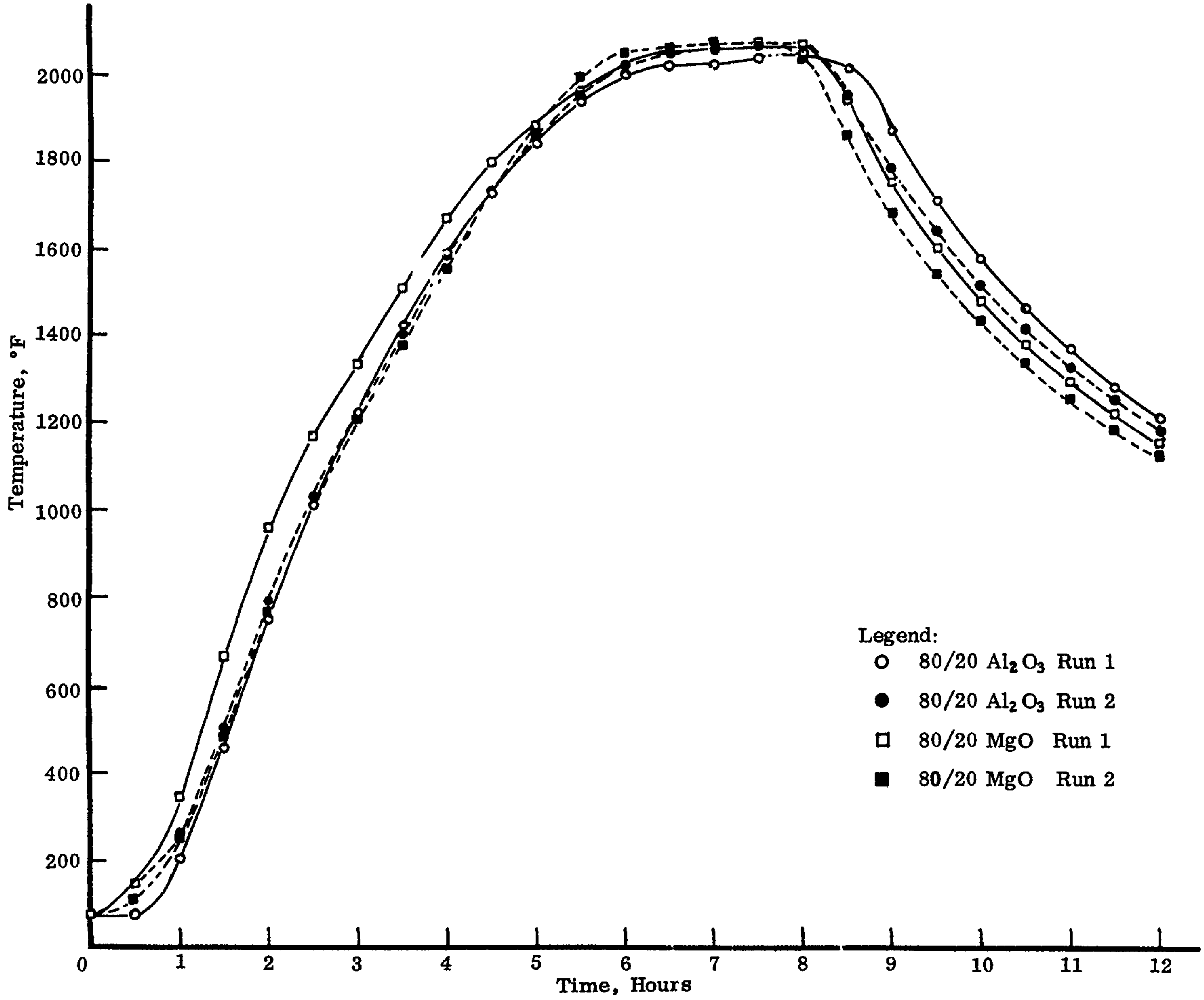


Fig. 11 Retort Temperature as a Function of Time, Runs 1 and 2 Compared.

TABLE 1. EFFECT OF FILLER PARTICLE SIZE AND TYPE ON HEAT FLUX IN RETORT--80% OF 20 MESH, 20% OF 240 MESH ALUMINA.

	Run 1			Run 2		
Time from start(hr)	Furnace thermo-couple(°F)	Retort edge thermo-couple(°F)	Retort center thermo-couple(°F)	Furnace thermo-couple(°F)	Retort edge thermo-couple(°F)	Retort center thermo-couple(°F)
0.5	530	250	R.T.	470	220	140
1.0	835	625	200	790	510	260
1.5	1055	930	455	1020	840	500
2.0	1210	1170	750	1185	1090	790
2.5	1360	1335	1010	1315	1265	1030
3.0	1535	1520	1220	1475	1420	1220
3.5	1660	1670	1420	1650	1605	1400
4.0	1770	1795	1590	1775	1750	1580
4.5	1860	1900	1725	1870	1865	1730
5.0	1945	1985	1840	1955	1955	1850
5.5	2005	2060	1935	2035	2040	1950
6.0	2010	2075	2000	2035	2070	2025
6.5	2010	2075	2020	2040	2080	2050
7.0	2010	2075	2025	2040	2090	2060
7.5	2010	2080	2040	2040	2090	2070
8.0	2010	2085	2050	1920	2060	2070
8.5	1750	1935	2020	1680	1830	1955
9.0	1580	1740	1875	1530	1665	1785
9.5	1450	1590	1710	1415	1535	1640
10.0	1345	1475	1575	1320	1430	1515
10.5	1250	1375	1465	1230	1340	1415
11.0	1175	1295	1370	1160	1260	1325
11.5	1105	1220	1280	1095	1195	1250
12.0	1040	1155	1210	1030	1130	1180

TABLE 2. EFFECT OF FILLER PARTICLE SIZE AND TYPE ON HEAT FLUX IN RETORT--100% OF 20 MESH ALUMINA.

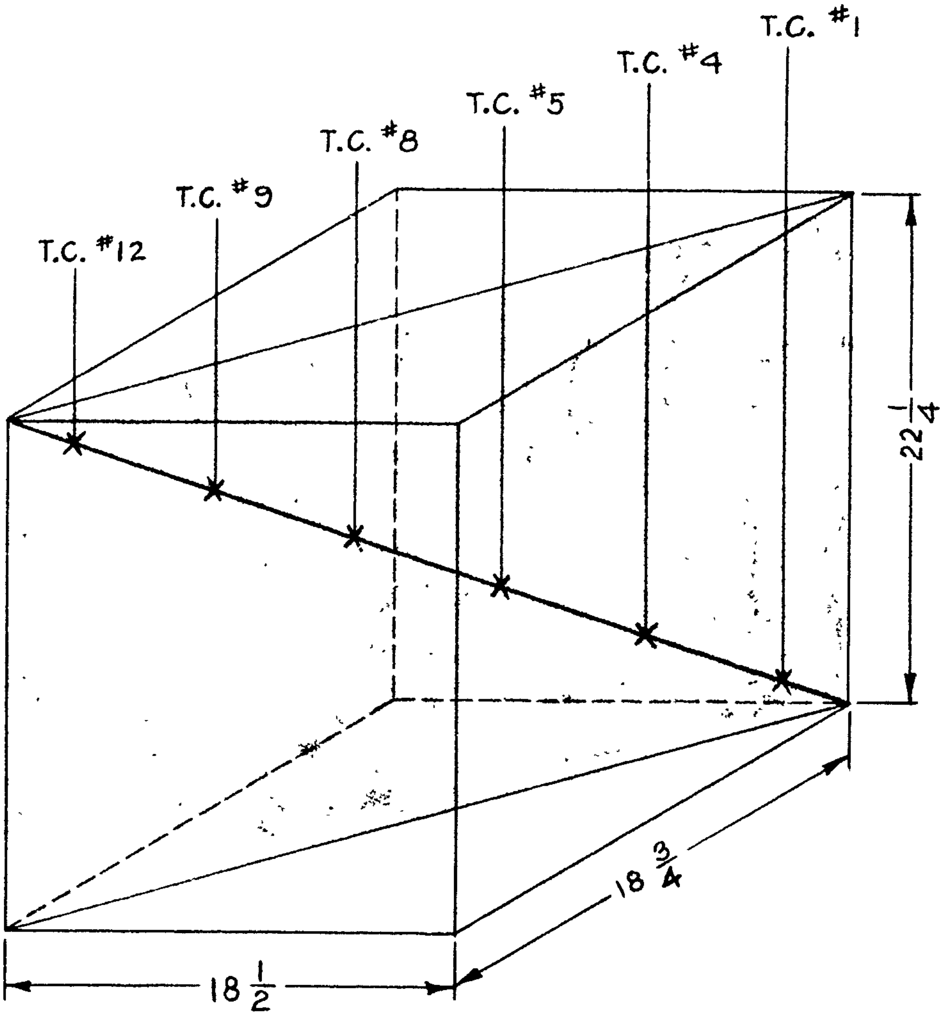
	Run 1			Run 2		
Time from start(hr)	Furnace thermo-couple(°F)	Retort edge thermo-couple(°F)	Retort center thermo-couple(°F)	Furnace thermo-couple(°F)	Retort edge thermo-couple(°F)	Retort center thermo-couple(°F)
0.5	530	140	120	470	180	160
1.0	835	450	225	790	500	290
1.5	1055	770	470	1020	840	530
2.0	1210	1055	775	1185	1095	830
2.5	1360	1255	1060	1315	1280	1095
3.0	1535	1445	1290	1475	1430	1295
3.5	1660	1615	1510	1650	1625	1495
4.0	1770	1750	1680	1775	1775	1680
4.5	1860	1850	1805	1870	1895	1820
5.0	1945	1945	1915	1955	1985	1930
5.5	2005	2020	2000	2035	2070	2020
6.0	2010	2045	2045	2035	2105	2080
6.5	2010	2045	2060	2040	2110	2095
7.0	2010	2045	2060	2040	2115	2100
7.5	2010	2050	2070	2040	2120	2110
8.0	2010	2050	2070	1920	2100	2095
8.5	1750	1935	2030	1680	1865	1930
9.0	1580	1740	1850	1530	1690	1755
9.5	1450	1590	1690	1415	1560	1615
10.0	1345	1475	1565	1320	1450	1500
10.5	1250	1375	1460	1230	1360	1405
11.0	1175	1295	1370	1160	1280	1325
11.5	1105	1220	1290	1095	1215	1255
12.0	1040	1155	1220	1030	1150	1190

TABLE 3. EFFECT OF FILLER PARTICLE SIZE AND TYPE ON HEAT FLUX IN RETORT--80% OF 20 MESH, 20% OF 220 MESH MAGNESIA.

	Run 1			Run 2		
Time from start(hr)	Furnace thermo-couple(°F)	Retort edge thermo-couple(°F)	Retort center thermo-couple(°F)	Furnace thermo-couple(°F)	Retort edge thermo-couple(°F)	Retort center thermo-couple(°F)
0.5	630	230	140	395	155	105
1.0	865	550	340	700	440	225
1.5	1100	870	660	885	715	480
2.0	1250	1115	955	1100	960	760
2.5	1380	1285	1165	1250	1175	1005
3.0	1510	1430	1330	1380	1335	1205
3.5	1685	1600	1505	1485	1465	1370
4.0	1800	1750	1665	1720	1660	1550
4.5	1870	1855	1795	1855	1825	1730
5.0	1940	1930	1880	1965	1955	1875
5.5	2015	2005	1965	2030	2045	1995
6.0	2035	2050	2025	2030	2070	2050
6.5	2040	2070	2055	2035	2070	2060
7.0	2040	2075	2060	2040	2080	2075
7.5	2040	2080	2065	2040	2085	2075
8.0	2040	2080	2070	1840	1995	2040
8.5	1720	1885	1945	1630	1780	1860
9.0	1560	1700	1750	1485	1620	1680
9.5	1435	1560	1600	1375	1490	1540
10.0	1335	1440	1475	1280	1385	1430
10.5	1250	1350	1375	1200	1300	1335
11.0	1175	1265	1290	1125	1220	1250
11.5	1105	1200	1215	1060	1155	1180
12.0	1045	1135	1150	1000	1095	1120

TABLE 4. EFFECT OF FILLER PARTICLE SIZE AND TYPE ON HEAT FLUX IN RETORT--100% OF 20 MESH MAGNESIA.

	Run 1			Run 2		
Time from start(hr)	Furnace thermo-couple(°F)	Retort edge thermo-couple(°F)	Retort center thermo-couple(°F)	Furnace thermo-couple(°F)	Retort edge thermo-couple(°F)	Retort center thermo-couple(°F)
0.5	630	380	190	395	150	190
1.0	865	790	370	700	470	360
1.5	1100	1080	680	885	750	600
2.0	1250	1280	985	1100	1000	860
2.5	1380	1420	1220	1250	1210	1105
3.0	1510	1550	1400	1380	1365	1280
3.5	1685	1725	1575	1485	1500	1440
4.0	1800	1855	1735	1720	1700	1625
4.5	1870	1935	1860	1855	1870	1810
5.0	1940	2005	1940	1965	1995	1950
5.5	2015	2075	2020	2030	2085	2060
6.0	2035	2110	2070	2030	2105	2085
6.5	2040	2110	2090	2035	2110	2085
7.0	2040	2110	2100	2040	2105	2090
7.5	2040	2110	2100	2040	2105	2090
8.0	2040	2105	2100	1840	2010	2025
8.5	1720	1840	1950	1630	1790	1815
9.0	1560	1665	1765	1485	1620	1650
9.5	1435	1530	1615	1375	1500	1520
10.0	1335	1425	1500	1280	1395	1415
10.5	1250	1335	1400	1200	1310	1325
11.0	1175	1260	1315	1125	1230	1245
11.5	1105	1190	1240	1060	1170	1180
12.0	1045	1130	1180	1000	1110	1120



THERMOCOUPLE NO.	DEPTH FROM TOP SURFACE (IN.)	DISTANCE ON FACE DIAGONAL FROM CORNER (IN.)
1	20.7	2.0
4	16.9	6.5
5	13.1	11.0
8	9.3	15.5
9	5.5	20.0
12	1.7	24.5

Fig. 12 Thermocouple Hot Junction Location in Large Retort

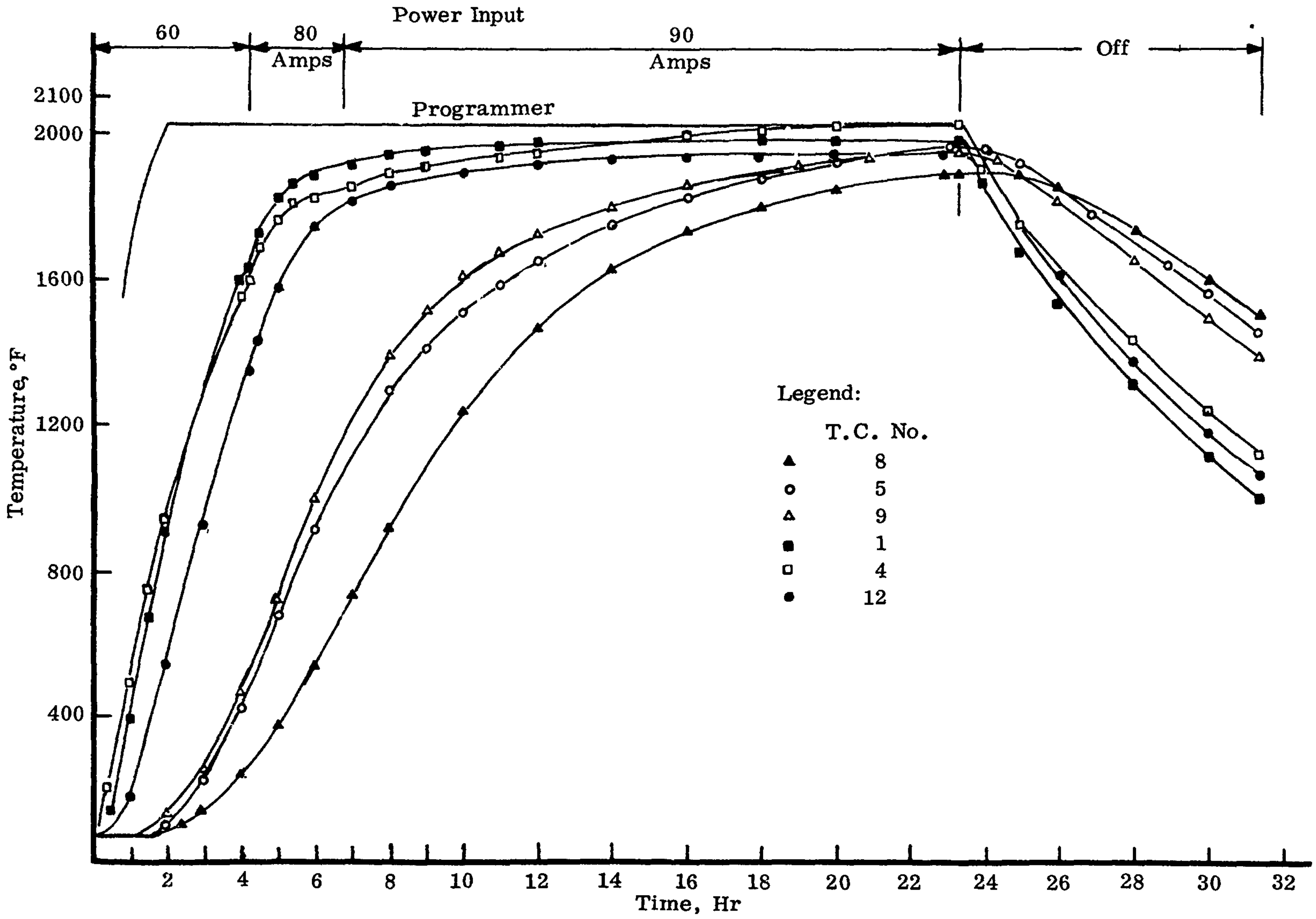


Fig. 13 Heat Transfer Study in Large Retort -- Run No. 1

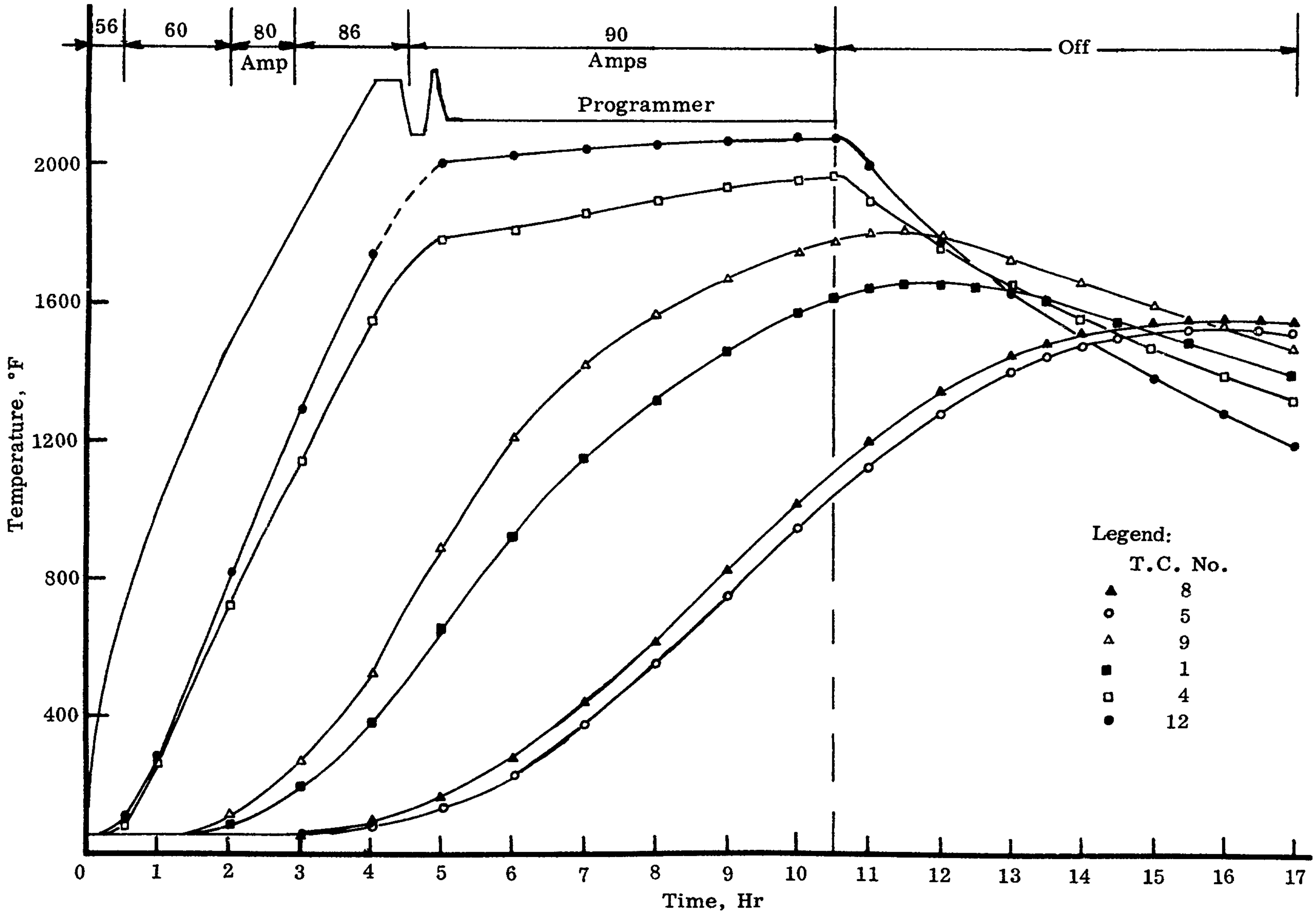


Fig. 14 Heat Transfer Study in Large Retort -- Run No. 2

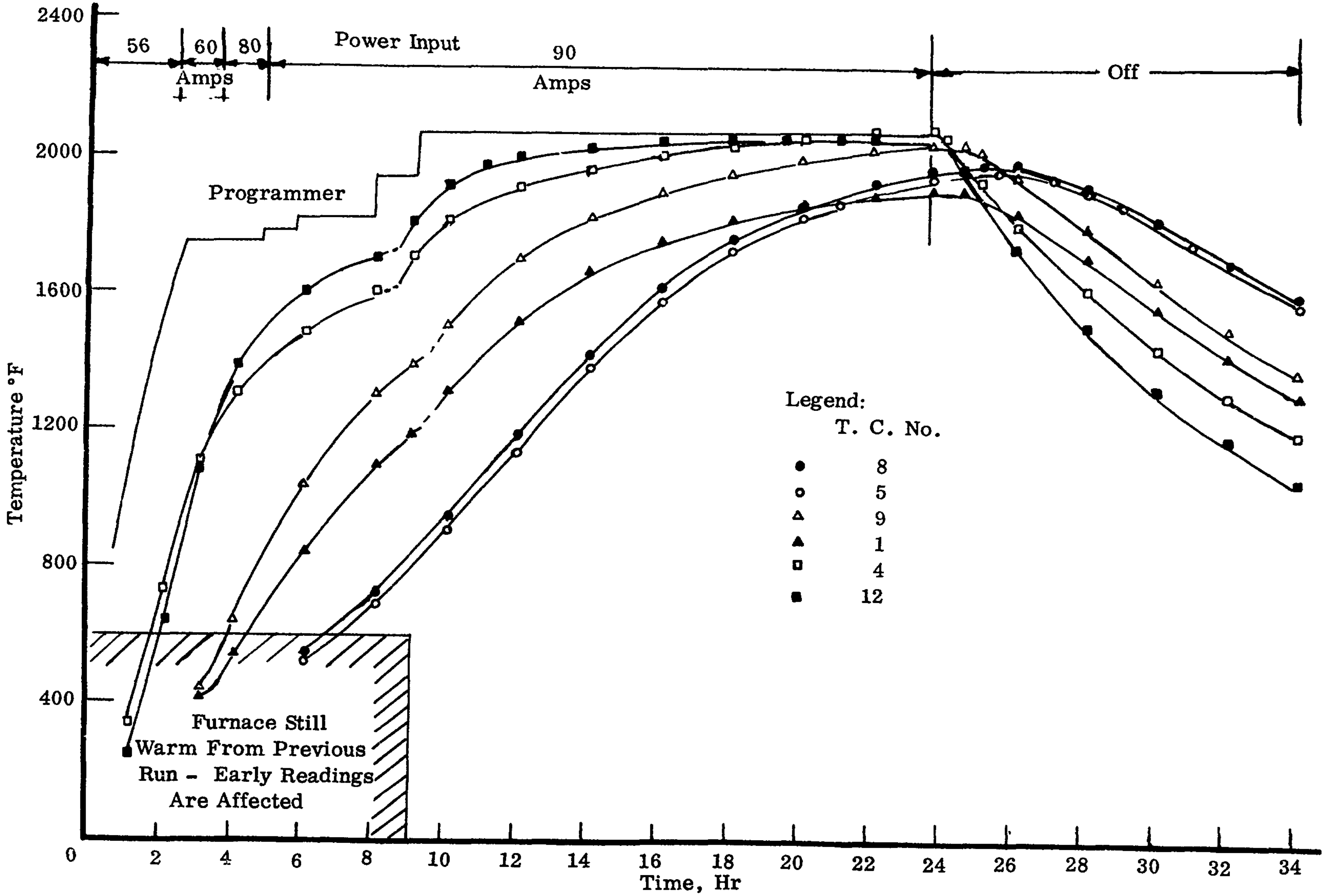


Fig. 15 Heat Transfer Study in Large Retort -- Run No. 3

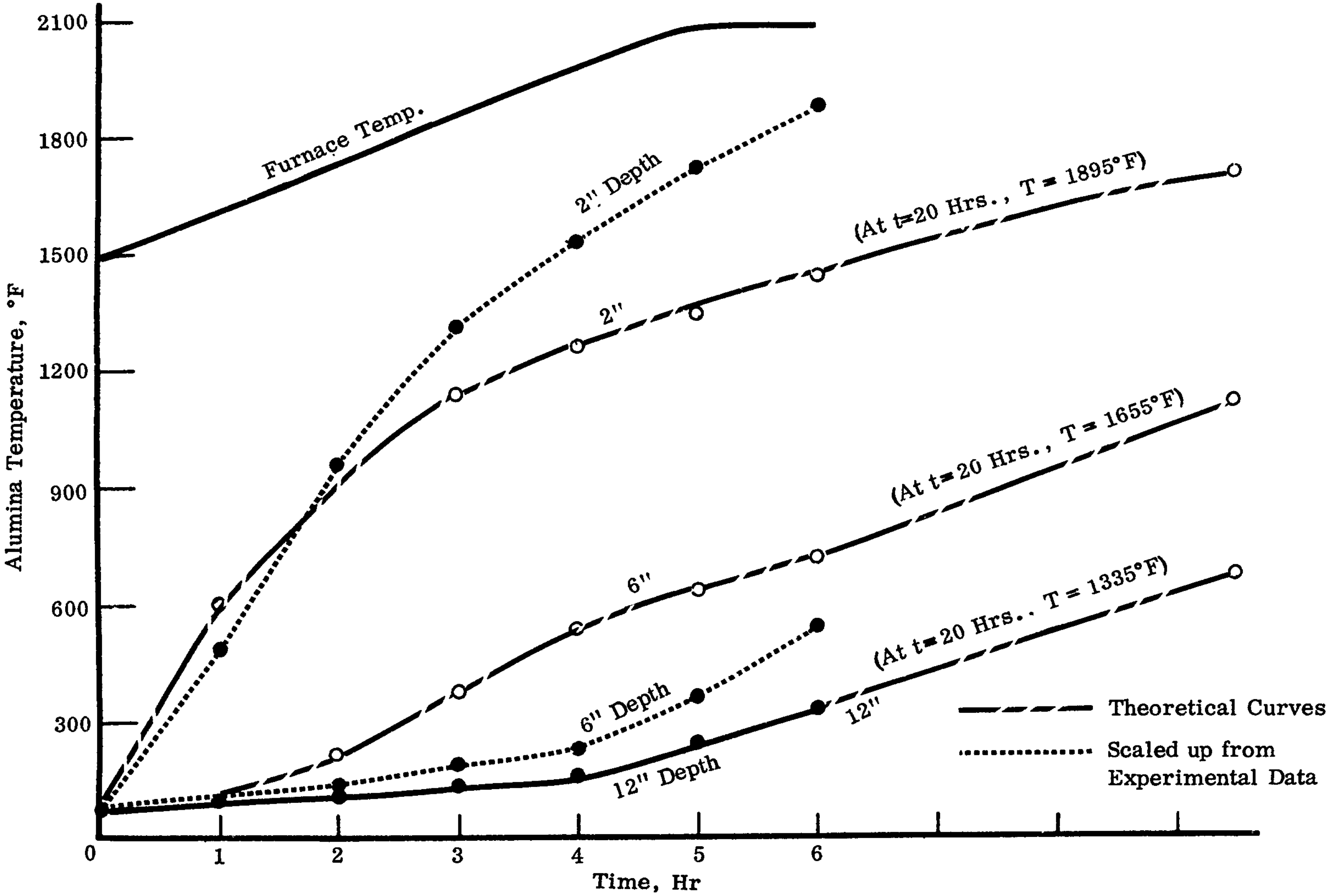


Fig. 16 Actual and Caloulated Heat Transfer Within Large Retort

inversely with particle size, i.e., the larger the columbium particles, the smaller the columbium area. Therefore the very nature of the coating process suggests that the particle size can have a marked effect on the characteristic of the coating.

A study was made of the effective protection afforded by three groups of coatings which differ only in the use of 40, 80, and minus 200 mesh columbium powders in the pack mixture. Several were made for each pack mixture. In each run, 22 Mo-5Ti samples measuring 1.5 by 3.0 by 0.030 in. were prepared and coated. The coated samples of each batch were evaluated as shown below:

Type of Test	No. Tested
High temperature oxyacetylene torch test	9
Guided bend to 1.5 in. radius plus oxyacetylene torch test	3
Guided bend to coating failure	3
Reserved for metallographic and other testing	7

Oxidation resistance performance data for the various batches (Tables 5,6,and 7) shows that the effect of the columbium particle size on lifetime in the size ranges studied is statistically insignificant. The relative independence of good coating properties upon columbium particle size adds a degree of freedom to the process and thus permits process adaptation to the cost and availability of a pack constituent. This same flexibility might not hold true if the amount of columbium were reduced below 2 weight percent, or if substantially coarser columbium particles were used.

Coating ductility, as evaluated in the bend test apparatus, was also statistically the same for the three groups of coatings (Tables 8, 9, and 10). Data on the high-temperature oxidation protection provided by the coated samples bent over a 1.5 in. radius prior to testing in the oxyacetylene torch facility is presented in Tables 11, 12, and 13.

3.2.2 Evaluation of Inert Filler Material

The results of the time-temperature (heat flux) studies with the 20 mesh alumina-filled retorts showed the advantage of higher heat transfer rates within the retort. To determine if this could be achieved, the type of alumina employed in the PFR-6 coating pack was varied. The proportion of alumina used in the composition remained at 86.5 weight percent, a part of this being the 20 mesh grit used previously and the balance consisting of either alumina spheres or alumina pellets in the following proportions:

- 76.5 weight percent grit, 10 weight percent spheres
- 76.5 weight percent grit, 10 weight percent pellets
- 66.5 weight percent grit, 20 weight percent spheres
- 66.5 weight percent grit, 20 weight percent pellets

Two coating runs were performed for each combination, 22 samples of Mo-5Ti being coated per run. The coated samples of each batch were evaluated in the manner described in section 3.2.1.

It was anticipated that replacing a portion of the alumina grit with alumina spheres or pellets would result in improved gas permeation, thereby decreasing the time required for the entire pack to reach coating temperature. Consequently, either the coating time at a stated temperature could be reduced or a thicker coating could be provided in the same time-temperature cycle.

The results of the oxyacetylene torch test show that protection against the high-temperature oxidizing atmosphere was not improved as anticipated. The variation in the average lifetimes for the different combinations (Tables 14 - 17) is not statistically meaningful. A comparison of the standard deviation of the batches processed with the spheres and pellets to that of the standard PFR-6 batches indicates that batch reproducibility, except for the 10 percent pellet study, does not differ to any great extent.

The bend-to-failure studies in the sphere/pellet evaluation (Table 18) indicate that room temperature coating ductility or formability is similar to that experienced in the standard PFR-6 (Table 10).

The standard deviations of post-bend oxyacetylene torch test data on coated samples (Tables 19-22) are comparable to those of the standard PFR-6 (Table 13) except for the 10 percent sphere study.

Since the substitution of a portion of the grit alumina by spheres or pellets does not improve the coating characteristics and does, in fact, result in less desirable coating coverage on edges and corners, the use of spheres or pellets as a portion of the inert filler material is not recommended.

3.2.3 Control of Coating Quality on Edges

Attempts to coat 10-mil substrate using the same procedure as that used on 30-mil material produced a high integrity coating along the large flat surfaces. However, the coating cracked badly at the corners and edges. Although some cracking was noted on 30-mil material, the problem was many times more severe in the case of the thinner material. Microscopic examination indicated that cracking was only a part of the problem. Coating deposition and growth along the edges and corners occurred in what is best described as a "unicorn" effect. This effect was caused by the achievement of a good coating on the flat surfaces and on the edges in planes nearly perpendicular to these surfaces, and almost no coating in the transition zones between the coated areas. This phenomenon is one of the characteristics of a diffusion coating which produces a "unicorn" or single horn appearance when the edge is viewed in cross-section (Fig. 17). Several attempts to eliminate this problem are described in the following paragraphs.

- Pack Cementation. It was postulated that the solution to this problem lay in controlling the diffusion rate and the rate of coating deposition. One method of controlling these rates involves varying the amount of pack carrier compound in the mixture while keeping other variables constant. Experiments were conducted in which the ammonium chloride content of the PFR-6 pack was reduced from 2.0 weight percent to 1.0, 0.5, 0.3, and 0.1 weight percent. Specimens so processed were evaluated in the oxyacetylene torch test facility.

With the lower halide contents there was marked improvement in the edge condition of the samples. However, the coating produced from the 0.1 weight percent ammonium chloride

Fig. 17 "Unicorn" Effect Produced by Improper Process Control

TABLE 5. COLUMBIUM PARTICLE SIZE STUDY: OXYACETYLENE TORCH TEST DATA, 40 MESH COLUMBIUM.

Batch description	Coating life at 3000°F[a] (hr)			Average life(hr)	s^2	s
PFR-6 40 mesh Cb No. 1	2.30 1.25 1.91	2.93 2.57 2.25	3.03 2.03 2.15	2.27	0.293	0.542
PFR-6 40 mesh Cb No. 2	2.75 1.78 1.73	2.63 1.50 1.91	1.85 1.25 1.42	1.87	0.264	0.514
PFR-6 40 mesh Cb No. 3	3.22 2.85 2.05	2.23 1.60 2.32	2.40 2.07 2.08	2.31	0.226	0.476
All	-	-	-	2.15	0.282	0.531

$$
\begin{aligned}
95\% \text{ confidence limit} &= \bar{X} \pm 1.96\sigma \\
&= 2.15 \pm 1.96(0.531) \\
&= 1.11 \text{ to } 3.19
\end{aligned}
$$

[a] 3000°F assuming emittance of 1.0 (3125°F assuming emittance of 0.8). Sample thermal shocked with 30 psi air blast every 0.5 hr.

TABLE 6. COLUMBIUM PARTICLE SIZE STUDY: OXYACETYLENE TORCH TEST DATA, 80 MESH COLUMBIUM.

Batch description	Coating life at 3000°F[(a)] (hr)			Average life(hr)	s^2	s
PFR-6 80 mesh Cb No. 1	3.05 2.80 2.83	2.25 1.50 1.87	1.70 1.95 2.00	2.22	0.294	0.548
PFR-6 80 mesh Cb No. 2	2.17 2.02 3.32	1.75 1.43 1.83	2.25 2.17 2.67	2.18	0.303	0.559
PFR-6 80 mesh Cb No. 3	2.12 2.45 1.77	3.18 1.72 2.40	2.90 2.25 2.40	2.35	0.227	0.476
All	-	-	-	2.25	0.260	0.509

$$
\begin{aligned}
\text{95\% confidence limit} &= \overline{X} \pm 1.96\sigma \\
&= 2.25 \pm 1.96(0.509) \\
&= 1.25 \text{ to } 3.25
\end{aligned}
$$

(a) 3000°F assuming emittance of 1.0 (3125°F assuming emittance of 0.8). Sample thermal shocked with 30 psi air blast every 0.5 hr.

TABLE 7. COLUMBIUM PARTICLE SIZE STUDY: OXYACETYLENE TORCH TEST DATA, -200 MESH COLUMBIUM.

Batch description	Coating life at 3000°F[a] (hr)			Average life(hr)	s^2	s
PFR-6 -200 mesh Cb No. 1	2.17	2.32	3.12	2.16	0.196	0.443
	1.57	2.32	1.95			
	2.25	1.75	1.98			
PFR-6 -200 mesh Cb No. 2	3.12	2.50	2.08	2.49	0.262	0.512
	1.88	2.75	2.00			
	3.20	2.83	2.00			
PFR-6 -200 mesh Cb No. 3	1.33	3.07	2.13	1.92	0.241	0.491
	1.67	1.78	1.67			
	2.00	2.00	1.67			
PFR-6 -200 mesh Cb No. 4	3.12	1.67	2.50	1.95	0.344	0.586
	1.78	1.37	1.65			
	2.18	1.25	2.00			
All	-	-	-	2.13	0.291	0.539

$$
\begin{aligned}
\text{95\% confidence limit} &= \overline{X} \pm 1.96\sigma \\
&= 2.13 \pm 1.96(0.539) \\
&= 1.07 \text{ to } 3.19
\end{aligned}
$$

[a] 3000°F assuming emittance of 1.0 (3125°F assuming emittance of 0.8). Sample thermal shocked with 30 psi air blast every 0.5 hr.

TABLE 8. COLUMBIUM PARTICLE SIZE STUDY: BEND TEST DATA, 40 MESH Cb

Batch description	Minimum bend radius prior to coating fracture[a] (in.)
PFR-6 40 mesh Cb No. 1	0.5 0.5 0.5
PFR-6 40 mesh Cb No. 2	0.5 0.5 0.5
PFR-6 40 mesh Cb No. 3	0.5 0.5 0.5
Average radius for coating fracture = $\overline{X}$ = 0.5 in.	

[a] Bend radius decreased in steps of 0.125 in. in guided bend test.

TABLE 9. COLUMBIUM PARTICLE SIZE STUDY: BEND TEST DATA, 80 MESH Cb.

Batch description	Minimum bend radius prior to coating fracture[a] (in.)
PFR-6 80 mesh Cb No. 1	0.5 0.5 0.5
PFR-6 80 mesh Cb No. 2	0.5 0.5 0.5
PFR-6 80 mesh Cb No. 3	0.5 0.5 0.5
Average radius for coating fracture = $\overline{X}$ = 0.5 in.	

(a)Bend radius decreased in steps of 0.125 in. in guided bend test.

TABLE 10. COLUMBIUM PARTICLE SIZE STUDY: BEND TEST DATA, -200 MESH Cb.

Batch description	Minimum bend radius prior to coating fracture[a] (in.)
PFR-6 -200 mesh Cb No. 1	0.5
	0.5
	0.5
PFR-6 -200 mesh Cb No. 2	0.5
	0.5
	0.5
PFR-6 -200 mesh Cb No. 3	0.5
	0.5
	0.5
PFR-6 -200 mesh Cb No. 4	0.5
	0.5
	0.75
Average radius for coating fracture = $\overline{X}$ = 0.521 in.	

[a] Bend radius decreased in steps of 0.125 in. in guided bend test.

TABLE 11. COLUMBIUM PARTICLE SIZE STUDY: POST-BEND OXYACETYLENE TORCH TEST DATA, 40 MESH COLUMBIUM.

Batch description	Post-bend coating life at 3000°F[a] (hr)[b]
PFR-6 40 mesh Cb No. 1	1.33 1.45 1.37
PFR-6 40 mesh Cb No. 2	2.97 2.17 2.87
PFR-6 40 mesh Cb No. 3	1.50 1.50 1.00

Average post-bend coating life = $\overline{X}$ = 1.80 hr

Variance = s^2 = 0.50 hr

Standard deviation = s = 0.71 hr

95% confidence limit = $\overline{X} \pm 1.96\sigma$

= $1.80 \pm 1.96(0.71)$

= 0.41 to 3.18 hr.

[a] 3000°F assuming emittance of 1.0 (3125°F assuming emittance of 0.8). Sample thermal shocked with 30 psi air blast every 0.5 hr.

[b] Samples bent over 1.5 in. radius prior to testing. Flame impingement on concave side of bent sample.

TABLE 12. COLUMBIUM PARTICLE SIZE STUDY: POST-BEND OXYACETYLENE TORCH TEST DATA, 80 MESH COLUMBIUM.

Batch description	Post-bend coating life at 3000°F[a] (hr)[b]
PFR-6 80 mesh Cb No. 1	2.37 1.52 2.17
PFR-6 80 mesh Cb No. 2	2.67 2.07 1.91
PFR-6 80 mesh Cb No. 3	- - -

Average post-bend coating life = $\overline{X}$ = 2.12 hr
Variance = s^2 = 0.15 hr
Standard deviation = s = 0.39 hr
95% confidence limit = $\overline{X} \pm 1.96\sigma$
= $2.12 \pm 1.96(0.39)$
= 1.35 to 2.89 hr.

[a] 3000°F assuming emittance of 1.0 (3125°F assuming emittance of 0.8). Sample thermal shocked with 30 psi air blast every 0.5 hr.

[b] Samples bent over 1.5 in. radius prior to testing. Flame impingement on concave side of bent sample.

TABLE 13. COLUMBIUM PARTICLE SIZE STUDY: POST-BEND OXYACETYLENE TORCH TEST DATA, -200 MESH COLUMBIUM.

Batch description	Post-bend coating life at 3000°F[(a)] (hr)[(b)]
PFR-6 -200 mesh Cb No. 1	2.50 1.81 1.37
PFR-6 -200 mesh Cb No. 2	0.97 1.81 1.38
PFR-6 -200 mesh Cb No. 3	0.50 0.43 0.37
PFR-6 -200 mesh Cb No. 4	0.50 0.78 0.50

Average post-bend coating life = $\overline{X}$ = 1.08 hr
Variance = s^2 = 0.48 hr
Standard deviation = s = 0.69 hr
95% confidence limit = $\overline{X} \pm 1.96\sigma$
= $1.08 \pm 1.96(0.69)$
= -0.28 to +2.44 hr
= 0 to 2.44 hr.

(a) 3000°F assuming emittance of 1.0 (3125°F assuming emittance of 0.8). Sample thermal shocked with 50 psi air blast every 0.5 hr.

(b) Samples bent over 1.5 in. radius prior to testing. Flame impingement on concave side of bent sample.

TABLE 14. ALUMINA PARTICLE VARIATION STUDY: OXYACETYLENE TORCH TEST DATA, 10% ALUMINA SPHERES.

Batch description	Coating life at 3000°F(a) (hr)			Average life(hr)	s^2	s
PFR-6 10% spheres No. 1	2.63 2.67 2.70	2.47 1.90 1.62	1.93 1.77 1.88	2.17	0.216	0.465
PFR-6 10% spheres No. 2	2.42 2.24 3.03	3.17 2.67 2.15	2.72 2.22 1.50	2.47	0.253	0.503
All	-	-	-	2.32	0.245	0.495

95% confidence limit $= \overline{X} \pm 1.96\sigma$

$= 2.32 \pm 1.96\ (0.495)$

$= 1.35$ to 3.29 hr.

(a) 3000°F assuming emittance of 1.0 (3125°F assuming emittance of 0.8). Sample thermal shocked with 30 psi air blast every 0.5 hr.

TABLE 15. ALUMINA PARTICLE VARIATION STUDY: OXYACETYLENE TORCH TEST DATA, 10% ALUMINA PELLETS.

Batch description	Coating life at 3000°F[a] (hr)			Average life(hr)	s^2	s
PFR-6 10% pellets No. 1	0.58	1.88	1.58	1.95	0.572	0.756
	3.30	1.95	2.62			
	1.90	2.23	1.48			
PFR-6 10% pellets No. 2	4.40	2.17	2.30	2.08	0.931	0.965
	2.38	1.55	1.57			
	1.70	1.17	1.45			
All	-	-	-	2.01	0.712	0.844

$$\begin{aligned} \text{95\% confidence limit} &= \bar{X} \pm 1.96\sigma \\ &= 2.01 \pm 1.96(0.844) \\ &= 0.36 \text{ to } 3.67 \text{ hr.} \end{aligned}$$

[a] 3000°F assuming emittance of 1.0 (3125°F assuming emittance of 0.8). Sample thermal shocked with 30 psi air blast every 0.5 hr.

TABLE 16. ALUMINA PARTICLE VARIATION STUDY: OXYACETYLENE TORCH TEST DATA: 20% ALUMINA SPHERES.

Batch description	Coating life at 3000°F[a] (hr)			Average life(hr)	s^2	s
PFR-6 20% spheres No. 1	2.08 0.95 1.78	2.40 2.25 2.68	2.68 1.72 1.48	2.00	0.332	0.577
PFR-6 20% spheres No. 2	2.07 1.97 1.85	1.73 2.58 1.67	2.63 2.15 1.78	2.05	0.125	0.354
All	-	-	-	2.02	0.216	0.465

$$\begin{aligned} \text{95\% confidence limit} &= \overline{X} \pm 1.96\sigma \\ &= 2.02 \pm 1.96(0.465) \\ &= 1.11 \text{ to } 2.93 \text{ hr.} \end{aligned}$$

[a] 3000°F assuming emittance of 1.0 (3125°F assuming emittance of 0.8). Sample thermal shocked with 30 psi air blast every 0.5 hr.

TABLE 17. ALUMINA PARTICLE VARIATION STUDY: OXYACETYLENE TORCH TEST DATA, 20% ALUMINA PELLETS.

Batch description	Coating life at 3000°F[a](hr)			Average life(hr)	s^2	s
PFR-6 20% pellets No. 1	2.00	2.35	2.27	1.98	0.121	0.348
	2.08	2.32	1.33			
	2.13	1.75	1.62			
PFR-6 20% pellets No. 2	2.13	2.00	1.88	1.87	0.052	0.229
	1.97	2.00	1.77			
	1.35	2.00	1.78			
All	-	-	-	1.93	0.085	0.291

$$
\begin{aligned}
95\% \text{ confidence limit } &= \overline{X} \pm 1.96\sigma \\
&= 1.93 \pm 1.96(0.291) \\
&= 1.36 \text{ to } 2.50 \text{ hr.}
\end{aligned}
$$

[a] 3000°F assuming emittance of 1.0 (3125°F assuming emittance of 0.8). Sample thermal shocked with 30 psi air blast every 0.5 hr.

TABLE 18. ALUMINA PARTICLE VARIATION STUDY: BEND TEST DATA.

Batch description	Minimum bend radius prior to coating fracture[a] (in.)
PFR-6 10% spheres No. 1	0.50 0.50 0.75
PFR-6 10% spheres No. 2	0.75 0.50 0.50
PFR-6 10% pellets No. 1	0.50 0.50 0.50
PFR-6 10% pellets No. 2	1.50(substrate fractured) 0.50 0.50
PFR-6 20% spheres No. 1	0.50 0.50 0.50
PFR-6 20% spheres No. 2	0.50 0.50 0.50
PFR-6 20% pellets No. 1	0.50 0.50 0.75
PFR-6 20% pellets No. 2	1.50(substrate fractured) 0.50 0.50

Averages: 10% spheres = 0.58 in.
10% pellets = 0.67 in.
20% spheres = 0.50 in.
20% pellets = 0.71 in.

[a] Bend radius decreased in steps of 0.125 in. in guided bend test, starting at 1.5 in.

TABLE 19. ALUMINA PARTICLE VARIATION STUDY: POST-BEND OXYACETYLENE TORCH TEST DATA, 10% ALUMINA SPHERES.

Batch description	Post-bend coating life at 3000°F[(a)] (hr)[(b)]
PFR-6 10% spheres No. 1	0.50 2.98 0.47
PFR-6 10% spheres No. 2	0.50 1.50 0.37

Average post-bend coating life = $\overline{X}$ = 1.05 hr
Variance = s^2 = 1.07 hr
Standard deviation = s = 1.03 hr
95% confidence limit = $\overline{X} \pm 1.96\sigma$
= $1.05 \pm 1.96(1.03)$
= 0 to 3.07 hr.

(a) 3000°F assuming emittance of 1.0 (3125°F assuming emittance of 0.8). Sample thermal shocked with 30 psi air blast every 0.5 hr.

(b) Samples bent over 1.5 in. radius prior to testing Flame impingement on concave side of bent sample.

TABLE 20. ALUMINA PARTICLE VARIATION STUDY: POST-BEND OXYACETYLENE TORCH TEST DATA, 100% ALUMINA PELLETS.

Batch description	Post-bend coating life at 3000°F[a] (hr)[b]
PFR-6 10% pellets No. 1	0.63
	0.62
	1.07
PFR-6 10% pellets No. 2	1.20
	1.00
	0.30

Average post-bend coating life = $\overline{X}$ = 0.80 hr
Variance = s^2 = 0.12 hr
Standard deviation = s = 0.34 hr
95% confidence limit = $\overline{X} \pm 1.96\sigma$
= $0.80 \pm 1.96(0.34)$
= 0.13 to 1.47 hr.

[a] 3000°F assuming emittance of 1.0 (3125°F assuming emittance of 0.8). Sample thermal shocked with 30 psi air blast every 0.5 hr.

[b] Samples bent over 1.5 in. radius prior to testing. Flame impingement on concave side of bent sample.

TABLE 21. ALUMINA PARTICLE VARIATION STUDY: POST-BEND OXYACETYLENE TORCH TEST DATA, 20% ALUMINA SPHERES.

Batch description	Post-bend coating life at 3000°F[a] (hr)[b]
PFR-6 20% spheres No. 1	1.50 1.50 0.98
PFR-6 20% spheres No. 2	1.00 0.67 0.63

Average post-bend coating life = $\overline{X}$ = 1.05 hr
Variance = s^2 = 0.15 hr
Standard deviation = s = 0.38 hr
95% confidence limit = $\overline{X} \pm 1.96\sigma$
= $1.05 \pm 1.96(0.38)$
= 0.30 to 1.80 hr.

(a) 3000°F assuming emittance of 1.0 (3125°F assuming emittance of 0.8). Sample thermal shocked with 30 psi air blast every 0.5 hr.

(b) Samples bent over 1.5 in. radius prior to testing. Flame impingement on concave side of bent sample.

TABLE 22. ALUMINA PARTICLE VARIATION STUDY: POST-BEND OXYACETYLENE TORCH TEST DATA, 20% ALUMINA PELLETS.

Batch description	Post-bend coating life at 3000°F[a] (hr)[b]
PFR-6 20% pellets No. 1	0.50 0.50 0.50
PFR-6 20% pellets No. 2	0.33 1.25 0.38

Average post-bend coating life = $\overline{X}$ = 0.58 hr
Variance = s = 0.11 hr
Standard deviation = s = 0.34 hr
95% confidence limit = $\overline{X} \pm 1.96\sigma$
= $0.58 \pm 1.96(0.34)$
= 0 to 1.24 hr.

[a] 3000°F assuming emittance of 1.0 (3125°F assuming emittance of 0.8). Sample thermal shocked with 30 psi air blast every 0.5 hr.

[b] Samples bent over 1.5 in. radius prior to testing. Flame impingement on concave side of bent sample.

TABLE 23. EFFECT OF HEATING RATE AND RETORT MATCH: OXYACETYLENE TORCH TEST AND COATING DATA.

Run	Av. coating life at 3000°F[(a)] (hr)	Standard deviation(hr)	95% confidence limit(hr)	Av. weight gain(gm)	Av. coating thickness increase per side(mil)	Process conditions
1	0.87	0.496	0 - 1.84	0.4908	1.2	Fast heating; weighted.
2	0.70	0.262	0.18 - 1.21	0.4641	1.1	Fast heating; not weighted.
3	1.19	0.197	0.80 - 1.92	0.5925	1.7	Slow heating; weighted.
4	0.86	0.148	0.57 - 1.15	0.5506	1.7	Slow heating; not weighted.

(a) 3000°F assuming emittance of 1.0 (3125°F assuming emittance of 0.8). Sample thermal shocked with 30 psi air blast every 0.5 hr.

batch in a 4 by 5 by 6 in. retort was relatively porous on the flat surface areas, resulting in an almost immediate failure when the test pieces were subjected to the oxyacetylene torch test.

Additional experimentation involving the relationship between chloride variation and increased retort volume (necessitated by larger samples) indicated that a new parameter was perhaps better suited to the control of coating quality. Specifically, it appeared that the amount of carrier compound required for optimum coating on both surfaces and edges was a function of the substrate surface area to be coated. (This aspect is discussed in a later section.) Although a limitation on the maximum weight percentage of ammonium chloride in the coating pack still appeared valid, the substrate surface area to be coated seemed to be a more sensitive criterion of the percentage actually required.

- Heating Rate Variation. A second approach to the problem is to control the coating deposition rate on the substrate with respect to the diffusion rate into the substrate The rate of coating deposition seems to be more strongly dependent upon temperature than is the rate of diffusion. Since both rates are temperature dependent, governing the retort heating schedule should effectively control the ratio of these rates.

In all previous work, the heating schedule consisted of an uninterrupted temperature increase from room temperature to coating temperature. In the first variation from this schedule, several retorts containing six 1.5 by 3.0 by 0.010 in. Mo-0.5Ti specimens in PFR-6 packs with various ammonium chloride contents were heated continuously from room temperature to 1850°F, held 1 hr at 1850°F, heated continuously to 2050°F, held for the remainder of the coating cycle at 2050°F, and then furnace-cooled to ambient temperature.

A second variation in the heating schedule used the same furnace load as in the first variation. This time the retorts were heated continuously to 2100°F, held 1 hr at temperature, cooled to 2050°F, held at this temperature for the remainder of the cycle, then furnace-cooled to ambient temperature. Evaluation of the coating quality on edges and corners of the test pieces with a binocular microscope preceded oxidation resistance testing.

In the first heating variation (1850°F hold plus 2050°F hold), the ratio of coating deposition rate to diffusion rate is comparatively low during the 1850°F hold. Thus, as the coating is deposited, an efficient diffusion process occurs to reduce the severity of the coating structure. Once the high quality diffusion layer is in place, the rate of coating deposition can be increased by a rise in temperature. Since the additional coating is now deposited upon the diffusion layer rather than on the virgin substrate, the coating growth should be unaffected by such variables as variation in substrate surface free energies and differing orientations of the substrate microstructure. Therefore the coating grows uniformly over the entire substrate. The samples coated in 0.3 weight percent ammonium chloride PFR-6 batch gave the best performance in the oxyacetylene torch test. As previously mentioned, however, this improved performance could probably be more accurately indexed by relating the substrate area to be coated to the weight of ammonium chloride, rather than to the percentage of chloride.

Quite aside from consideration of the coating deposition and diffusion rates, the "hold" in the heating cycle can improve heat transfer throughout the retort. Previous tests and calculations have shown that as the cross-section dimensions of a retort are increased, the temperature gradient within the retort during heating also increases. Since this gradient increase causes difficulties in process control and coating reproducibility. a decrease in temperature gradient has obvious benefits. By introducing a hold in the heating portion of the coating cycle, the thermal gradient, especially in intermediate size retorts, is reduced.

The second variation (2100°F hold, plus 2050°F hold) was based on the concept that a high deposition rate compared with the diffusion rate would produce a high concentration gradient at the interface between the coating and the substrate. The driving force toward equilibrium through diffusion would therefore be increased, again resulting in a high integrity coating.

The results of oxyacetylene torch tests on samples coated using the second heating variation did not indicate any statistical improvement over those samples coated by the first heating variation. The 0.3 weight percent ammonium chloride batch in a 4 by 5 by 6 in. retort produced coatings with the best oxidation resistance as indicated by the oxyacetylene torch test results, and, in addition, produced good coatings on edges and corners. The possibility that the ratio of weight of ammonium chloride to substrate surface area again may have been the most important factor in the process cycle should not be overlooked, however.

In a slightly different approach to the heating rate variation, the length of time from room temperature to coating temperature was varied. Two 4 by 5 by 6 in. retorts, each containing nine 1.5 by 3.0 by 0.030 in. Mo-0.5Ti specimens in 0.3 weight percent ammonium chloride PFR-6 pack mixture, were heated from room temperature to 2050°F in approximately 1 hr. A 40-lb weight was placed on one of these retorts during the entire processing cycle to provide a tighter fit between retort and cover. Although this additional weight would not greatly increase the sealing pressure if the entire bearing area is considered, it may be seen that the actual very small line-contact area and high temperatures involved in the process do promote a better seal with the additional weight.

Another run was made using identical conditions throughout except for heating time, which was changed from 1 hr to 6 hr. After heating, all four retorts were held at 2050°F for 7 hr. Thickness and weight measurements were taken before and after coating. Data obtained on samples coated using these two widely different heating rates are given in Table 23.

Heating from ambient to process temperature in approximately 1 hr resulted in high deposition rates at the deposition temperature. This rate, as indicated by the weight gain data, was even greater in the retort with the weighted cover because the tighter fit retained a larger amount of the gaseous halide within the retort.

A 6 hr heating period made possible a slow, uniform deposition of the coating (Table 23, Runs 3 and 4). The increased heating period allows more time at a temperature above the coating reaction initiation temperature. The increase in average weight gain is approximately 20 percent. The value of slower deposition and a resulting lower deposition-to-diffusion ratio is apparent when coating life and coating reproducibility, as indicated by standard deviation, are considered. Once again the retort with a weighted cover (Table 23, run 3) produced a greater weight gain.

The condition of the coating on edges and corners on samples heated slowly to processing temperature was greatly improved over those heated rapidly. The slow heating rate allows more nuclei of coating to be formed and results in a less severe unicorn effect. It also gives a more favorable deposition-to-diffusion ratio, improving the quality of the coating at the edges and corners.

- Edge Preparation. The differences in coating condition at the edges and corners between 10- and 30-mil material processed under similar conditions may be partially explained by the maximum, uniform edge radii possible on the two thicknesses. In both cases, this maximum uniform radius is given by t/2, where t is the substrate thickness.

Several 10, 20, and 30-mil Mo-0.5Ti specimens in the rough cut condition were processed for 8 hr in a vibratory finisher to evaluate this method of edge and corner preparation prior to coating. In addition, the edges and corners of nine 30-mil Mo-0.5Ti samples were prepared by other methods, three in each of the following: (1) polishing to a mirror finish, (2) regular edge and corner preparation on wet belt grinder, and (3) regular edge and corner preparation on wet belt grinder plus sandblasting with minus 240 grit alumina.

All samples were subsequently coated in 0.3 weight percent ammonium chloride PFR-6 pack mixture in 4 by 5 by 6 in. retorts. The samples prepared in the vibratory finisher were coated in one retort, the remainder in a second one.

The edges and corners prepared by the vibratory finishing method were highly uniform. The 10-mil material had an edge radius approximately half the thickness of the sample (or 5 mils). The 20- and 30-mil materials also had edge radii of approximately 5 mils. Examination of these samples after coating showed that the coating was very uniform over the edges and corners. Some small cracks and discontinuities were present, indicating that for this process, the edge radius should be slightly increased whenever material thickness permits.

The polishing process was performed on 30-mil specimens. As far as was possible, a perfectly rounded edge and corner (radius 15 mils, half the sample thickness) was formed and polished. The coating over edges prepared in this manner was very good, showing only a few slight indications of cracking. However, the time required to polish the samples to a mirror finish was prohibitive.

The regular preparation plus sandblast on the edges and corners proved slightly better than the regular grinding alone, since the coating showed fewer cracks and discontinuities. Apparently the sandblasting removed some minor imperfections and irregularities resulting from finishing with the wet belt grinder. However, consideration must be given to the amount of material removed and the distortion of the part in the use of sandblast. Of course, the coating over the mirror-finished edge was superior to that over either of these two types of edges.

Reviewing the preparation methods, a direct comparison of coatability could be made only on the 30-mil material, and this is not particularly valid because of the differing radii resulting from edge preparation. Of the four methods discussed, vibratory finishing is the most desirable because it provides a uniform radius, it is far less subject to human variations, and it does not require the constant attention of an operator or technician.

- Torch Tests on Edges. A series of 1.5 by 3.0 in. Mo-0.5Ti and TZM specimens, both 10 and 30 mils thick, were processed in 8 by 8 by 4 in. retorts for 1 hr at 1850°F, plus 6 hr at 2050°F. The PFR-6 packs contained 0.1 weight percent ammonium chloride. The coated samples were tested at 2600°F and 2960°F both on edges and in the centers in the high temperature oxyacetylene torch test facility. The results of these tests (Tables 24 and 25) do not show a definite superiority of either edges or centers. Difficulty was experienced, however, in determining the failure point on the edge test samples. Because of the nature of the test set-up, it is easier to miss the exact failure point on the edge test than on the center test.

TABLE 24. EDGE COATING STUDY: OXYACETYLENE TORCH TEST AND COATING DATA.

Material	Substrate thickness (mil)	Av. coating life(hr)	Test temp. (°F)	Standard deviation(hr)	Av. weight gain(gm)	Av. coating thickness increase per side(mil)	Condition of edges
TZM	30	0.50	3000[(a)]	0.182	0.4525	1.2	Very good
		10.38	2600[(b)]	6.096	0.4991	1.4	Very good
	10	0.98	3000[(a)]	0.433	0.4921	1.4	Good
		7.15	2600[(b)]	2.467	0.4582	1.2	Fair
Mo-0.5 Ti	30	0.62	3000[(a)]	0.183	0.4833	1.4	Very good
		7.18	2600[(b)]	3.325	0.4628	1.3	Very good
	10	1.84	3000[(a)]	1.004	0.5217	1.8	Good
		8.61	2600[(b)]	3.986	0.4556	1.9	Good

(a) 3000°F assuming emittance of 1.0; 3125°F assuming emittance of 0.8. Sample thermal shocked with 30 psi air blast every 0.5 hr.

(b) 2600°F assuming emissivity of 1.0. Sample thermal shocked with 30 psi air blast every 0.5 hr.

TABLE 25. CENTER COATING STUDY: OXYACETYLENE TORCH TEST AND COATING DATA

Material	Substrate thickness (mil)	Av. coating life(hr)	Test temp. (°F)	Standard deviation(hr)	Av. weight gain(gm)	Av. coating thickness increase per side(mil)	Condition of edges
TZM	30	0.81	3000[a]	0.544	0.5505	1.3	Very good
		8.97	2600[b]	3.059	0.5057	1.5	Very good
	10	0.38	3000[a]	0.277	0.4987	1.4	Good
		10.83	2600[b]	5.110	0.5382	1.5	Good
Mo-0.5 Ti	30	0.98	3000[a]	0.479	0.5426	1.4	Very good
		1.56	2600[b]	1.840	0.4976	1.5	Very good
	10	0.95	3000[a]	0.830	0.5352	1.8	Fair
		5.57	2600[b]	2.969	0.5573	1.7	Fair

(a) 3000°F assuming emittance of 1.0; 3125°F assuming emittance of 0.8. Sample thermal shocked with 30 psi air blast every 0.5 hr.

(b) 2600°F assuming emissivity of 1.0. Sample thermal shocked with 30 psi air blast every 0.5 hr.

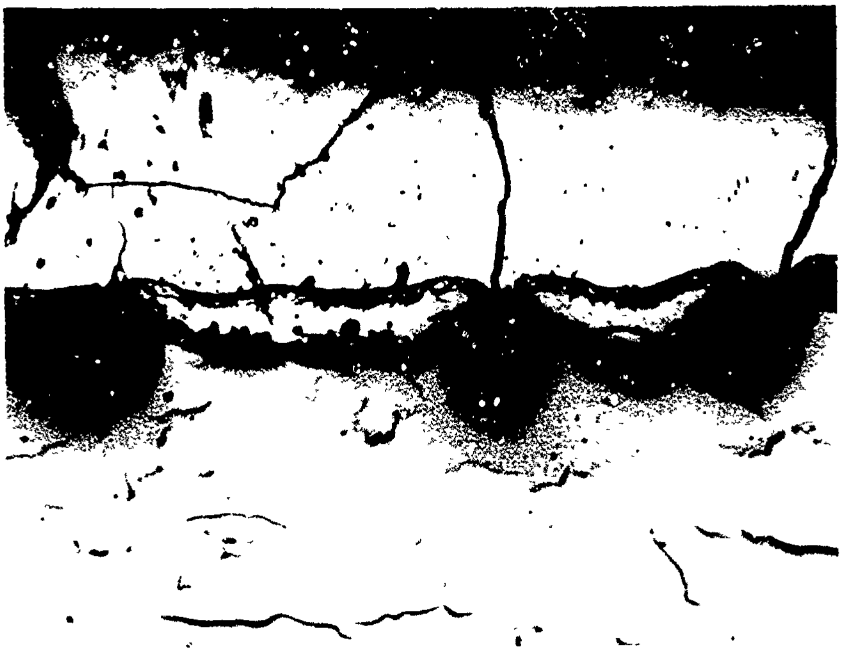


Fig. 18 Oxidized Mo-0.5Ti Substrate Resulting from Cracks in PFR-6 Coating

3.2.4 Coating Process Time

In an effort to determine, among other things, the effect of coating process time upon coating thickness, a series of Mo-0.5Ti and TZM samples were coated at 2050°F for process times of 3, 9, 14, and 19 hr, respectively. These samples were subsequently sectioned, mounted, polished, and forwarded to Advanced Metals Research Corporation in Sommerville, Massachusetts for electron microprobe analysis. The results of this analysis showed that the over-all coating thickness was only very slightly affected by coating process time. Coating thicknesses (converted from a plot of the 45 degree electron probe survey of coating) ranged from 2.2 to 2.6 mils per side. No composition gradient or structure variation was indicated by this study.

3.2.5 Surface Preparation

The study of several methods of surface preparation was prompted by the possibility that thin, adherent molybdenum oxide or some other undesirable surface film was not being completely removed during the standard polish-plus-wash preparation. Such a surface contaminant could possibly act as a barrier to the application of a diffusion coating, resulting in an inferior coating and relatively poor oxidation protection.

Six methods of substrate surface preparation prior to coating were investigated on 10-mil Mo-0.5Ti. These were as follows:

- Vibratory finishing
- Liquid honing (vapor blast)
- Ultrasonic cleaning
- Chemical etching
- Low-pressure abrasive blasting
- Polish-plus-wash (standard method).

Vibratory finishing (discussed in section 3.2.3 as a method of edge preparation) proved satisfactory for cleaning surfaces in preparation for coating. This technique permits cleaning of all surfaces, including re-entrant and blind area, and in addition, is independent of the skill of the operator. When using this method, it is desirable to provide a means of controlling the abrasive particle size since the very small particles will tend to imbed themselves, thus contaminating surfaces to be coated. Such control may be gained by recirculating the abrasive.

Liquid honing the surfaces to be coated provides good preparation. This technique is governed to some extent by operator skill and is somewhat limited insofar as preparing blind areas. Therefore, it was not considered beyond the preliminary investigation.

Preparation of surfaces by ultrasonic cleaning is limited to the removal of surface oils and dirt. Because adherent oxide or other foreign matter is not removed, this method as a sole means of preparation was eliminated.

The three most promising methods of substrate surface preparation prior to coating were evaluated in detail on 10-mil Mo-0.5Ti. These were chemical etching (HNO_3, plus water wash, plus HCl, plus water wash), low-pressure abrasive blasting (minus 240 grit aluminum oxide at 30 psi), and the standard polish-plus-wash methods. Cleaning by the chemical etch and sandblast methods reduced the substrate thickness approximately 20 percent. The prepared specimens were handled with tweezers and gloves to avoid contamination of the surfaces.

Three groups of these prepared specimens were coated with PFR-6 at 2050°F for 7.5 hr. A comparison was made to determine the effect of the different surface preparations with respect to the protective life of the coating as indicated in the oxyacetylene torch test facility. Results of these tests showed no statistical difference among the three groups, with the exception of a single sandblasted specimen that lasted 3.38 hr.

Upon close examination of the mode of failure, it was noted that all torch test specimens, with the exception of that with 3.38-hr lifetime, failed because of specimen deformation. As the test piece was heated in the flame, the thermal stresses created in the specimen exceeded its yield strength at the test temperature, resulting in a relatively severe deformation in the hot area. This deformation caused ruptures or discontinuities in the coating, reducing its oxidation protection. The forerunner of failure--a small bright spot within the hot zone--occurred in the same manner as has been noted in the past with PFR-6 coatings on 30-mil test pieces.

In the single sample lasting 3.38 hr, no deformation was apparent in the test specimen hot area during testing. The lack of specimen deformation accounts for only a part of the increased lifetime of this test piece, however. A lifetime of 3.38 hr is far outside the 95% confidence limit (0.81 to 1.91 hr) previously established for 30-mil specimens coated with PFR-6. No explanation is available for the surprising oxidation resistance of this sample.

Of special interest in the metallographic examination of torch-tested specimens was the mode of failure. The coating rupture or discontinuity caused by the thermally induced deflection of the specimen during testing is shown in Fig. 18. The large, dark, semicircular spots at the interface of the coating and the substrate were caused by substrate oxidation during oxidation testing. The cracks (dark lines) extending from these spots through the coating to the surface permitted enough oxygen to reach the attacked area to cause oxidation. Failure therefore occurred rapidly and was recognized by the evolution of the characteristic molybdenum trioxide smoke from the side opposite flame impingement, accompanied by the sudden rising of sample temperature.

3.2.6 Post-Coating Treatment

In an effort to increase the protective life of the PFR-6 coating, three separate post-coating treatments were applied to PFR-6 coated samples. The treatments were 25-min oxidation in slowly flowing air at 1700°, 2000°, and 2300°F. The results of the oxyacetylene torch tests on test pieces which had been treated indicated that no improvement in the protective life was gained over untreated control samples evaluated in the same manner. Although a slight improvement in average protective life of the specimens oxidized at 2000°F over the specimens oxidized at 1700°F was recorded in the oxyacetylene torch test, the difference is not statistically meaningful. In all cases, the protective lifetimes were within the 95 percent confidence limit established by the oxyacetylene torch tests of the unoxidized control samples. This fact is important since post-coating oxidation is an accepted technique for control of emittance as well as a proof test for determining coating integrity. It is believed the post-coating treating temperatures were not high enough to give significant improvement in protection of the coating.

TABLE 26. PFR-6 COATINGS ON Mo-0.5% Ti AND TZM ALLOYS: WEIGHT GAIN AND COATING THICKNESS.

Alloy	Thickness(mil)	Weight % NH_4Cl	Average weight gain (gm)	Thickness increase per side(mil)
Mo-0.5 Ti	30	0.3	0.6075	1.9
		0.1	0.3785	1.3
	10	0.3	0.6669	2.7
		0.1	0.4203	1.3
TZM	30	0.3	0.7490	2.1
		0.1	0.4562	1.4
	10	0.3	0.6672	2.3
		0.1	0.4256	1.5

3.3 ALTERNATE MOLYBDENUM ALLOYS

As required under this contract, three different molybdenum-base metals were to be investigated as substrates for coating with PFR-6. It was proposed initially that the three alloys be Mo-0.5Ti, TZM, and TZC. As the contract work proceeded however, it became obvious that TZC could not be used in coating studies because the metal producers were unable to fabricate it in sheet form. Pure sintered powder molybdenum was therefore substituted for the third alloy in the coatability study.

3.3.1 Molybdenum - 0.5% Titanium

As has been previously established (ASD TR 61-241), the average coating life in the high-temperature oxyacetylene torch test for PFR-6 on 30-mil Mo-0.5Ti is 1.36 hr and the 95 percent confidence interval in this case is 0.81 to 1.91 hr. The variation in halide content of the pack material and modifications in the heating rate to achieve a satisfactory edge and corner condition have not changed these values markedly.

Most of the experimental work based on 10-mil Mo-0.5Ti alloy has been conducted in the course of two-cycle or riveted assembly studies and is reported in section 3.6. Comparative studies were run with both 10-mil and 30-mil Mo-0.5Ti samples to evaluate weight gain and thickness increase resulting from the coating process.

The results of this study (Table 26) indicate that the coating characteristics of 10-mil Mo-0.5Ti are somewhat different from those of the 30-mil material. The weight gain and thickness increase per side are both greater in the case of the thinner material whether processed in 0.3 weight percent or 0.1 weight percent ammonium chloride PFR-6. One possible explanation for the change in behavior with a change in substrate thickness is the effect of the thickness reduction process itself, because the additional rolling required to reduce the material thickness changes its grain structure. Since the alloy silicide coating formation is based upon diffusion, which, in turn, depends upon the base metal structure, the additional working could explain the change in weight gain and coating thickness values between the 30- and 10-mil substrate.

The effects of reduction of carrier compound percentage when coating both 30- and 10-mil substrates are as expected. In the coating operation, the coating thickness decreases in a 1.5 to 1 ratio and the weight gain decreases in a 1.6 to 1 ratio as the ammonium chloride decreases in a 3 to 1 ratio. This would indicate that the entire amount of halide initially placed in the pack mixture is not required for the coating itself. That portion of the chloride which is lost through the seal during processing varies, however. Assurance is therefore necessary that a sufficient amount of carrier compound be present within the retort to permit the formation of an effective coating.

3.3.2 TZM Alloy

In conjunction with the study of the coatability of Mo-0.5Ti, an exact duplicate study was performed using TZM as the substrate. A comparison of the results for 10-mil and 30-mil TZM samples, coated with PFR-6, shows that the average weight gain for the thinner material is about 10 percent lower in both the 0.3 and 0.1 weight percent ammonium chloride PFR-6 processes--exactly the opposite of that experienced with the Mo-0.5Ti alloy. The average thickness increase per side is very nearly equal for both 10-mil and 30-mil substrate.

A comparison of the 30-mil Mo-0.5Ti and TZM shows that the latter has the higher average weight increase in the coating process. Yet the average coating thickness, as determined by micrometer, is approximately the same for both alloys. This would suggest that the thickness of the interdiffusion zone is greater in the TZM alloy, but it remains to be proven metallographically.

The results of a comparison of coating data for the 10-mil Mo-0.5Ti and TZM alloys again indicate that the interdiffusion layer in the TZM alloy is greater. In this case, however, the average weight gains are approximately equal while the TZM has a noticeably lower average thickness increase.

In a study of the high-temperature oxidation resistance of the PFR-6 coating on 10-mil TZM alloy, nine specimens were placed in each of four 4 by 5 by 6 in. retorts containing 0.3 weight percent ammonium chloride PFR-6 pack mixture. These retorts were heated for 1 hr at 1850°F, plus 6 hr at 2050°F, and furnace cooled. The increase in weight and thickness of the test pieces resulting from the coating process were then determined.

The average coating life of the test pieces processed in retort 2 is considerably greater than that of pieces processed in retort 1 (Table 27). Both of these average lifetimes are markedly greater than those for samples processed in retorts 3 and 4, and both values are somewhat higher than usual. Because of this, the individual oxyacetylene torches were checked, but were found to be operating properly. The average coating thickness was the same for both batches. The average weight gain, however, was greater for samples coated in retort 1 than in retort 2, indicating that the rate of deposition was slower in retort 2. This may account to some degree for the improved average lifetime.

It should also be noted that the standard deviations for retorts 1 and 2 are a good deal higher than usual. Since the torch facility has been found satisfactory and both batches are apparently similar in process, this anomaly remains unexplained.

The average coating lives and standard deviations of samples processed in retorts 3 and 4 were nearly equal, as could have been anticipated by comparing the weight and thickness increase data for these two runs. Indeed, a longer average lifetime in retorts 1 and 2 was not unexpected, based upon the weight and thickness increase data for these samples. Despite the shorter torch test coating life in retorts 3 and 4, these runs produced more desirable results, since their reliability is considerably higher as shown by the standard deviation.

The coatability of 30-mil TZM alloy was also studied extensively. Results of these studies (Tables 28 and 29) indicate that 30-mil TZM substrate may be suitably coated with PFR-6 and that such coated pieces possess a satisfactory resistance to oxidation at high temperatures. Initial studies showed oxidation test results comparable to PFR-6 on Mo-0.5 Ti alloy. It was noted, however, that the coating on the TZM alloy failed in the guided bend test at a radius of 1.0 in., in contrast with a 0.55 in. radius determined for the coated Mo-0.5Ti. Since this reduction in ductility was not a serious limitation, studies on TZM were continued.

The additional investigations demonstrated the effect of slightly modified process cycles. Several process runs were made using the following variations:

A: 7 hr at 2050°F

B: 1 hr at 1850°F, plus 6 hr at 2050°F

C: 1 hr at 1850°F, plus 6 hr at 2100°F

D: 1 hr at 1850°F, plus 6 hr at 2150°F

Detailed results are shown in Table 28. The data summary shown in Table 29 indicates that the processing cycle, particularly the second hold temperature, significantly affects the coating life, and also shows that coatings produced in processes A and D are inferior to coatings produced under the other process conditions. The reproducibility of the different processes, indicated by the standard deviation and consideration of adequate lifetime, suggests processes B and C to be superior. Because of its lower process temperature, process B is to be preferred since it is less apt to cause recrystallization of the substrate.

Reduction of the amount of carrier compound in the pack mixture and control of the heating schedule have been needed to control the condition of the coating along the edges and corners of the test sample. As discussed previously, proper control of the ratio of coating deposition rate to coating diffusion rate is required to prevent a unicorn condition at these places. Although this unicorn condition was originally investigated with regard to 10-mil Mo-0.5Ti substrate, the general principles found true in this investigation are applicable also to the coating of 30-mil TZM samples.

A comparison of runs 1 and 2, 3 thru 5, and 6 thru 8 (Table 29) shows that control of the retort heating schedule combined with reduced amounts of carrier compound causes only a slight lowering of the average coating life. The standard deviation, however, is improved up to 50 percent by the heating and carrier compound modification. The overall effect of the change in coating conditions, then, is twofold: (1) it provides a coating with slightly reduced average life but markedly improved reliability, as evaluated in the oxyacetylene torch test, and (2) it eliminates probable weak spots in the coating resulting from the unicorn condition along edges and at corners of test samples.

3.3.3 Pure Molybdenum

For a preliminary examination of the coatability of PFR-6 on pure molybdenum base metal, nine 1.5 by 3.0 by 0.030 in. specimens were placed in each of three 4 by 5 by 6 in. retorts filled with 0.3 weight percent ammonium chloride PFR-6 pack mixture, processed for 1 hr at 1850°F plus 6 hr at 2050°F, and then furnace-cooled. The results of these runs (Table 30) indicate that the PFR-6 coating is certainly compatible with pure molybdenum and that satisfactory protection from high-temperature oxidation is possible. One will note that the third run was markedly inferior to the first two runs. This difference cannot be explained by large variations in the weight or thickness increases due to coating. Examination of coated samples from the third run before testing in the oxyacetylene torch facility showed some unusual coloring on one end of several samples, indicating that an impurity may have been present in the pack. The lack of additional base metal prevented a further search for other explanations of the variation.

3.4 COATING PARAMETERS

As experimental work on the scale-up of PFR-6 from a laboratory-size operation to an intermediate-size process continued, it became more obvious that high-temperature oxyacetylene torch test data and metallographic coating thickness data are useful only on an experimental basis. Although effects of coating process variation may be satisfactorily evaluated by testing samples to failure in the torch test or by measuring the coating thickness metallographically, both of these procedures are destructive. They are, therefore, obviously unacceptable for coated parts that are to perform as components of reentry vehicles. It was therefore necessary to develop non-destructive tests which would provide some estimate of the actual coating characteristics. Several parameters have been extensively investigated and are discussed in the subsequent sections.

3.4.1 Ratio of Carrier Compound Weight to Substrate Surface Area

Previous studies designed to optimize the PFR-6 coating on thin (10-mil) Mo-0.5Ti substrate indicated that both the actual weight of pack carrier compound (ammonium chloride) and its percentage of the entire pack affected the coating integrity. In smaller retorts (less than 120 cu in.), a PFR-6 pack containing 0.3 weight percent carrier compound provided optimum protection from high-temperature oxidation and eliminated the unicorn effect of the coating on the edges and corners of the substrate. When this same pack composition was used in larger retorts, however, the unicorn effect became more pronounced as retort volume increased. This indicated that the weight percentage of carrier compound was not the best measure of the integrity of the coating on the substrate corners and edges, leading to consideration of a new parameter: the ratio of ammonium chloride weight to substrate surface area to be coated.

Studies of the effect of this ratio were conducted on 30-mil Mo-0.5Ti substrate. Several carrier compound to surface area ratios were used. Three process times (3, 5, and 9 hr) at 2050°F were used to investigate the effect of time-at-temperature upon this ratio. Weight and thickness increase measurements were made of the coated specimens, followed by evaluation in the torch test facility. The results of this study are given in Tables 31 thru 33, and are presented graphically by least square plots in Fig. 19.

Two immediately apparent results of this study were: (1) an increase in oxidation protection with a larger ammonium chloride to surface area ratio, and (2) an increase in oxidation protection with longer process time. Both of these relationships are to be expected from consideration of the principles of the pack cementation process. Not shown by these least square plots, but equally important, was the condition of the coating at the substrate edges and corners. As in the studies on 10-mil substrate, the unicorn effect became increasingly evident with increasing amounts of carrier compound. It was therefore apparent that the oxidation protection of the coating on a localized spot on the flat surface of the test sample (indicated by torch test life) is not the only criterion of coating integrity, but that the quality of the coating on all portions of the test specimen must be considered.

The relatively steep slopes of these plots indicate that this parameter could be valuable in determining the amount of ammonium chloride to be used in the pack mixture for coating one or more specific parts. Since the parameter indicates pack composition prior to coating rather than the performance of the part after coating, it is uniquely applicable in this respect

TABLE 27. PFR-6 COATING ON 10-MIL TZM ALLOY: OXYACETYLENE TORCH TEST AND COATING DATA.

Retort	Average coating life at 3000°F[a] (hr)	Standard deviation(hr)	95% confidence limit(hr)	Av. weight gain per sample(gm)	Av. coating thickness increase per side(mil)
1	2.47	1.54	0 - 5.49	0.8122	2.3
2	3.62	1.42	0.84 - 6.39	0.7393	2.3
3	1.33	0.34	0.67 - 2.00	0.5370	1.9
4	1.44	0.37	0.72 - 2.16	0.5571	2.0

[a] 3000°F assuming emittance of 1.0; 3125°F assuming emittance of 0.8. Sample thermal shocked with 30 psi air blast every 0.5 hr.

TABLE 28. PFR-6 COATING ON TZM ALLOY: OXYACETYLENE TORCH TEST DATA.

Run	Average coating life at 3000°F[a] (hr)	Standard deviation(hr)	95% confidence limit(hr)	Weight Percent NH_4Cl	Process[b]
1	0.92	0.236	0.45 - 1.38	2.0	A
2	1.85	0.486	0.89 - 2.80	2.0	A
3	1.28	0.334	0.63 - 1.94	0.3	B
4	1.29	0.315	0.67 - 1.91	0.3	B
5	1.30	0.592	0.14 - 3.46	0.3	B
6	1.66	0.289	1.09 - 2.22	0.3	C
7	1.33	0.136	1.06 - 1.60	0.3	C
8	1.06	0.279	0.51 - 1.60	0.3	C
9	1.65	0.409	0.85 - 2.45	0.3	D
10	0.59	0.171	0.26 - 0.93	0.3	D
11	0.85	0.218	0.43 - 1.28	0.3	D

[a] 3000°F assuming emittance of 1.0 (3125°F assuming emittance of 0.8). Sample thermal shocked with 30 psi air blast every 0.5 hr.

[b] Process conditions keyed as follows:

A = 7 hr at 2050°F.
B = 1 hr at 1850°F plus 6 hr at 2050°F.
C = 1 hr at 1850°F plus 6 hr at 2100°F.
D = 1 hr at 1850°F plus 6 hr at 2150°F.

TABLE 29. PFR-6 COATING ON TZM ALLOY: OXYACETYLENE TORCH TEST DATA. SUMMARY OF TABLE 28.

Run	Average coating life at 3000°F[a] (hr)	Standard deviation (hr)	95% confidence limit (hr)	Weight Percent NH_4Cl	Process[b]
1,2	1.38	0.607	0.19 - 2.57	2.0	A
3,4,5	1.29	0.309	0.67 - 1.89	0.3	B
6,7,8	1.35	0.343	0.68 - 2.02	0.3	C
9,10,11	1.03	0.533	0 - 2.07	0.3	D

[a] 3000°F assuming emittance of 1.0 (3125°F assuming emittance of 0.8). Sample thermal shocked with 30 psi air blast every 0.5 hr.

[b] Process conditions are keyed as follows:

A = 7 hr at 2050°F.
B = 1 hr at 1850°F plus 6 hr at 2050°F.
C = 1 hr at 1850°F plus 6 hr at 2100°F.
D = 1 hr at 1850°F plus 6 hr at 2150°F.

TABLE 30. PFR-6 COATING ON PURE MOLYBDENUM: OXYACETYLENE TORCH TEST AND COATING DATA.

Run	Average coating life at 3000°F[(a)] (hr)	Standard deviation(hr)	95% confidence limit(hr)	Av. weight gain per sample(gm)	Av. coating thickness increase per side(mil)
1	1.88	0.606	0.69 - 3.069	0.5959	1.8
2	1.47	0.485	0.52 - 2.42	0.6520	2.0
3	0.36	0.351	0 - 1.04	0.6507	1.5
Ave	1.24	0.809	0 - 2.82	0.6329	1.8

(a) 3000°F assuming emittance of 1.0; 3125°F assuming emittance of 0.8. Sample thermal shocked with 30 psi air blast every 0.5 hr.

TABLE 31. EFFECT OF RATIO OF CARRIER COMPOUND WEIGHT TO SUBSTRATE SURFACE AREA: OXYACETYLENE TORCH TEST AND COATING DATA, 3 HR AT 2050°F COATING PROCESS.

Number of Samples	Weight Percent NH_4Cl	Ratio: Wt. NH_4Cl to surface area (gm/cm^2)	Av. coating thickness(mil)	Av. weight gain each sample(gm)	Av. unit area wt. gain each sample(gm/cm^2)	Av. torch test life, $\overline{X}$(hr)
9	0.1	0.0071	1.2	0.2814	4.70×10^{-3}	0.00
9	0.3	0.0212	2.0	0.6650	11.11×10^{-3}	1.14
9	0.5	0.353	1.8	0.6488	10.82×10^{-3}	0.84
9	1.0	0.0706	2.0	0.7227	12.06×10^{-3}	1.08

TABLE 32. EFFECT OF RATIO OF CARRIER COMPOUND WEIGHT TO SUBSTRATE SURFACE AREA: OXY-ACETYLENE TORCH TEST AND COATING DATA, 5 HR AT 2050°F COATING PROCESS.

Number of Samples	Weight percent NH_4Cl	Ratio: Wt. NH_4Cl to surface area (gm/cm^2)	Av. coating thickness(mil)	Av. weight gain each sample(gm)	Av. unit area wt. gain each sample(gm/cm^2)	Av. torch test life, $\overline{X}$(hr)
9	0.1	0.0069	0.6	0.1670	2.79×10^{-3}	0.02
9	0.3	0.0206	1.2	0.4594	7.68×10^{-3}	0.72
9	0.5	0.0344	1.4	0.5568	9.31×10^{-3}	0.75
9	1.0	0.0687	1.7	0.7309	12.22×10^{-3}	1.36

TABLE 33. EFFECT OF RATIO OF CARRIER COMPOUND WEIGHT TO SUBSTRATE SURFACE AREA: OXY-ACETYLENE TORCH TEST AND COATING DATA, 9 HR AT 2050°F COATING PROCESS.

Number of Samples	Weight percent NH_4Cl	Ratio: Wt. NH_4Cl to surface area (gm/cm^2)	Av. coating thickness(mil)	Av. weight gain each sample(gm)	Av. unit area wt. gain each sample(gm/cm^2)	Av. torch test life, $\overline{X}$(hr)
9	0.1	0.0071	1.7	0.5558	9.29×10^{-3}	0.66
9	0.3	0.0212	2.2	0.6139	10.26×10^{-3}	1.11
9	0.5	0.0353	1.8	0.6569	10.99×10^{-3}	1.30
9	1.0	0.0706	2.3	1.0087	18.15×10^{-3}	1.74

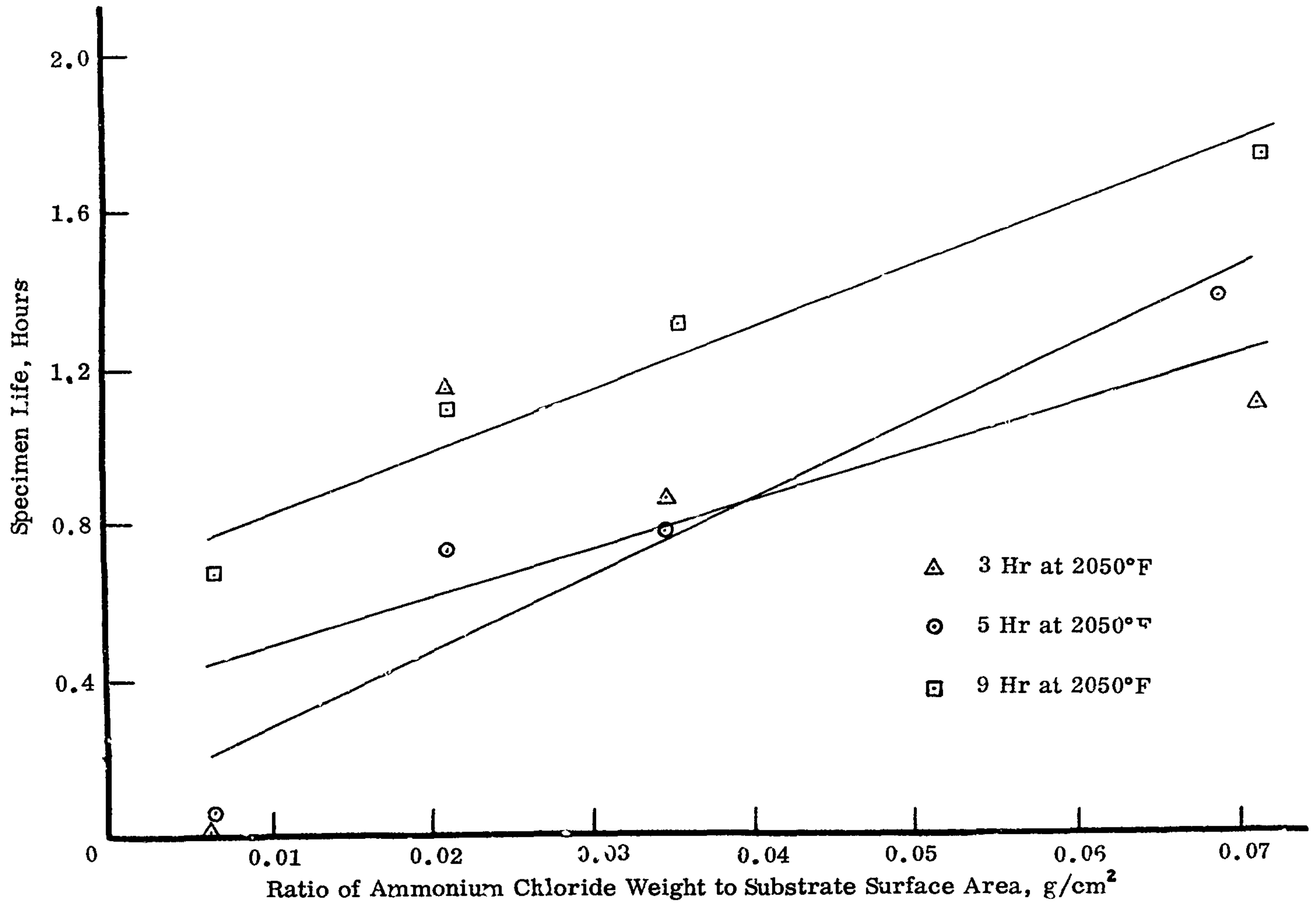


Fig. 19 Specimen Life as a Function of the Carrier Compound to Surface Area

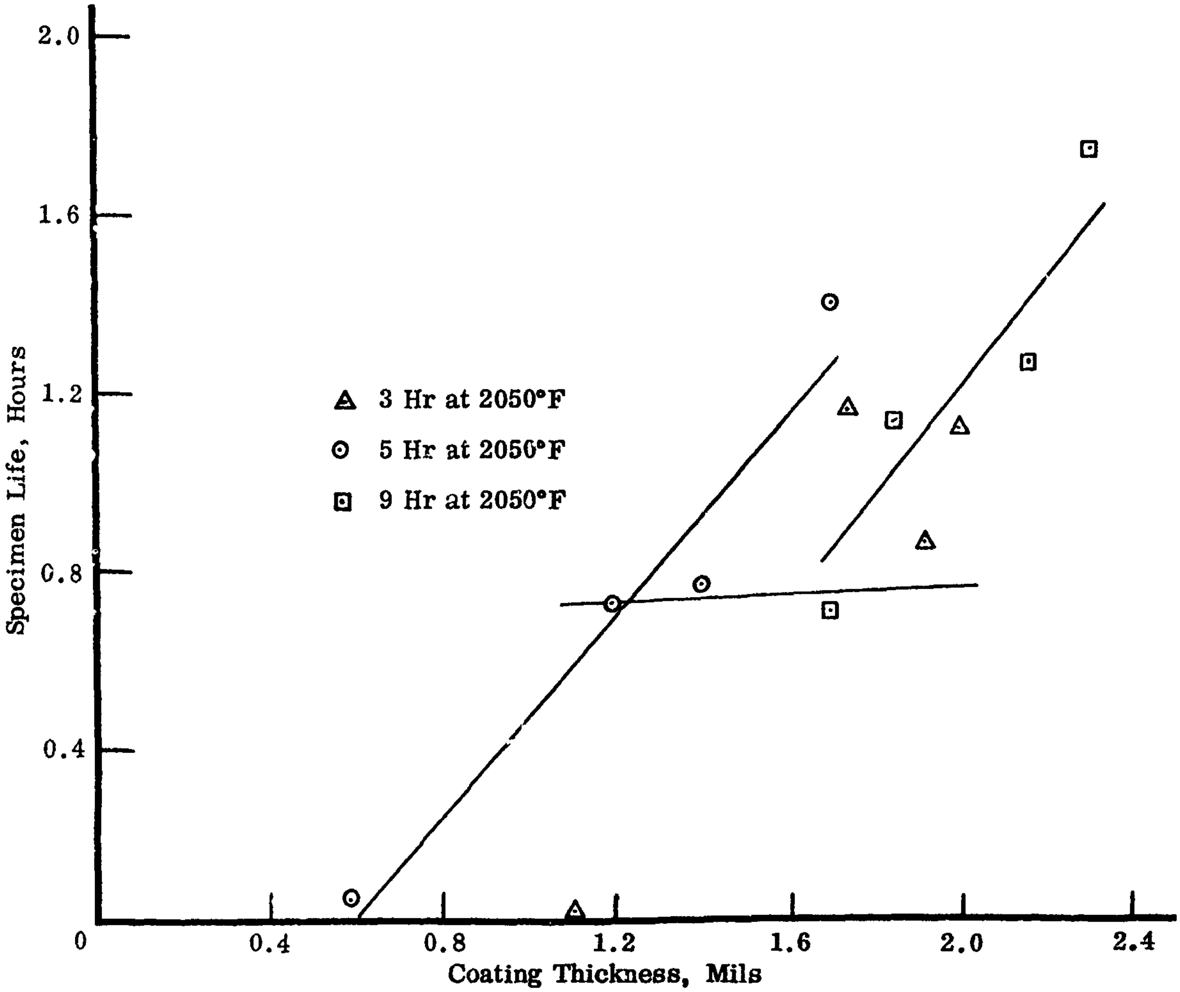


Fig. 20 Specimen Life as a Function of Coating Thickness

among the parameters discussed. Its value is further enhanced by the fact that the only information required for use of the parameter is the total surface area of the parts to be coated.

3.4.2 Performance Life vs Coating Thickness

If micrometer measurement of the thickness increment could be used as a means of predicting the oxidation resistance of the coating it would be useful because it is simple and non-destructive. Attempts were made to correlate coating thicknesses measured by micrometer with results of oxyacetylene torch tests on coated 30-mil Mo-0.5Ti specimens in order to acheive a simple non-destructive test for coating life. The measurement of the coated specimen was compared to the measurement of the uncoated specimen and the apparent incremental thickness was used as an approximation of coating life. The apparent incremental thickness is, of course, the sum of the coating thickness on both sides, and its use assumes that the two coating thicknesses are identical. Equality of thickness may be assured by appropriate placement of the specimens in the retort. The results of the correlation between coating thickness and performance life are given in Tables 31 thru 33 and shown as least square plots in Fig. 20.

The least square plot of coating thickness and torch test life indicates that small differences in coating thickness have a pronounced effect on the oxidation protection afforded by the coating. The individual data points have a slightly better relation to the least square line in the 9-hr process cycle than in the 3-hr process cycle. This is explained by the characteristics of the coating. Metallographic examination of those samples processed in the shorter coating cycle showed a "hill and valley" pattern. The process time was evidently not long enough to produce a coating of uniform thickness. Since the coating is attacked nearly uniformly over the entire surface when subjected to oxidation at high temperatures, the failure occurs first in the regions of the thin coating, i.e. in the valleys. The period of protection offered by the coating, then, is limited by the protection provided by the thinnest segment of coating.

The micrometric thickness measurements do not provide a sufficiently sensitive indication of the variation in coating thickness because such measurement gives the coating thickness from the tops of the hills on one side to the tops of the hills on the opposite side of the coated substrate. Metallographic examination of the samples processed at 2050°F for 9 hr showed that the "hill and valley" variation is markedly decreased, accounting for the more accurate relationship between micrometric measurement of the sample and torch test life. The relatively low slope of the plots of performance life vs coating thickness in relation to the slopes of the plots of other parameters indicates that the oxidation protection estimates based upon micrometrically measured coating thickness are not as accurate as desired. For this reason, another method of estimation was investigated and is discussed below.

3.4.3 Performance Life vs Unit Area Weight Gain

A comparison of the 2.0 weight percent ammonium chloride batches processed at 2050°F for 3 and 9 hr, respectively, showed that specimen thickness increase did not always indicate the corresponding increase in the oxidation protection that might be expected. The large difference in weight gain which occurred during the coating process indicated that this parameter might be a more accurate guide to coating oxidation protection than is coating thickness. Weight gain used by itself, however, without regard to the surface area coated is not a satisfactory parameter. In the experimental batches, all test pieces were similar in size and the same number of pieces were used per batch so that weight gain alone did not have an effect. This would not be the case in processing actual re-entry vehicle components. Therefore, care was taken to make sure that the data obtained from these intermediate scale-up studies would be useful for extension to a production-sized operation. It was accomplished by using the "unit area weight gain" parameter, which is defined as weight gained during the coating cycle per unit area of substrate surface coated. Thus the unit takes into account both weight gain resulting from coating and surface area coated. Weight gain measurements and torch tests were made on coated 30-mil Mo-0.5Ti processed in runs with various carrier compound contents and held at 2050°F for 3, 5, and 9 hr. The results are given in Tables 31 thru 33 and as least square plots in Fig. 21.

The least square plot of unit area weight gain as a function of specimen life gives the expected positive relationship. The variables required for the calculation of unit area weight gain, i.e. substrate surface area and weight gain, may be measured easily and accurately. The resultant correlation between the unit area weight gain and the torch life is therefore expected. It must be noted, however, that the same restriction holds with regard to process time in this case as in the case of torch life as a function of specimen thickness [illegible]. The process time must be of sufficient length that coating thickness irregularities characteristic of a short time process cycle are not present to influence the relationship between parameters.

The relationship between the unit area weight gain and coating performance is somewhat better than that between coating thickness per side and coating life, or the ratio of ammonium chloride weight to substrate surface area and performance life, although the latter parameter, as discussed in section 3.4.1, is of a slightly different nature in that it may be used as a pre-coating parameter as well. The estimates of coating oxidation protection based upon the unit area weight gain parameter should therefore be somewhat more accurate than those based upon either of the other relationships. The actual unit area weight gain value for optimum performance life must be determined after the optimum ratio of ammonium chloride volume to retort volume has been established for the several retort sizes.

The value of unit area weight gain as an index of coating performance is enhanced by the ease of its determination and its non-destructive nature. As parts for coating become larger, methods for controlling thermal gradients will become more important. With the assurance that a uniform over-all coating has been deposited, quality control samples may be placed in the process retort and coating performance estimated on the basis of data calculated from these control samples.

3.5 PACK MIXTURE REUSE

The purpose of studying the possibility of pack material reuse is to reduce the cost of applying PFR-6. The raw materials used in each batch of PFR-6 coating mixture are expensive. If the pack material could be reused a number of times, each time adding only the relatively inexpensive carrier and atmosphere control compounds, a substantial saving would be achieved. It must be pointed out, however, that reuse of the pack material cannot be arbitrarily adopted until the performance and statistical reliability of the resulting coatings have been demonstrated.

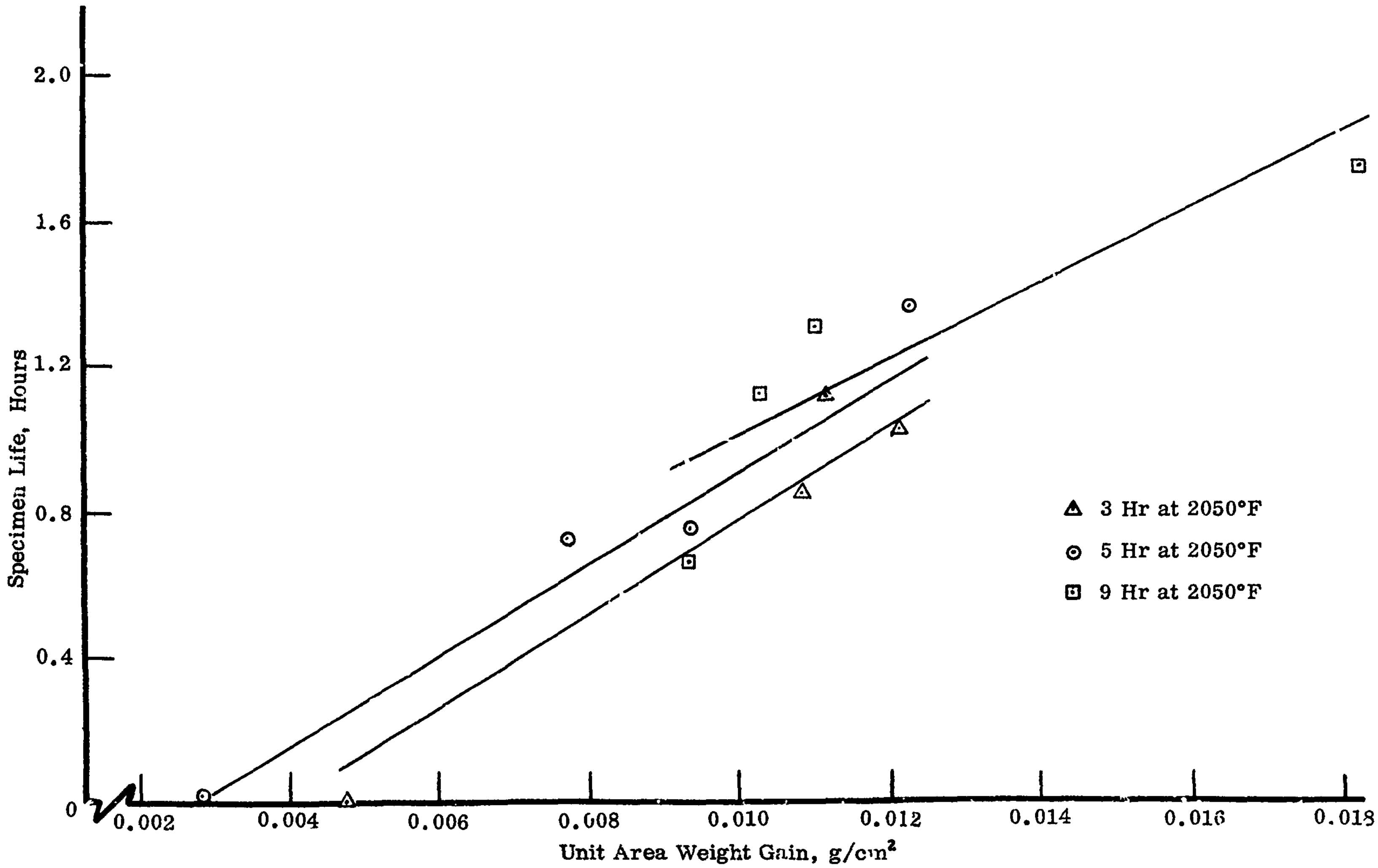


Fig. 21 Specimen Life as a Function of Unit Area Weight Gain

TABLE 34. EFFECT OF PACK REUSE ON COATING LIFE: OXYACETYLENE TORCH TEST AND WEIGHT GAIN DATA, 1 HR AT 1850°F PLUS 6 HR AT 2050°F PROCESS.

Run	Average coating life at 3000°F[a] (hr)	Standard deviation (hr)	95% confidence limit (hr)	Average weight gain per sample (gm)
Initial				
A	12	0.302	0.53 - 1.71	0.7056
B	1.19	0.233	0.73 - 1.64	0.6214
1st Reuse				
A	1.08	0.262	0.57 - 1.60	0.6562
B	0.88	0.128	0.63 - 1.13	0.6471
2nd Reuse				
A	1.64	0.306	1.04 - 2.24	0.8101
B	1.71	0.259	1.20 - 2.21	0.8147

[a] 3000°F assuming emittance of 1.0; 3125°F assuming emittance of 0.8. Sample thermal shocked with 30 psi air blast every 0.5 hr.

TABLE 35. ADDITIONAL STUDY ON EFFECT OF PACK REUSE ON COATING LIFE: OXYACETYLENE TORCH TEST AND WEIGHT GAIN DATA, 1 HR AT 1850°F PLUS 6 HR AT 2050°F PROCESS.

Run	Average coating life at 3000°F[a] (hr)	Standard deviation(hr)	95% confidence limit(hr)	Average weight gain per sample(gm)
Initial				
C	1.21	0.191	0.84 - 1.59	0.6330
D	0.93	0.176	0.58 - 1.27	0.5462
1st Reuse				
C	0.61	0.212	0.20 - 1.02	0.5139
D	0.57	0.330	0 - 1.21	0.5400
2nd Reuse				
C	1.14	0.206	0.74 - 1.54	0.6214
D	1.14	0.303	0.55 - 1.74	0.5965

[a] 3000°F assuming emittance of 1.0; 3125°F assuming emittance of 0.8. Sample thermal shocked with 30 psi air blast every 0.5 hr.

TABLE 36. INVESTIGATION OF COATING CYCLE FOR COMPONENTS TO BE ASSEMBLED BY RIVETING: OXYACETYLENE TORCH TEST AND PROCESS DATA.

Run	Av. coating life at 3000°F[a] (hr)	95% confidence limit(hr)	Av. weight gain(gm)	Retort size(in.)	Wt.% NH_4Cl	Complete process[b]	Condition of edges
1	0.08	0.04 - 0.13	0.4049	4x5x6	0.3	E	Fair
2	0.17	0 - 0.39	0.4777	4x5x6	0.3	E	Fair
3	0.16	0.02 - 0.30	0.7160	4x5x6	0.3	E + F	Fair
4	2.51	0.77 - 4.25	0.8426	4x5x6	0.3	E + A	Fair
5	0.13	0.08 - 0.18	0.3995	8x8x4	0.3	E + A	Poor
6	0.22	0 - 0.47	0.7891	8x8x4	0.1	E + A	Fair
7	1.58	0 - 4.03	0.7713	8x8x4	0.05	E + A	Good
8	0.76	0 - 2.68	0.8075	4x5x6	0.1	E + A	Good

[a] 3000°F assuming emittance of 1.0: 3125°F assuming emittance of 0.8. Sample thermal shocked with 30 psi air blast every 0.5 hr.

[b] Process conditions are keyed as follows:

A = 7 hr at 2050°F. (postassembly process)
E = 1 hr at 1850°F plus 2 hr at 2050°F. (preassembly process)
F = 3 hr at 2050°F. (postassembly process)

Such factors as change, consumption, classification, or partial loss of pack material during processing or discharging of retorts may introduce unexpected variables in the coating process. Furthermore, the lack of high temperature thermodynamic data makes it impossible to predict the exact reactions occurring in the coating cycle. It must be assumed, therefore, that the components remaining in the used pack material are not the same as those in a fresh batch. As an example, silicon does not remain completely in its elemental form after the coating cycle. Although the parameters of the coating performance already studied may remain unchanged, certain other coating characteristics, such as emittance, should also be evaluated before reuse of pack material can be safely accepted as a part of the standard operating procedure.

To study the effect of reusing PFR-6 pack material, two 4 by 5 by 6 in. retorts, each containing nine 1.5 by 3.0 by 0.030 in. Mo-0.5Ti specimens, were processed. The weight and thickness of each specimen were recorded before and after the coating cycle. The pack material from each retort was then reused in two more cycles. Each time, the ammonium chloride and urea were replenished. In order to substantiate the initial data, a second series of batches was processed. The number of specimens and the coating cycle were identical in all runs.

Results of the initial studies of reuse of pack materials (Table 34) indicated that average specimen life decreases slightly when reusing the pack material the first time, although the confidence limits showed considerable overlap. In the second reuse of the pack material, however, a reversal of this trend occurred. Average specimen life in this case showed a 0.75-hr increase over that realized in the first reuse of the pack mixture and a 0.5-hr increase over specimen life of the samples coated in new pack material.

The relatively wide variation in specimen life is not unexpected. The anticipated trend in specimen life, however, has not been realized. It was expected that the longest life would result from specimens coated in the initial batch. Then, since some of the coating materials would have been consumed or changed during this first use, subsequent reuse of the material would provide a coating with decreased oxidation protection. Such a trend appeared only in the first reuse but not in the second.

The data from the second series of batches processed (Table 35) show comparable results. This time a decrease in specimen life of about 0.5 hr was observed in the first reuse. In the second reuse of the pack, an increase in specimen life again occurs, this time to approximately that realized in the initial use. The overlap of confidence limit experienced in the preliminary study is again noted.

Since this preliminary study has been completed, information derived from the composition of the used pack material has given a possible explanation for the unexpected specimen life variation. Various amounts of iron, chromium, and nickel, in addition to the expected aluminum oxide, silicon, and columbium were present in the pack mixture after a single use. None of these elements has been shown by electron probe to be present in the coating applied in the initial use of the pack material. It is theorized that the first three elements mentioned are present as a result of the powerful corrosive effect of the high-temperature halides during processing on the retort itself. It is quite possible that continued reuse of the pack material causes the iron, chromium, and nickel contents to increase to a point where they have a significant effect on the coating life.

Several samples of used PFR-6 pack mixture were submitted to the Technology Department of Union Carbide Metals Company, Niagara Falls, New York for chemical analysis. It was determined that the iron, chromium, and nickel present in the pack mixture after a single use were well below 0.1 percent. The amount of these metals present after multiple reuse has not yet been determined, so the possibility still exists that these elements do affect subsequent reuse of the pack material.

Also of interest in these chemical analyses was the amount of silicon and columbium remaining in the pack mixture after a single use. Silicon content amounted to approximately 7.7 percent and columbium to approximately 1.9 percent. Since the pack mixture initially contains 8.5 and 2.0 percent of these elements, respectively, it can be seen that pack reuse remains a definite technical and economic possibility.

3.6 COATINGS FOR RIVETED ASSEMBLIES

Riveting is presently the method most widely used for assembling molybdenum alloy components since welding results in brittle joints. Assembly by riveting is not without problems, however. If the parts are assembled in the uncoated condition and coated after assembly, the mating surfaces of components and rivets have no protection against oxidation. Although the pack cementation coating process has a high throwing power, the intimate contact between the tightly mated parts prevents coating deposition in these areas. When the assembly is subjected to elevated temperatures in an oxidizing environment, rapid failure of the part through oxidation of the uncoated areas will result.

Prevention of this rapid failure requires the elimination of uncoated areas by coating the individual components before assembly. Preassembly coating, however, does not satisfy the requirements for oxidation protection. During riveting, the upset portion of the rivet often develops cracks, rupturing the coating and reducing protection against oxidation. Quite often the coating on the component in the area immediately adjacent to the rivet is also ruptured. The need to restore the coating in both affected areas makes a second, or postassembly, coating cycle mandatory.

Several combinations of preassembly and postassembly coating cycles have been evaluated in small and intermediate-sized retorts. Results of these investigations are given in Table 36. Runs 1 and 2 were used as the standard preassembly coating. Runs 3 to 8 were processed in both preassembly and postassembly cycles.

Results of investigations of the pack cementation process in general have indicated that equal weights of coating deposited at different rates provide varying degrees of oxidation protection. The coatings formed at slower rates (lower deposition-to-diffusion ratio) provided greater oxidation protection than coatings of equal weight increase formed at higher deposition rates. Since both the process temperature and the amount of pack carrier compound affect the coating rate, control of either variable can be used to control the coating deposition rate. In Runs 5 through 7 (Table 36) and 5A through 7A (Table 37), the temperature was held constant, and the quantity of ammonium chloride carrier compound was varied as indicated. The quantity of ammonium chloride, therefore, controlled the coating reaction rate and, consequently, the oxidation protection provided by the coating. The coatings resulting from processing in Runs 7, 6A, and 7A provided the longest specimen life, indicating that coating conditions were near optimum in those cases.

It was observed that use of reduced amounts of ammonium chloride resulted in improved edge conditions, i.e. the unicorn effect was minimized or eliminated. For experiments carried out in smaller retorts, reducing the carrier content while holding all else constant resulted in shortened specimen life. This may be compensated for, to a certain extent, by longer processing times for the batches with lower chloride content. Again in the larger retorts, a reduction in ammonium chloride content resulted in improved edges and corners as expected. The specimen life, however, did not decrease as markedly as one would expect from the results of the study conducted in 4 by 5 by 6 in. retorts.

That part of the study involving a second cycle in 8 by 8 by 4 in. retorts was repeated. The average specimen life after preassembly coating is shown for Runs 1A and 2A in Table 37. It should be noted that these lives were somewhat greater than those resulting from the tests of the preassembly coating evaluated in the previous study (Table 36). This must be kept in mind since it affects, to some degree, the subsequent data. The results of the evaluation of these test pieces after the second coating cycle (simulating the coating after riveting, or postassembly coating) again show that the condition of the edges and corners improved with decreasing amounts of carrier compound (Table 37). In this repeated study, however, the amount of carrier compound was decreased further than in the previous study. Once again the specimen life improved with reduced amounts of pack carrier compound, but the improvement reached a maximum and then dropped off markedly as the carrier compound content decreased to less than 0.05 weight percent.

As expected, the average weight gain per sample in both the first and second experiments decreased with decreasing pack carrier compound content. The only variation in this relationship occurred in the second study in which the average weight gain increased as the carrier compound was reduced from 0.05 to 0.01 weight percent. No explanation is available for this behavior.

In a further investigation of the 2-cycle processes required for riveted assemblies, 22 specimens of 10-mil Mo-0.5Ti and 22 specimens of 10-mil TZM were processed in separate retorts for 1 hr at 1850°F plus 2 hr at 2050°F in 0.1 percent ammonium chloride PFR-6 pack mixtures. All test pieces were weighed and measured before and after the coating cycle to determine changes in weight and thickness. Three of the coated samples from each batch were tested in the oxyacetylene torch facility to evaluate their oxidation resistance after this simulated preassembly coating cycle (items 1 and 2, Table 38).

In a simulated postassembly coating cycle, nine precoated samples of each type of base metal were processed for 7 hr at 2050°F in a 0.1 weight percent ammonium chloride PFR-6 pack and nine each in a 0.05 weight percent PFR-6 pack. All samples were again weighed and measured after this second coating cycle.

Several items should be noted in a study of the resultant data (Table 38). The preassembly coating cycle has resulted in slightly higher average coating life than in previous studies. When considered in combination with the data in section 3.3.2, it appears that the increased value in the case of the TZM alloy may be characteristic of the coatability of 10-mil TZM. TZM coated with PFR-6 has a higher average coating life and a narrower range of confidence than the coated Mo-0.5Ti, indicating that the two alloys differ somewhat in coating characteristics. The weight increase resulting from the coating process is greater in the case of TZM than in that of Mo-0.5Ti. The average coating thickness is essentially the same for both alloys, again indicating a thicker interdiffusion zone for the TZM alloy.

TABLE 37. ADDITIONAL INVESTIGATION OF COATING CYCLE FOR COMPONENTS TO BE ASSEMBLED BY RIVETING: OXYACETYLENE TORCH TEST AND PROCESS DATA.

Run	Av. coating life at 3000°F[(a)] (hr)	95% confidence limit(hr)	Av. weight gain(gm)	Retort size(in.)	Wt.% NH_4Cl	Complete process[(b)]	Condition of edges
1A	0.62	0 - 2.37	0.4241	4x5x6	0.3	E	Fair to good
2A	0.83	0.80 - 0.86	0.3977	4x5x6	0.3	E	Fair
5A	0.82	0 - 2.81	0.7877	8x8x4	0.3	E + A	Poor to fair
6A	2.30	0.49 - 4.10	0.6568	8x8x4	0.1	E + A	Fair
7A	2.00	0.89 - 3.10	0.5246	8x8x4	0.05	E + A	Good
9	0.41	0 - 0.95	0.6892	8x8x4	0.01	E + A	Fair to good

(a) 3000°F assuming emittance of 1.0; 3125°F assuming emittance of 0.8. Sample thermal shocked with 30 psi air blast every 0.5 hr.

(b) Process conditions are keyed as follows:

A = 7 hr at 2050°F. (postassembly process)
E = 1 hr at 1850°F plus 2 hr at 2050°F. (preassembly process)

TABLE 38. INVESTIGATION OF COATING CYCLE FOR COMPONENTS TO BE ASSEMBLED BY RIVETING: OXYACETYLENE TORCH TEST, COATING, AND PROCESS DATA.

Item number	Substrate material	Av. coating life at 3000°F[(a)] (hr)	95% confidence limit(hr)	Av. weight gain(gm)	Av. coating thickness(mil)	Wt.% NH_4Cl	Complete process[(b)]	Condition of edges
1	Mo-0.5%Ti	0.77	0 - 1.90	0.3850	1.6	0.1	E	Fair
2	TZM	1.12	0.27 - 1.97	0.4627	1.7	0.1	E	Fair
3	Mo-0.5%Ti	0.56	0 - 1.82	0.5486	2.0	0.1	E + A	Poor to fair
4	TZM	2.08	0.08 - 4.07	0.6238	1.9	0.1	E + A	Poor to fair
5	Mo-0.5%Ti	1.77	0.84 - 2.71	0.5114	1.9	0.05	E + A	Fair to good
6	TZM	2.12	1.43 - 2.91	0.6013	1.6	0.05	E + A	Fair to excellent

(a) 3000°F assuming emittance of 1.0; 3125°F assuming emittance of 0.8. Sample thermal shocked with 30 psi air blast every 0.5 hr.

(b) Process conditions are keyed as follows:
A = 7 hr at 2050°F. (postassembly process)
E = 1 hr at 1850°F plus 2 hr at 2050°F. (preassembly process)

TABLE 39. LOW TEMPERATURE STATIC OXIDATION TESTS: SPECIMEN DATA AFTER 37 HOURS OF EXPOSURE

Parameter	Specimen		
	No. 1	No. 2	No. 3
Initial weight (gm)	25.0901	24.2798	24.0315
Weight after coating (gm)	25.5918	24.8970	24.5882
Weight gain due to coating (gm)	0.5017	0.6172	0.5567
Weight after testing (gm)	25.5979	24.9020	24.5936
Weight gain due to testing (gm)	0.0061	0.0050	0.0054
Initial thickness (mil)	33.0	33.1	32.9
Thickness after coating (mil)	35.4	36.9	36.2
Coating thickness (mil)	1.2	1.9	1.6
Thickness after testing (mil)	35.4	36.9	36.2
Thickness gain due to testing (mil)	0.0	0.0	0.0

TABLE 40. STATIC OXIDATION TEST: WEIGHT AND THICKNESS CHANGES.

Test temperature(°F)	Material	Overall weight change (gm) after			Overall thickness change (mil) after		
		8 hr	16 hr	24 hr	8 hr	16 hr	24 hr
800	Mo-0.5Ti TZM	-0.0001 +0.0003	+0.0007 +0.0001	+0.0004 0.0000	+0.1 -0.3	+0.1 -0.5	0.0 0.0
900	Mo-0.5Ti TZM	+0.0008 +0.0013	+0.0009 +0.0011	+0.0009 +0.0014	0.0 0.0	0.0 0.0	0.0 +0.2
1000	Mo-0.5Ti TZM	+0.0006 +0.0011	+0.0008 +0.0011	+0.0006 +0.0008	+0.2 +0.3	0.0 +0.1	+0.1 0.0
1100	Mo-0.5Ti TZM	+0.0003 +0.0004	+0.0002 +0.0007	+0.0008 +0.0793	0.0 +0.2	+0.1 0.0	+0.1 +0.6
1200	Mo-0.5Ti TZM	+0.0006 -0.0001	+0.0002 -0.0005	+0.0002 -0.0007	0.0 -0.2	+0.1 -0.5	0.0 0.0
1300	Mo-0.5Ti TZM	+0.0003 +0.0004	+0.0009 -0.0001	+0.0009 -0.0066	+0.2 +0.3	0.0 +0.2	0.0 0.0

In the simulated postassembly coating cycle employing 0.1 weight percent ammonium chloride PFR-6 pack mixture (item 3 in Table 38), the average coating life of the coated Mo-0.5Ti was lower than that resulting from the preassembly coating cycle alone (item 1 in Table 33). The reliability of the coating, as indicated by the confidence limit and standard deviation, decreased slightly after the postassembly coating cycle. Average weight gain and coating thickness increased as expected.

The TZM samples processed in a postassembly cycle (item 4, Table 38) demonstrated an average coating life nearly twice that achieved by preassembly coating alone (item 2, Table 38). The reliability of the coating, however, is quite poor as shown by the wide confidence limit. It should be noted that the TZM alloy again has a greater weight increase than the Mo-0.5Ti, although the coating thicknesses are approximately the same.

The edge and corner coatings of both TZM and Mo-0.5Ti samples processed in the postassembly cycle using 0.1 weight percent ammonium chloride were somewhat rough. This roughness, when viewed with the binocular microscope, consists of tiny cracks and a slight unicorn effect, suggesting the possibility of reduced oxidation protection along the edges and corners.

A reduction of the carrier compound content from 0.1 to 0.05 weight percent reveals several benefits as shown by comparing items 3 and 5 in Table 38. The average coating life at 3000°F is tripled, the reliability is slightly improved, and the coating condition at the edges and corners is improved.

The effect of the same carrier compound reduction on TZM alloy coatings is shown by comparing item 4 with item 6 in Table 38. The average coating life remains approximately the same, but a marked increase in reliability is realized as indicated by comparison of the confidence limits. As in the case of the Mo-0.5Ti alloy, only a slight decrease in average weight gain is recorded, although the ammonium chloride content of the pack has been reduced by 50 percent. Again, the coating condition at edges and corners shows great improvement.

3.7 STATIC OXIDATION TESTING

Since failure by oxidation of molybdenum disilicide coatings at temperatures far below their expected maximum useful temperature has been reported as silicide pest by Fitzer, Long, Maxwell, et al., preliminary tests to check this condition were initiated. Three PFR-6 coated Mo-0.5Ti test pieces were supported on high-temperature firebrick in an electric furnace and held at the temperatures listed below. A visual examination was made after each half-hour of test and the results of the observation are noted in the chart below.

The specific data for these samples after 37 hr of test (Table 39) indicated that the visual observations every half-hour were adequate to check for failure at these low temperatures. Testing resulted in a weight increase of approximately one percent of the coating weight. No measurable increase in specimen thickness resulted from this test.

Temperature (°F)	Time at Temperature (hr)	Observation
1100	3.0	no failure
1150	3.0	no failure
1200	3.5	no failure
1250	3.0	no failure
1300	3.0	no failure
1350	3.0	no failure
1400	3.0	no failure
1450	3.0	no failure
1500	3.0	no failure
1550	3.5	no failure
1600	3.0	no failure
1650	3.0	no failure

This preliminary work indicated that the PFR-6 coating was not subject to silicide pest under the test conditions used. It was recognized, however, that the few data available from this test should be verified by additional work. Therefore, 24-hr tests were performed over a wider temperature range, using PFR-6 coated Mo-0.5Ti and TZM 10-mil specimens.

Three coated samples of each type were tested in a static oxidizing atmosphere at temperatures from 800°F to 1300°F inclusive for periods up to 24 hr. The test results (Table 40) show that in only two cases were samples influenced by these exposures. In the TZM specimen exposed for 24 hr at 1300°F, two spots of white molybdenum trioxide powder and one hole in the substrate were visible, accounting for the weight loss. It is obvious that they were caused by weak spots in the coating which could possibly have developed in the handling of these specimens while hot. The other noteworthy event occurred after a 24-hr exposure of a TZM specimen at 1100°F. The relatively large weight gain and thickness increase were accompanied by an opaque white film covering most of the surface of the test sample.

An attempt was made to duplicate this phenomenon by conducting additional static oxidation tests at 1100°F on 10-mil samples of both Mo-0.5Ti and TZM alloys. Although tests were conducted for well over 100 hr, nothing resembling the previous phenomenon was noted. The greatest over-all weight change among any of the samples was 0.003%. As a result of this extended work, it appears that the PFR-6 coating is not subject to silicide pest under the conditions of test.

3.8 COATING COMPOSITION

A series of coating runs, using TZM specimens, were processed for 3, 9, 14, and 19 hr at 2050°F. One specimen from each run (labeled A, B, C, and D, respectively) was sectioned, mounted, and polished. These samples were then sent to Advanced Metals Research Corporation, Somerville, Massachusetts for electron beam microanalysis of their molybdenum, silicon, columbium, and zirconium content. The complete report from AMR is presented in Appendix II. Comments on specific aspects of the work are given below.

In all samples, the coating was found to be approximately 58 weight percent molybdenum and 42 weight percent silicon. These concentrations are very close to the calculated values for $MoSi_2$. The concentrations of molybdenum and silicon are quite constant over the coating layer. A sharp gradient exists at both the outer edge and the interface. The coating is therefore primarily $MoSi_2$, with only negligible amounts of other molybdenum silicides (Mo_3Si, Mo_3Si_2) or free silicon present.

The electron beam scans for columbium were complicated by the presence of large amounts of background interference. As a result, it was stated with some certainty that if any columbium were present, its concentration was less than 0.2 weight percent. In the light of this information, the coating on a series of samples was removed by severe bending. The coating thus obtained was sent to The Charles C. Kawin Co. in Chicago for spectroanalysis to determine the columbium content. Results of this examination showed the columbium content to be 0.05 percent.

Electron beam analysis for zirconium required a technique similar to that used for columbium. The background intensity in the zirconium analysis was such that the sensitivity was not as good as for columbium. However, it indicated that the zirconium concentration is less than 0.4 weight percent, with a 50 percent certainty that it is less than 0.2 weight percent.

Increasing process times caused a slight increase in the coating thickness, as may be seen in Fig. 2 thru 9 of Appendix II. It should be noted that these plots result from a scan of the coating at 45 degrees to the edge and thus any differences are actually 0.707 times as much as is indicated.

4. CONCLUSIONS

4.1 SPECIFIC CONCLUSIONS

As a result of the extensive experimental work reported in the preceding section, certain specific conclusions have been reached regarding the PFR-6 process and its parameters. These are summarized topically in the following paragraphs.

4.1.1 Statistical Evaluation of Optimized Process

The calculated average life and reliability of the PFR-6 coating applied on the intermediate scale under optimum conditions remains essentially the same as that originally determined in the first year's laboratory work. Departure from the original values is believed to be the result of normal experimental variation. The average life is approximately 1.4 hr in an oxidizing oxyacetylene torch test at a temperature exceeding 3000°F.

4.1.2 Preparation of Surface of Substrate

Proper surface preparation is necessary to obtain a satisfactory coating. The vibratory process, if controlled to avoid impregnation by small particles of abrasive, appears to be the most satisfactory of the several techniques investigated. Acid etching is also suitable, but requires special care in rinsing to avoid subsequent hydrogen embrittlement and excessive removal of substrate.

4.1.3 Preparation of Edges and Corners of Substrate

Edge and corner preparation is important if good coating protection is to be achieved. Minimum corner radius should be 0.125 in. and the minimum edge radius should be 0.005 in. (t/2 radius is desired, where t is material thickness). Vibratory finishing of the edges produced the most uniform radiusing and, in addition, did not require constant attention from the operator.

4.1.4 Coatable Alloys

It has been determined that a satisfactory PFR-6 coating can be applied to pure molybdenum, Mo-0.5Ti, and TZM.

4.1.5 Heat Transfer in the Retort

Because of the nature of the pack cementation process and the problems inherent in its scale-up, considerable effort must be expended in studying the kind of inert pack filler and its composition, size, and shape, in order to maximize heat transfer rate within a retort. Temperature gradient and heat flux studies must be conducted empirically because of the complexity of the system and the lack of thermodynamic data over the range of temperatures of interest. It was found that the most satisfactory inert filler material (considering heat transfer, coating quality, and coating life) is minus 20 mesh aluminum oxide grit. All other materials and combinations of materials that were investigated offered various objections which made them less satisfactory.

4.1.6 Control of Coating Quality on Edges

The quality of PFR-6 coating on the edges of the substrate was found to be influenced by the ratio of the coating deposition rate to the coating diffusion rate into the substrate. Fortunately it was found possible to influence this ratio by controlling both the carrier compound (ammonium chloride) concentration in the pack mixture and also the heating schedule for the retort. Optimum conditions for these variables are as follows: (1) depending on surface area to be coated and the volume of the retort, the ammonium chloride concentration varies inversely with retort volume in the range 0.1 to 0.3 weight percent of the pack, and (2) heating of the retort from room temperature to 2050°F should take no less than 5 hr, including a 1 hr hold at 1850°F.

4.1.7 Optimum Proportion of Carrier Compound

The ratio of carrier compound weight to substrate surface area was found to be a parameter useful for determining the amount of ammonium chloride to be used in the pack mixture for retorts of different sizes. The value of the ratio is established from consideration of retort volume, substrate surface area to be coated, required coating life, and coating condition along the edges of the substrate to avoid the unicorn effect.

4.1.8 Columbium Particle Size

Variation of the columbium powder particle size over the range from 40 mesh to minus 200 mesh does not statistically affect coating life and other properties.

4.1.9 Pack Material Reuse

Because several of the pack components are relatively expensive, reuse of the pack mixture would reduce the cost of applying PFR-6 coating. It was found that the amounts of silicon and columbium in the used pack mixture were only slightly reduced from those initially present. However, reuse of the pack mixture produced samples with lifetimes in the test torch that did not follow a regular pattern so that it could not be demonstrated that the coating was either definitely affected or unaffected. Reuse of the pack remains a technical and economic possibility, but much more work must be done on the effect of reuse on the statistical lifetime of the coating.

4.1.10 Coating of Riveted Assemblies

Assembly of component parts of a composite refractory metal structure is best accomplished at present by riveting. Components to be riveted together require two coating cycles, one before assembly and the second after assembly, in order to assure good overall oxidation resistance

4.1.11 Non-Destructive Determination of Coating Life

Although it is acknowledged that positive proof of coating life is demonstrated only by actual test, an attempt was made to find an indication of expected coating life from some non-destructive measurement. Two parameters that were found suitable for this purpose are coating thickness and gain in weight of a unit area of substrate due to the deposition of the coating. The second parameter has been termed unit area weight gain. As is to be expected, coating life varies with both coating thickness and unit area weight gain. Furthermore, for a given parameter, coating life is increased by longer process times.

4.1.12 Silicide Pest

PFR-6 coated samples were exposed to a static oxidizing atmosphere for lengths of time up to 100 hr at temperatures from 800 to 1650°F. There was no evidence that PFR-6 coating is subject to silicide pest under these test conditions.

4.2 GENERAL CONCLUSIONS

The PFR-6 coating process, initially developed on a laboratory scale, has been improved to the point where it can be effectively employed on an intermediate scale to protect several molybdenum alloys and their riveted assemblies, retaining essentially the same statistically-proved reliability and lifetime. Despite the problems in heat flux distribution and the process reactions engendered by the scale-up to substantially larger retorts, it was possible to demonstrate conclusively that coating of large components of the order of 1.5 ft in the longest dimension could readily be accomplished. At the same time, process conditions and process parameters were optimized to attain the most satisfactory overall coating quality.

5. RECOMMENDATIONS

It is recommended that manufacturing-scale methods be developed for the PFR-6 coating process. The objective is to attain a capability of coating full-size, complex reentry vehicle components fabricated from molybdenum alloys so as to provide reliable oxidation protection at temperatures up to 3000°F for a statistically-proven lifetime. In this investigation, general process principles upon which may be based the scale-up of future cementation coatings would be evolved. Simultaneously, process studies should be continued to establish optimum conditions under which the coating process can be employed on an industrial scale.

APPENDIX I

EXPERIMENTAL PFR-6 COATING PROCESS SPECIFICATION

1. BASE MATERIAL

1.1 UNALLOYED MOLYBDENUM SHEET

1.1.1 Manufacture

The molybdenum shall be a product of consumable electrode,vacuum-arc-cast ingots or electron beam melted ingots.

1.1.2 Chemical Composition

The chemical analysis shall show 99.900% molybdenum minimum with all other elements at 0.100% maximum. Carbon shall be 0.010% minimum and 0.040% maximum.

1.1.3 Structure

The structure shall exhibit fibered grains with a maximum of 4% recrystallization visible metallographically. After heating for 0.5 hr at 1800°F, not more than 10% recrystallization shall be visible metallographically.

1.1.4 Mechanical Properties

The tensile properties shall be as follows:

Parallel to Rolling	Minimum
Ultimate (psi)	93,000
Yield, 0.2% offset (psi)	85,000
Elongation, % in 2 inches	10

Transverse to Rolling	Minimum
Ultimate (psi)	95,000
Yield, 0.2% offset (psi)	87,000
Elongation, % in 2 inches	8

The room temperature bend ductility on samples 0.75 in. wide by 2 in. long bent through 105 deg at a moderate rate shall be 2t (t = thickness) maximum as bend either in the rolling direction or transverse to the rolling direction. Bend transition temperature shall be 100°F maximum on samples bent either in the rolling direction or transverse to rolling. Room temperature hardness shall be 240 DPH minimum and 280 DPH maximum.

1.1.5 Finish

All sheet shall exhibit a hot-cold rolled, descaled surface with sheared edges unless a 120-grit belt ground surface is specified.

1.1.6 Quality

All material shall be clean, smooth, and free of visual defects such as slivers, cracks, and laminations.

1.2 MOLYBDENUM-0.5% TITANIUM SHEET (Mo-0.5Ti)

1.2.1 Manufacture

The Mo-0.5Ti sheet shall be a product of consumable electrode, vacuum-arc-cast ingots or electron beam melted ingots.

1.2.2 Chemical Composition

The chemical analysis shall show 99.340% molybdenum minimum. Carbon shall be 0.010% minimum and 0.040% maximum. Titanium shall be 0.400% minimum and 0.550% maximum.

1.2.3 Structure

The structure shall exhibit fibered grains with a maximum of 4% recrystallization visible metallographically. After heating for 0.5 hr at 2100°F, not more than 10% recrystallization shall be visible metallographically.

1.2.4 Mechanical Properties

The tensile properties shall be as follows:

Parallel to Rolling	Minimum
Ultimate (psi)	100,000
Yield, 0.2% offset (psi)	95,000
Elongation, % in 2 inches	6

Transverse to Rolling	Minimum
Ultimate (psi)	115,000
Yield, 0.2% offset (psi)	100,000
Elongation, % in 2 inches	4

The room temperature bend ductility on samples 0.75 in. wide by 2 in. long bent through 105 deg at a moderate rate shall be 2t (t = thickness) as bent parallel to rolling and 3t as bent transverse to rolling. Bend transition temperature shall be 100°F maximum on samples bent either in the rolling direction or transverse to rolling. Room temperature hardness shall be 285 DPH minimum and 312 DPH maximum.

1.2.5 Finish

All sheet shall exhibit a hot-cold rolled, descaled surface with sheared edges unless a 120-grit belt ground surface is specified.

1.2.6 Quality

All material shall be clean, smooth, and free of visual defects such as slivers, cracks, and laminations.

1.3 MOLYBDENUM-0.5% TITANIUM-0.08% ZIRCONIUM SHEET (TZM)

1.3.1 Manufacture

The TZM sheet shall be a product of consumable electrode, vacuum-arc-cast ingots or electron beam melted ingots.

1.3.2 Chemical Composition

The chemical analysis shall show 99.25% molybdenum minimum. Carbon shall be 0.01% minimum and 0.03% maximum. Titanium shall be 0.40% minimum and 0.55% maximum. Zirconium shall be 0.06% minimum and 0.12% maximum.

1.3.3 Structure

The structure shall exhibit fibered grains with a maximum of 4% recrystallization visible metallographically. After heating for 0.5 hr at 2200°F, not more than 10% recrystallization shall be visible metallographically.

1.3.4 Mechanical Properties

The tensile properties shall be as follows:

Parallel to Rolling	Minimum
Ultimate (psi)	125,000
Yield, 0.2% offset (psi)	105,000
Elongation, % in 2 in.	7
Transverse to Rolling	**Minimum**
Ultimate (psi)	135,000
Yield, 0.2% offset (psi)	110,000
Elongation, % in 2 in.	5

The room temperature bend ductility on samples 0.75 in. wide by 2 in. long bent through 105 deg at a moderate rate shall be 2t (t = thickness) as bent parallel to rolling and 3t as bent transverse to rolling. Bend transition temperature shall be 100°F maximum on samples bent either in the rolling direction or transverse to rolling. Room temperature hardness shall be 290 DPH minimum and 315 DPH maximum.

1.3.5 Finish

All sheet shall exhibit a hot-cold rolled, descaled surface with sheared edges unless a 120-grit belt ground surface is specified.

1.3.6 Quality

All material shall be clean, smooth, and free of visual defects such as slivers, deep scratches, cracks, and laminations.

2. PACK MATERIALS

2.1 COLUMBIUM POWDER

Particle size: -200 mesh

Chemical analysis:

Cb	99.00% min.
C	0.50% max.
Ta	0.50% max.
Ti	0.04% max.
Fe	0.01%

2.2 SILICON POWDER

Particle size: -48 mesh

Chemical analysis:

Si	97.00% min.
SiO_2	1.80% max.
Fe	0.70% max.
C	0.50% max.

Other impurities: trace

2.3 UREA CRYSTALS

Technical Grade

2.4 AMMONIUM CHLORIDE

Technical Grade

2.5 ALUNDUM (FUSED ALUMINUM OXIDE) GRIT

Particle size: -20 mesh straight grit

Chemical analysis:

Al_2O_3	99.49% min.
SiO_2	0.05% max.
Fe_2O_3	0.10% max.
TiO_2	0.01% max.
Na_2O	0.35% max.

3. PROCESS PROCEDURE

3.1 METAL CUTTING

The base metal shall not be overheated during cutting operations. A water flooded shellac wheel saw (or equivalent) shall be used.

3.2 EDGE, CORNER, AND SURFACE PREPARATION

The metal surface shall be ground on a 120-grit wet belt, well flooded at all times, unless the metal is supplied in this condition. The corners of the specimen shall be ground to a 0.125 in. radius on a 50-grit wet belt. The edges of the specimen shall be ground to a 0.005 in. minimum radius (t/2 minimum desired, where t is material thickness) on a 120-grit wet belt. The edges and corners shall then be ground with a 240-grit wet belt. The entire sample shall then be polished with polishing compound on a cotton fabric wheel until all contamination and stains are completely removed.

3.3 CLEANING

The metal samples shall be scrubbed with a warm detergent solution, thoroughly rinsed, and then dried between paper towels. The samples shall be soaked in acetone for a minimum of 15 minutes and redried immediately prior to packing into the retort. After the acetone wash, clean tweezers or clean cotton gloves shall be used to handle the samples.

3.4 POWDER WEIGHING AND MIXING

Each constituent shall be weighed carefully and accurately to within 0.1 percent of required weight. All the constituents shall be blended together immediately and mixed thoroughly to insure homogeneity of the packing compound. Use of a twin-cone blender is preferred.

3.5 RETORTS

All retorts shall be constructed of 1/4 in. or 3/8 in. type 304 stainless steel or Inconel, bent and arc welded to the desired shape and size. The section of the retort that fits tightly against the cover shall be milled level and flat to insure close contact with the cover. The inside of the retort shall be sandblasted thoroughly with aluminum oxide grit before packing to prevent contamination of the batch.

3.6 PACK COMPOSITION

The pack shall be prepared as follows, employing materials specified in section 2:

Material	Weight Percent
Columbium powder	2.0
Silicon powder	8.5
Urea crystals	1.0
Ammonium chloride	0.1 to 0.3*
Alundum	balance

*Varies with retort size.

3.7 PACKING

Part of the blended powders shall be placed in the retort to provide a suitable support for the samples. The samples or parts shall then be placed in this powder and aligned so that a minimum distance of 0.5 in. is maintained between samples or between a sample and the retort walls. A minimum of 1.5 in. shall be maintained between any sample and the top of the retort. The remaining pack composition shall be charged around and over the samples, insuring good contact at every point. The retort cover shall be fitted tightly in place and the entire retort inverted so that the cover is underneath.

3.8 RETORT SEALING

The sealing compound (glass frit) shall be packed around the retort. The retort cover shall be so designed that a channel exists between the lip of the cover and the retort wall. This will allow the seal to be placed completely around the retort. The retort shall then be placed in a suitable furnace for processing.

3.9 PROCESSING THE BATCH

After the retort is in the furnace and the furnace is closed, the temperature recording equipment and the exhaust fan system shall be turned on. The temperature control unit shall be set to 2050°F and the power turned on. The retort shall be heated to 1500°F in 2.5 to 3 hr and from 1500°F to operating temperature in 1.5 to 2 hr. Once the processing temperature is reached, the timer control shall be set for 7 hr at operating temperature. After the cycle is completed, the power shall be turned off and the retort allowed to cool in the furnace until a temperature of 800°F maximum is reached. The retort shall then be removed from the furnace and air-cooled or water-spray cooled. The retort shall be opened and the samples removed. The spent pack compound shall be removed and stored for later processing.

3.10 CLEANING AND HANDLING OF COATED SPECIMENS

Samples removed from the retort shall be brushed off with a fiber brush or washed in clean warm water to remove any pack compound that may be clinging to the specimens. The samples shall then be placed in suitable envelopes or other containers, or wrapped in paper towels, depending on ultimate disposition. Containers shall be identified to indicate the sample history.

APPENDIX II

ELECTRON BEAM MICROANALYSIS OF PFR-6 PROTECTIVE COATINGS

Prepared by

Advanced Metals Research Corp.

The concentration gradients of Mo and Si were determined in four samples of the Pfaudler PFR-6 coating on molybdenum. A search for the presence of Nb and Zr was also carried out. As anticipated, the coatings were shown to be MoSi$_2$ in all cases. Although Cb is expected to contribute to the coating formation, none was found. No Zr in excess of 0.2 w/o was detected anywhere in the coating layer or substrate.

The concentration determination was performed with the AMR electron beam microanalyzer (Fig. 1).* A beam of electrons is accelerated with a high potential and focussed by means of electromagnetic lenses to a diameter of about 1-2 microns at the surface of the specimen to be investigated. As in an x-ray tube the specimen will act as a primary source of x-rays. A continuous or white spectrum is produced as well as fluorescent x-rays characteristic of the elements excited by the electron beam. A chemical analysis of the excited area is afforded by analysis of the characteristic x-ray lines by means of a single crystal x-ray spectrometer.

A curved mica crystal focussing goniometer employing a helium path and flow-proportional counter was set up to record the Si Kα, Mo Lα, Nb Lα and Zr Lα characteristic x-ray lines.

Four samples of the PFR-6 coating A, B, C and D were mounted and polished at Pfaudler. Copper slabs were used to separate each sample and to protect the coating edges during polishing.

Although previous analysis of these coatings (AMR 1167) had been performed by "point counting" in fixed steps across the coating layers, past experience has indicated that a second procedure provides as much statistical accuracy and allows a greater number of scans to be taken. This procedure involves motor driving the specimen beneath the beam while chart recording the available x-ray intensity. The spectrometer is aligned to record the radiation of a particular characteristic line such as Si Kα and the traverses are taken at an angle of 45° to the coating-matrix interface.

The intensity distributions obtained are calibrated as a function of concentration by means of calculations described in AMR 1167. In short, however, these involve corrections for absorption and fluorescence applied to intensity ratios obtained by comparing the alloy intensities to those from pure element standards.

In general, a few scans were taken and the most representative chosen for presentation. Metallographic examination had revealed that the coatings were fairly uniform in thickness. A few pores or cracks were noted. Under polarized light, the individual grains in the coating could be seen. This examination revealed an apparent interface, or line, generally paralleling the metal-coating interface and located between the surface and substrate interface. No concentration deviations ascribable to this feature were noted.

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*Deleted from this text.

Fig. 2-5 are typical chart records obtained for the Mo distributions in samples A-D, respectively. Fig. 6-9 are similar records for the Si distribution.

The gradients are similar to those obtained in every examination of coatings of this type. The layer exhibits a constant composition of Mo and Si and rather a sharp gradient at the coating-substrate interface.

An infinitely sharp interface would be represented by a gradient over a distance of 4μ or less (scans at 45° to interface). Therefore, any gradients noted which extend over somewhat larger distances must be considered as real.

The concentrations of Mo and Si are about 58 and 42 w/o, respectively. These concentrations, accurate to ± 5% of the amount present (calculation uncertainties) are quite close to those of $MoSi_2$ as expected.

The Si scan obtained on Sample C appears a little lower than the others but this is not significant. Actually, the only real differences in the scans are a result of the traversing of pores, cracks or foreign included matter.

Columbium is an intentional addition to the coating formation procedure and might be expected to contribute to the superior performance of the PFR-6 coating. For this reason, rather an extensive effort was made to affirm the presence of Cb in the coating layer. Unfortunately, none was found.

In addition to a large number of scans across the coating, searches along the coating at various positions in the coating layer and even at the surface were performed. No reproducible intensity increases over background were noted.

Fig. 10-13 are typical chart records obtained for the intensity distributions with the spectrometer aligned for $NbL\alpha$. As indicated in Fig. 14 these scans are simply representative of the background intensity variations. In fact, the off-peak background determined is even slightly higher than the intensity recorded at the correct diffraction angle. This effect is not unusual, however, and is simply the result of intensity variations due to the presence of nearby strong Mo L series peaks.

It can be stated with some certainty that if any Cb is present its concentration is less than 0.2 w/o.

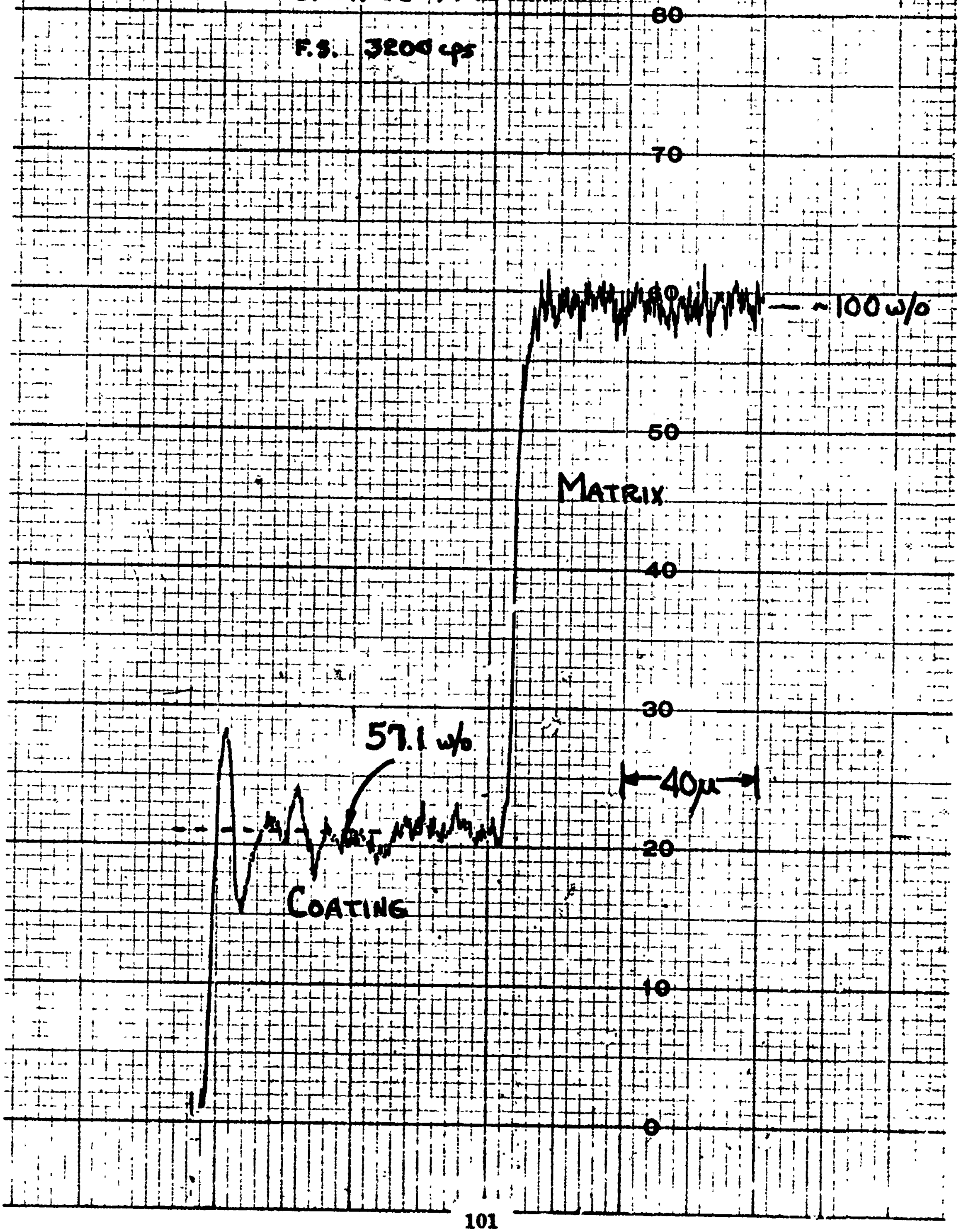
Zirconium had been reported as a possible impurity addition resulting from deterioration of the furnace lining used during production. The same careful search for Zr as for Nb was made. Due to the spectral position of a nearby Mo L series line, rather a drastic change in background intensity at the $Zr\ L\alpha$ position occurs. As a result the sensitivity of the analysis is not as good as that for Nb.

There is no need to exhibit the recorded distribution scans but it can be stated that the Zr concentration is less than 0.4 w/o. Actually there is a 50% certainty that the concentration is even less than 0.2 w/o.

In conclusion, the usual $MoSi_2$ layer has been found for all coating samples analyzed. Just as with other PFR-6 coatings examined, the presence of Cb could not be established. If Zr is present as an impurity its concentration is extremely low.

FIG. 2 Mo DISTRIBUTION

SAMPLE A



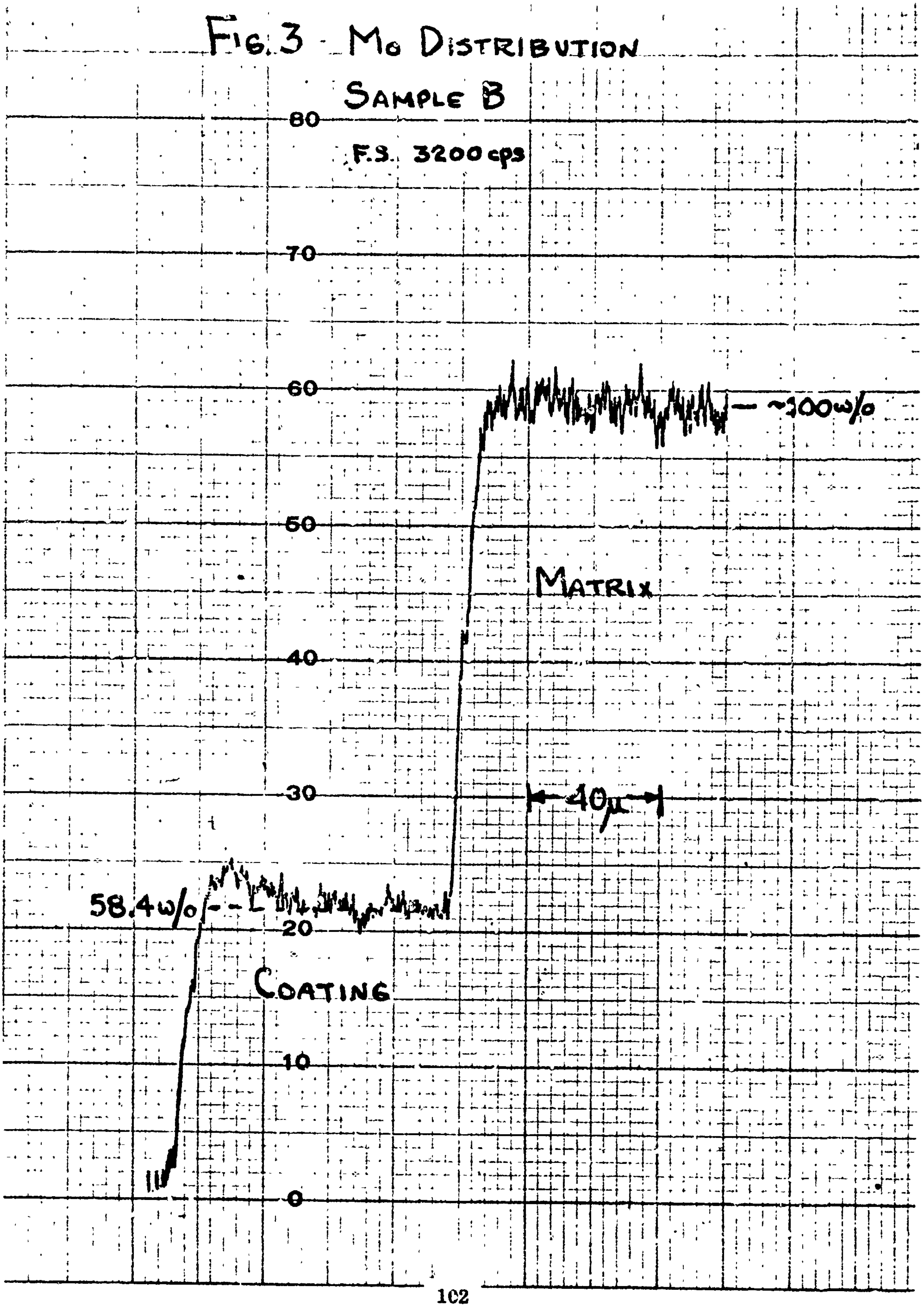


Fig. 3 Mo Distribution

Sample B

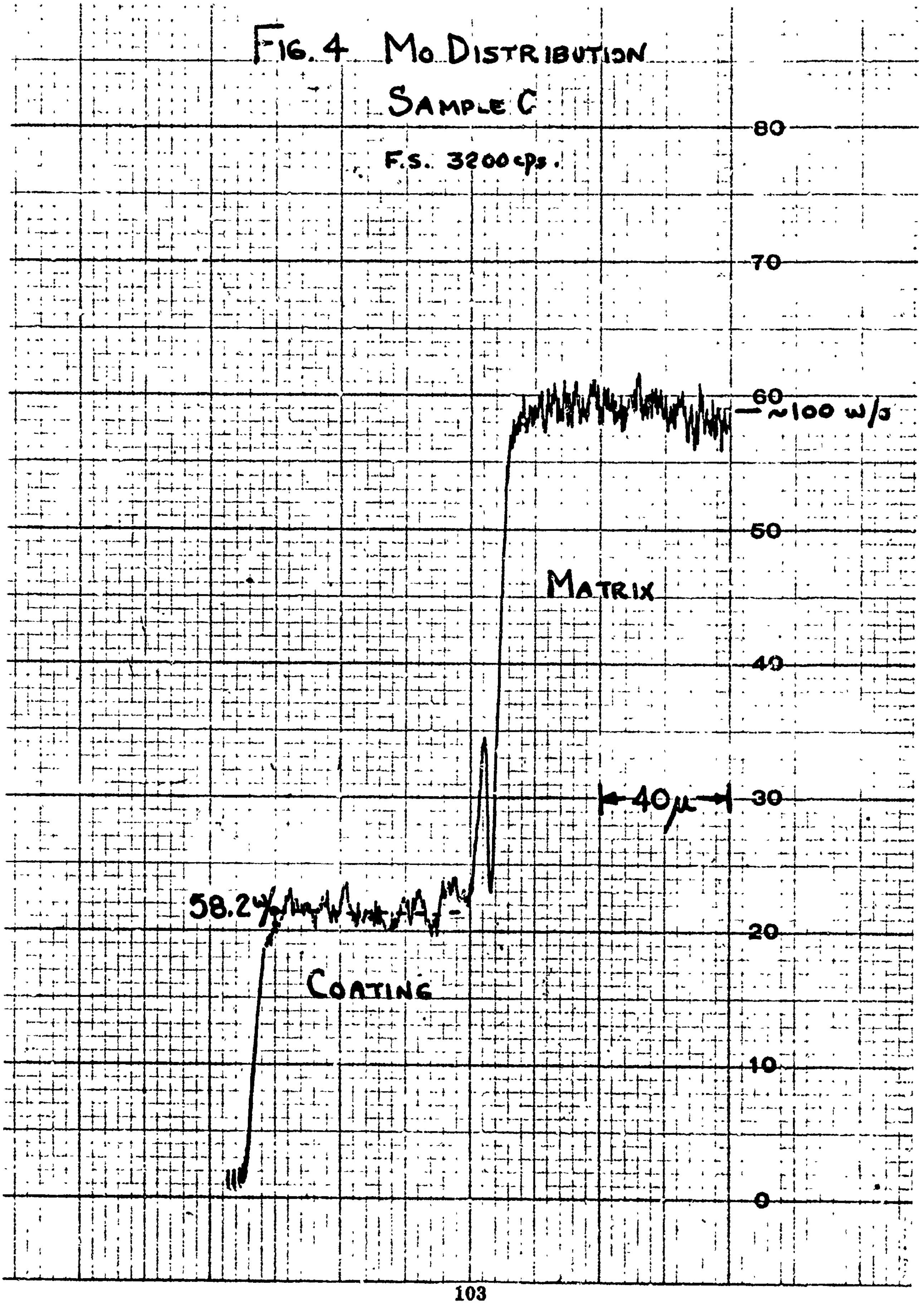
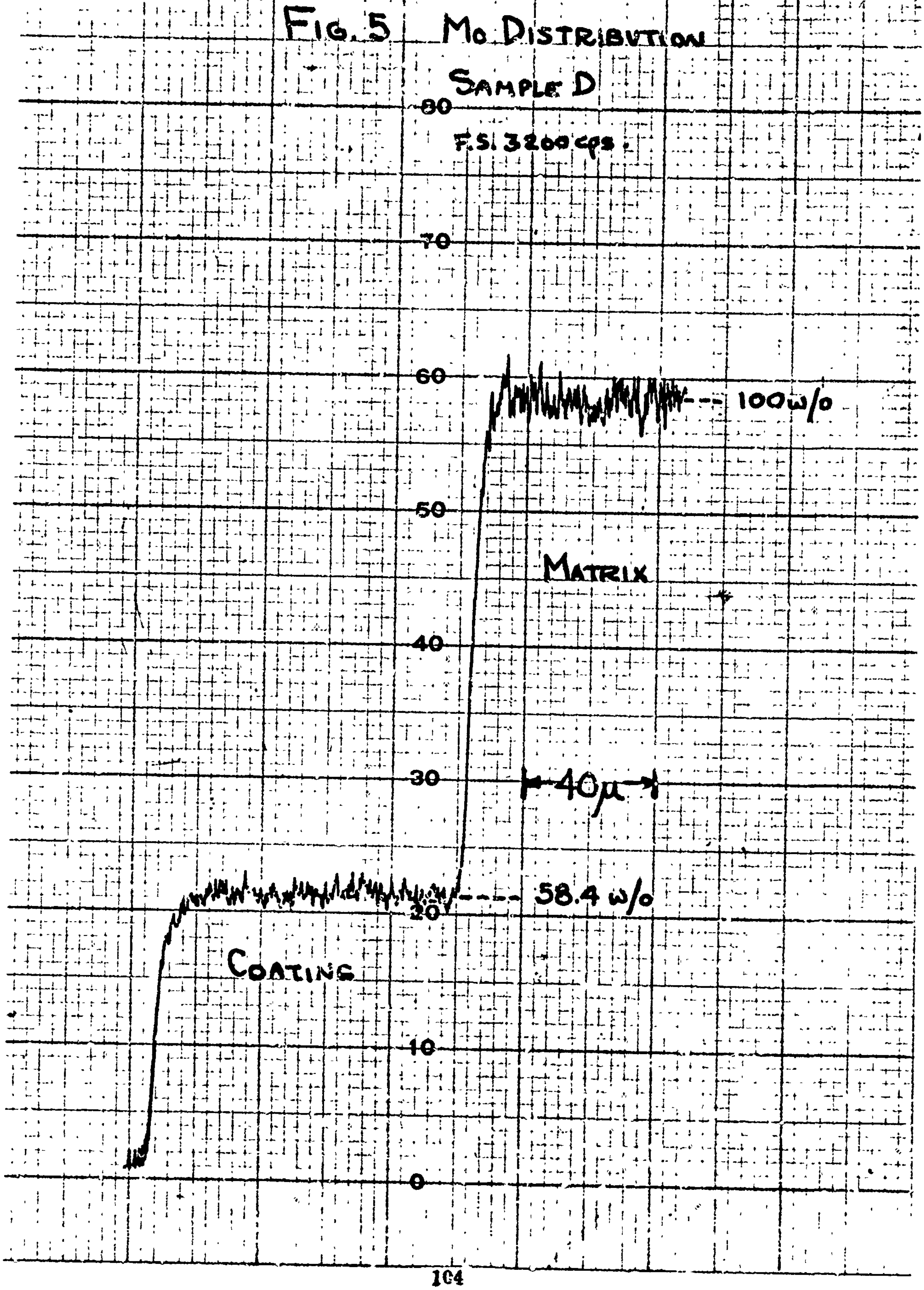


FIG. 4 Mo DISTRIBUTION

SAMPLE C

F.S. 3200 cps.

FIG. 5 Mo DISTRIBUTION



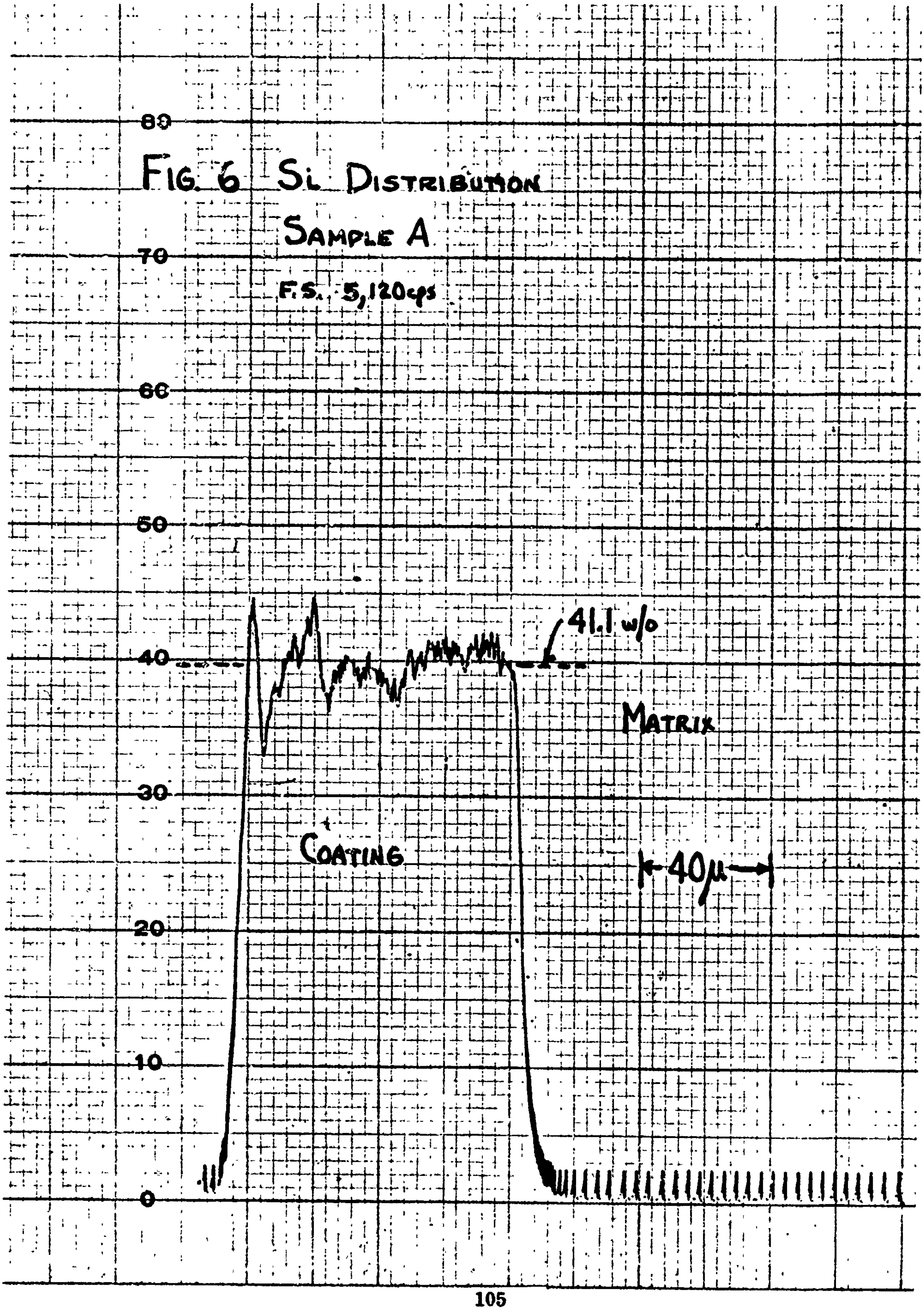


FIG. 6 Si DISTRIBUTION
SAMPLE A
F.S. 5,120cps
80
70
60
50
41.1 w/o
40
MATRIX
30
COATING
40μ
20
10
0

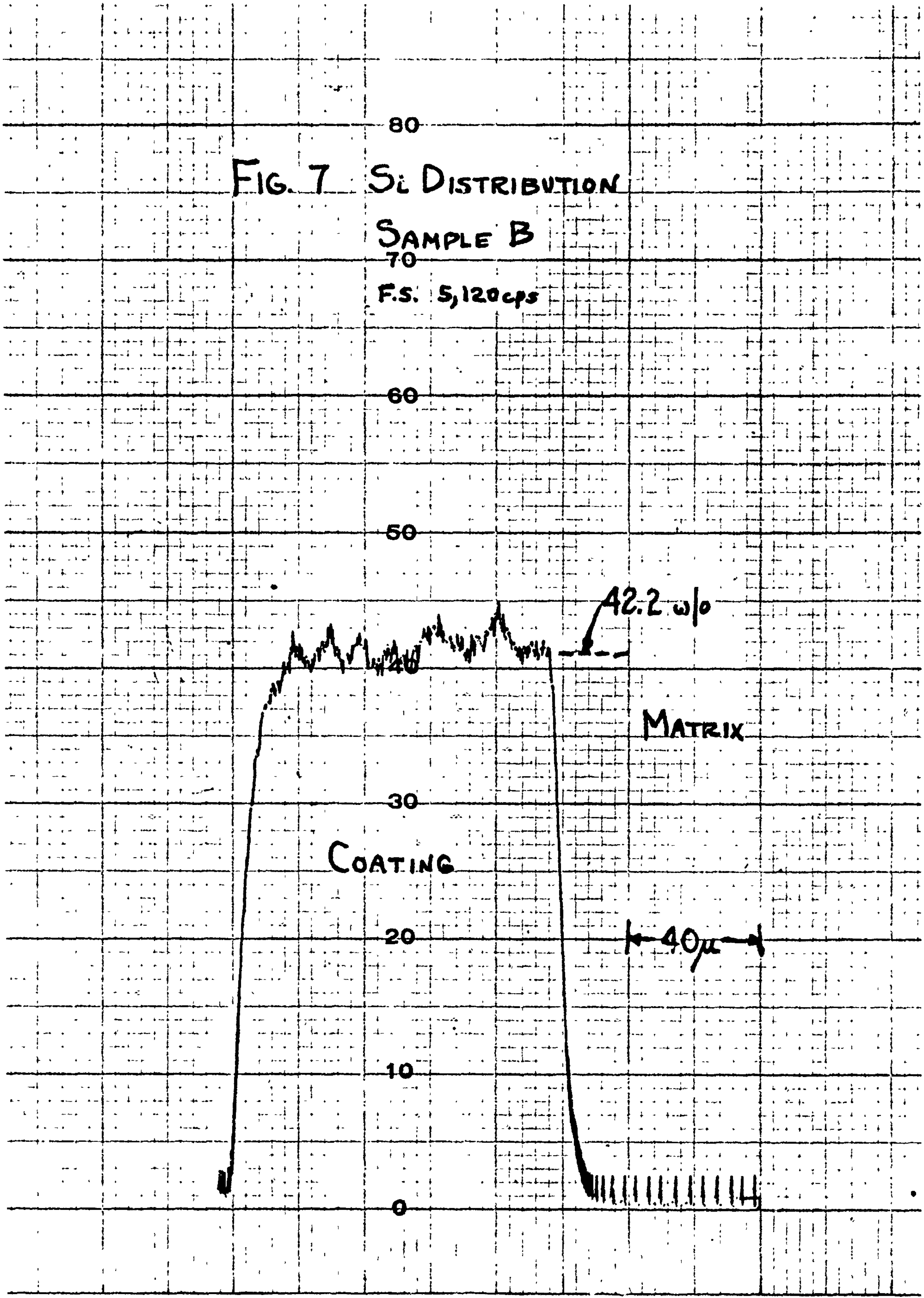


FIG. 7 Si DISTRIBUTION

SAMPLE B

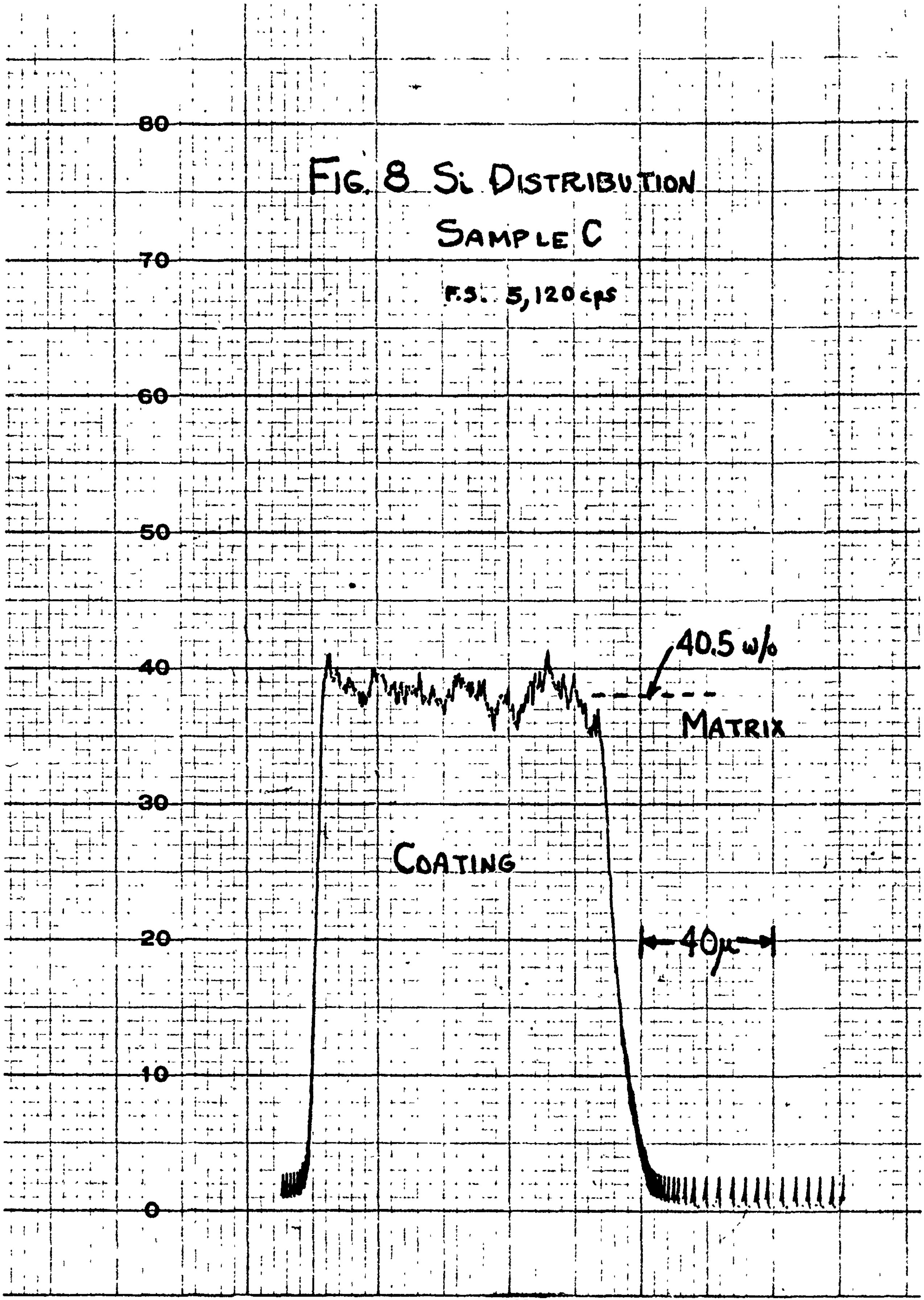


FIG. 8 Si DISTRIBUTION
SAMPLE C
F.S. 5,120 cps
80
70
60
50
40
30
20
10
0
40.5 w/o
MATRIX
COATING
40μ

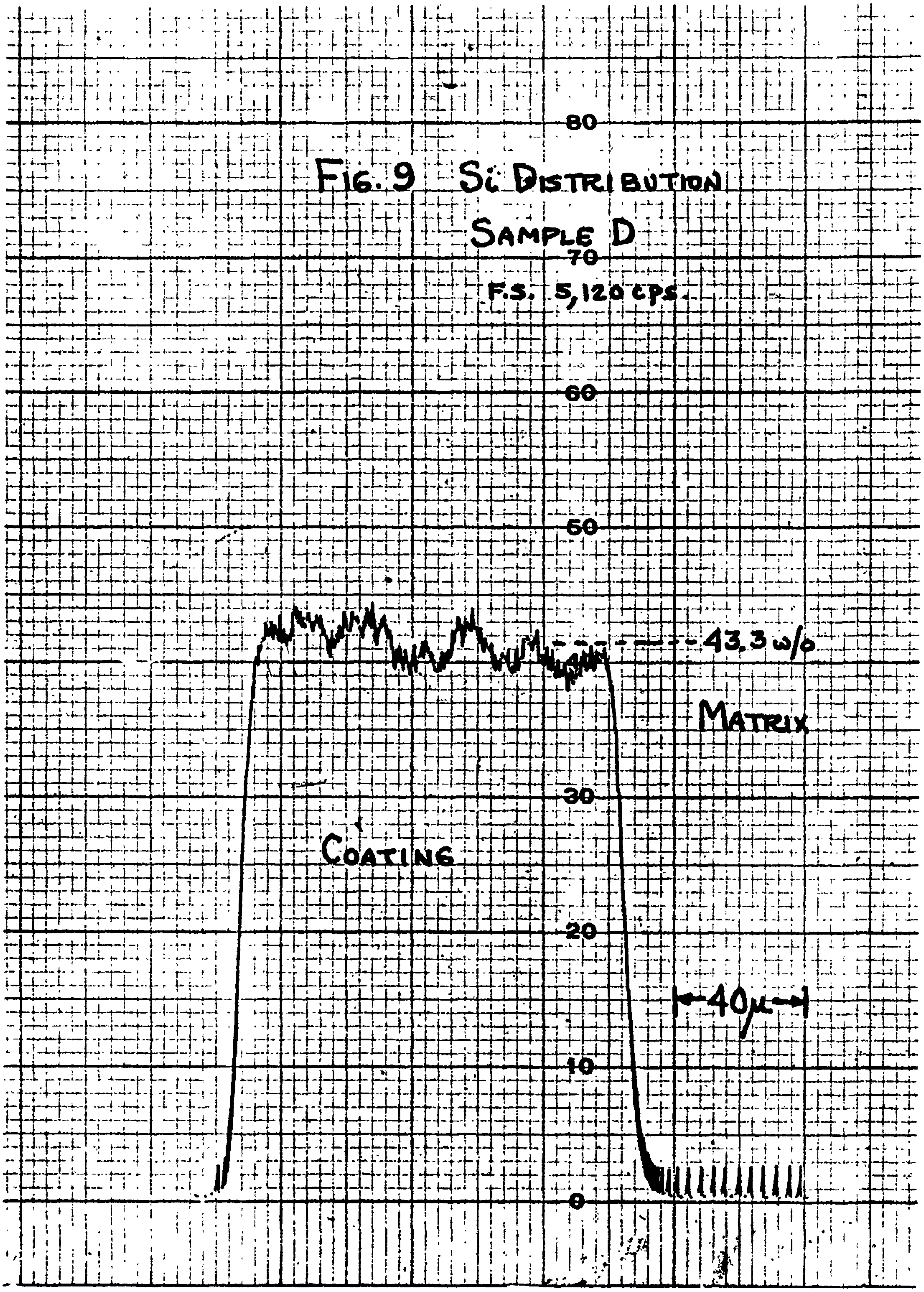


FIG. 9 Si DISTRIBUTION
SAMPLE D

F.S. 5,120 cps.

FIG. 10 Nb (Cb) DISTRIBUTION

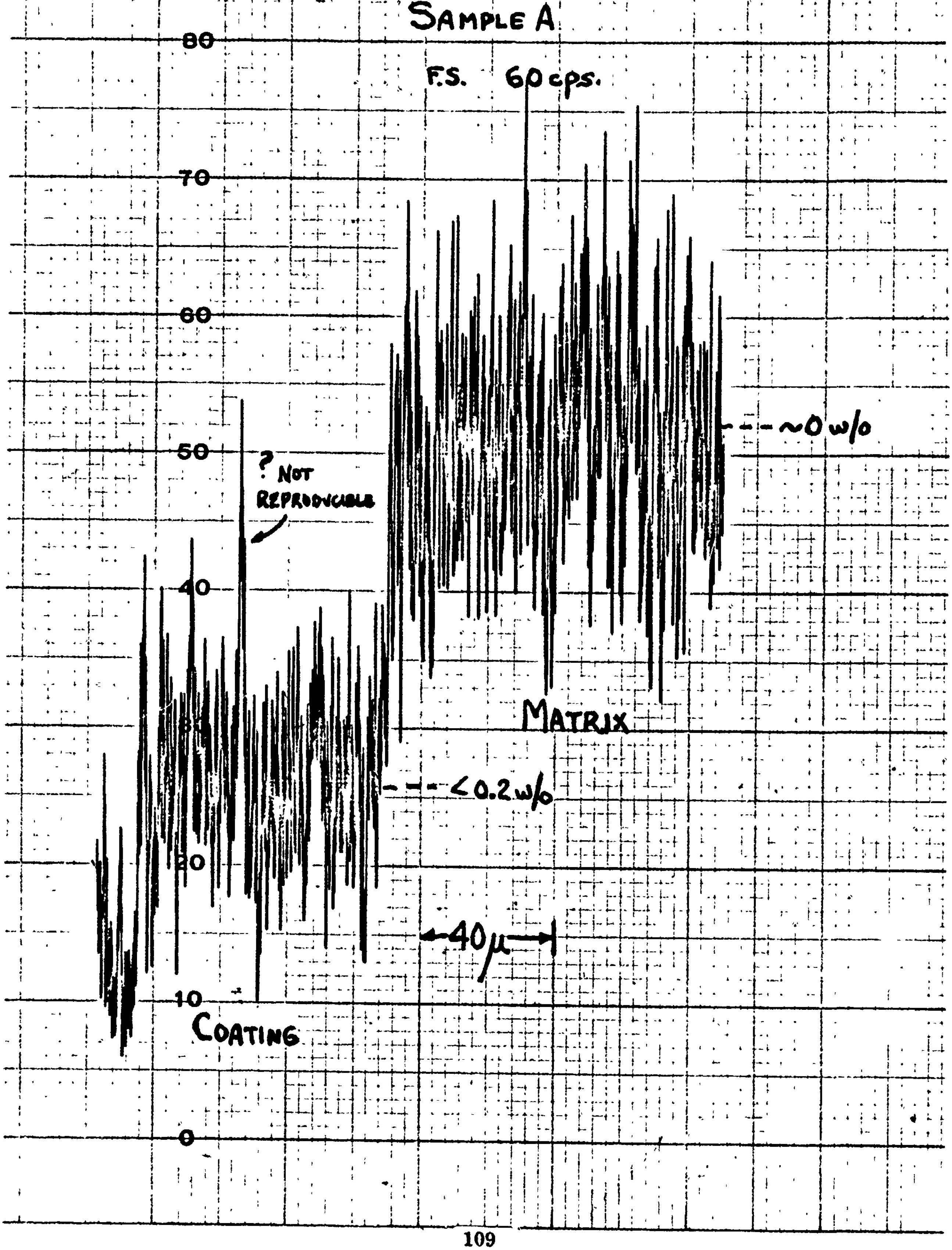
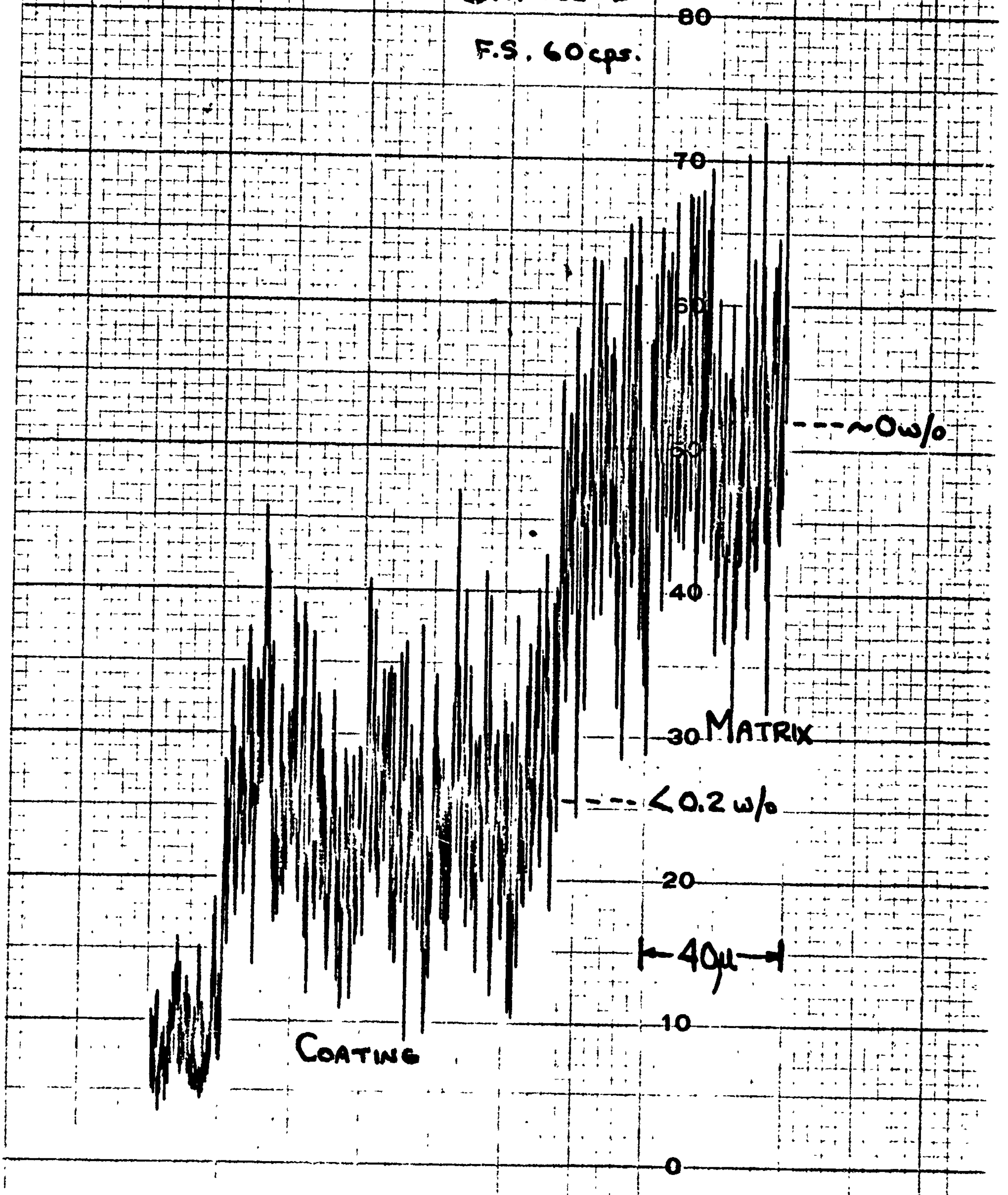


FIG. 11 Cb DISTRIBUTION

SAMPLE B



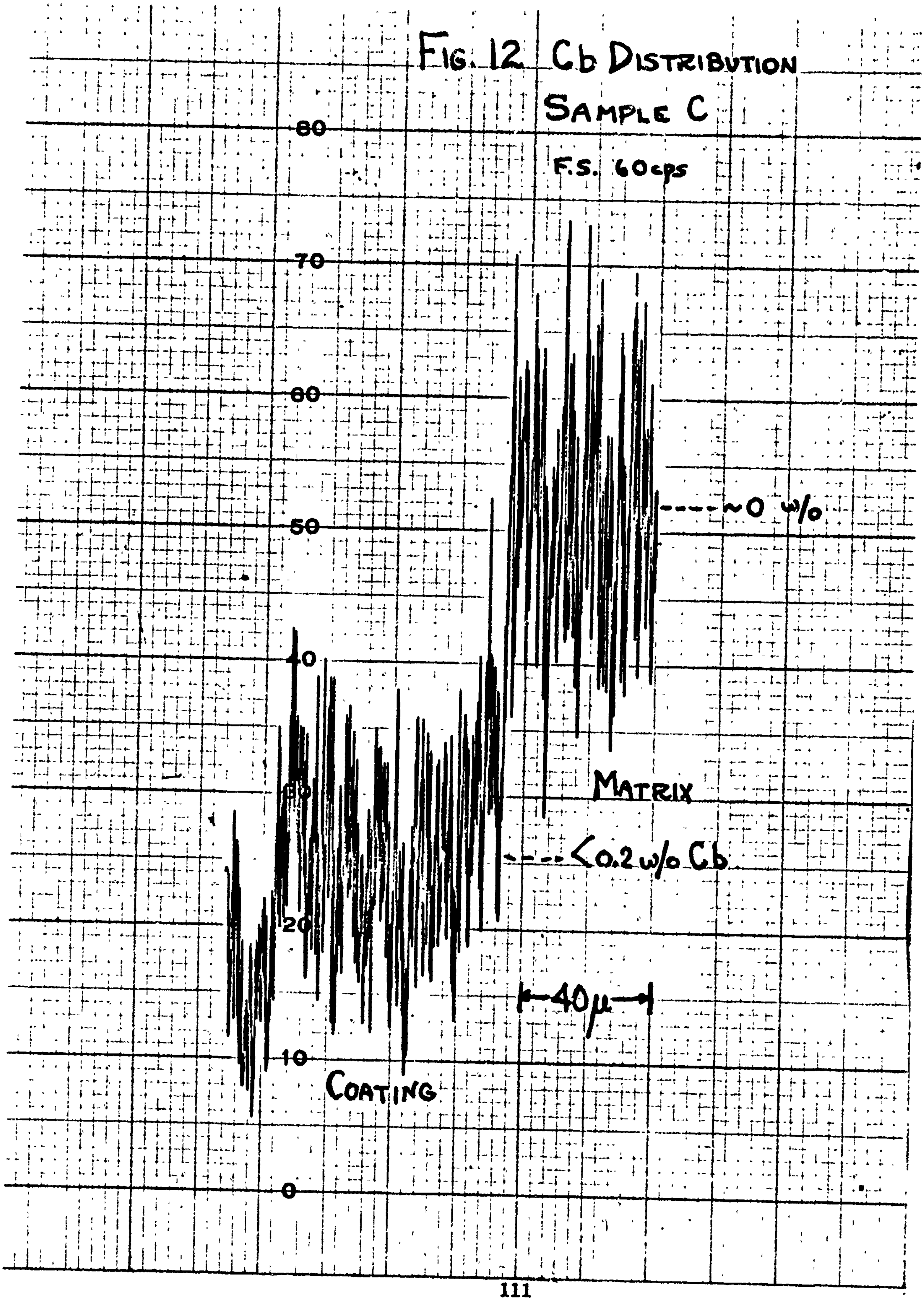


Fig. 12 Cb Distribution

Sample C

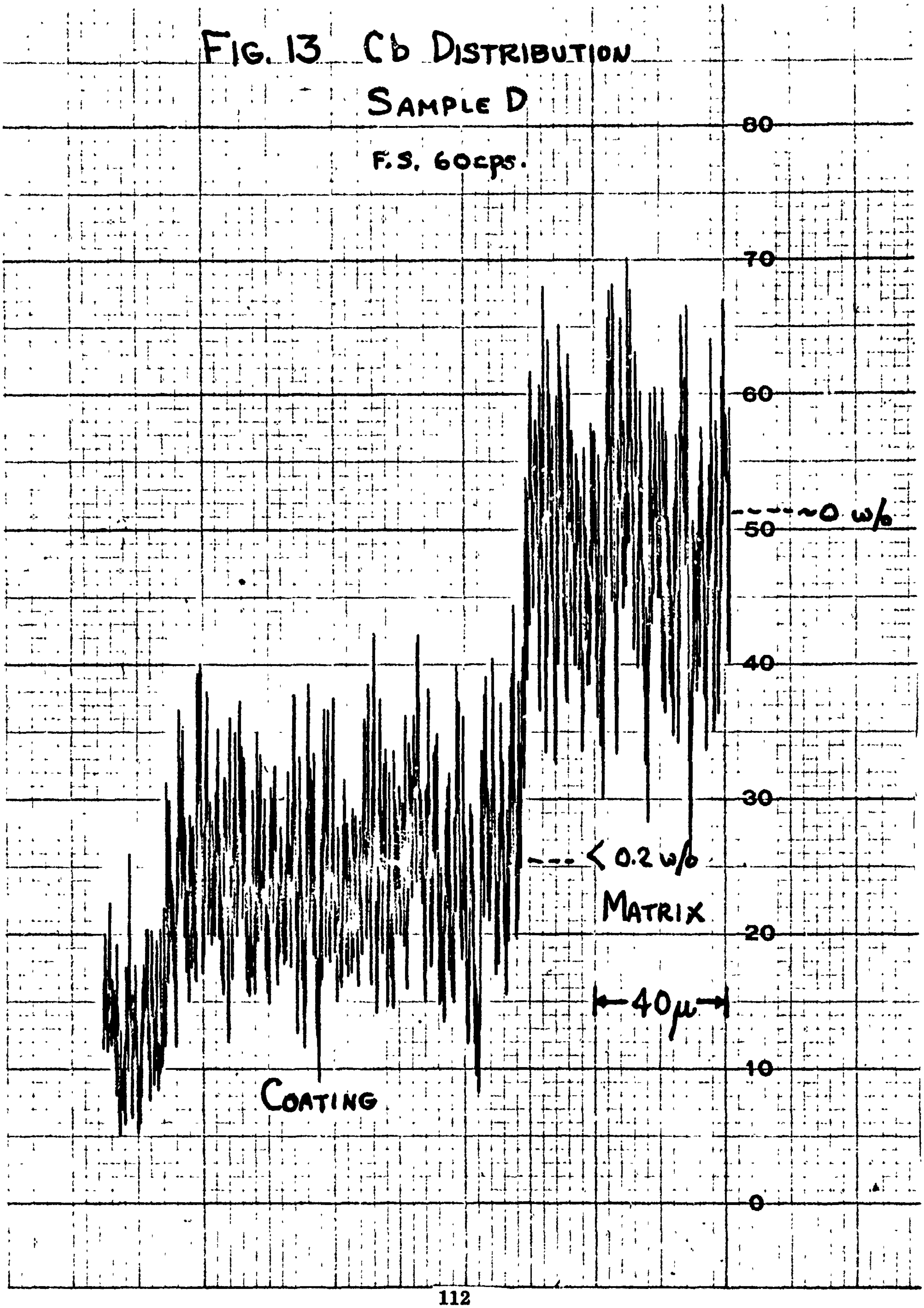


FIG. 13 Cb DISTRIBUTION

SAMPLE D

F.S. 60cps.

FIG. 14 COMPARISON OF BACKGROUND INTENSITY TO Cb DISTRIBUTION

F.S. 60 cps.