ML TDR 64-74

AD0603021 - A

DEVELOPMENT OF A POWDER AND/OR GAS CEMENTATION PROCESS FOR COATING MOLYBDENUM ALLOYS FOR HIGH TEMPERATURE PROTECTION.

TECHNICAL DOCUMENTARY REPORT No. ML TDR 64-74

JUNE 1964

AIR FORCE MATERIALS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
= US AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

[redacted]

Project No. 7381, Task No. 738102

[redacted]

(Prepared under Contract No. AF 33(616)-7383 by the
Chromalloy Corporation, W. Nyack, New York;
Herman Blumenthal and Neil Rothman, authors.)

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500 - July 1964 - 162-44-902

FOREWORD

This report was prepared by Chromalloy Corporation under USAF Contract No. AF33(616)-7383. Battelle Memorial Institute was a major subcontractor. The contract was initiated under Project 7381, Task No 738102. The work was administered under the Air Force Materials Laboratory, Research and Technology Division with L. N. Hjelm acting as Project Engineer.

All coating preparations and most of the oxidation testing were done by H. Blumenthal and N. Rothman at Chromalloy Corporation.

The authors wish to express their gratitude to Dr. C. A. Krier of Battelle who conducted the metallographic and chemical analyses and Dr. G. A. Beatty of Battelle who designed the statistical experiment and evaluated the data. The valuable comments of Drs. D. N. Williams and R. Ogden of Battelle and Messrs. M. Epner and R. L. Wachtell of Chromalloy during the course of this program were of invaluable aid.

ABSTRACT

As prepared W-2 coating on Mo-0.5Ti was found to be essentially $MoSi_2$. Upon exposure at 2700°F. the coating becomes three phase and develops an oxidation resistant glaze.

A statistically designed experiment was run on two levels of each of nine process variables in order to optimize the W-2 coating process. This experiment indicated that the three most important process variables were time and temperature of processing and mixing of the coating powders. Soundness of the Mo-0.5Ti surface and acid etching of the surface were of secondary importance. Purity, particle size and age of powder mixture and retort material were, statistically, minor in importance.

The recommended optimum coating would be produced by processing uncontaminated surface Mo-0.5Ti etched and honed. The work piece should be immersed in a commercial purity, -60 plus 150 mesh powder that is well mixed. The work should be processed twice (12 hours at temperature each time) at 1900°F. in a steel retort. The coating produced should have a wear life of 47 hours and a standard deviation of 8 hours at 2700°F. under the oxidation conditions used in this program.

This report has been reviewed and is approved.

W. P. Conrardy

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I. INTRODUCTION

A. General

Present requirements for high temperature materials have focused attention on the refractory metals, molybdenum, columbium, tantalum and tungsten. Of these metals, molybdenum is favored because it is relatively low in cost, presently available in many shapes, sizes, in quantity, and has good high temperature properties.

The greatest drawback to the use of molybdenum as a structural material for high temperature applications has been its complete lack of oxidation resistance at these elevated temperatures. At temperatures above 1450°F., the oxidation product, MoO_3, volatilizes catastrophically. Under the designation "W-2" Chromalloy Corporation has developed a coating which protects molybdenum at 3000°F. in oxidizing atmospheres for several minutes without failure. At 2000°F., W-2 coated parts have withstood oxidation for 7200 hours and at 2700°F. up to 76 hours.

Another property of the W-2 coating is its excellent thermal shock resistance. Specimens have survived thirty cycles of thermal shock for 2600°F. to room temperature. They were held at 2600°F. for 15 seconds and cooled by an oxygen blast.

B. The W-2 Coating Process

The W-2 coating is produced by embedding the part in a powder mixture containing the elements to be transferred to the molybdenum substrate, an inert filler and energizer.

Upon heating, the energizer volatilizes and reacts with the coating elements, forming gaseous compounds which then react at the molybdenum surface depositing the coating.

The parts placed in W-2 pack mixture are contained in a molybdenum or steel box. This box is inserted in a retort which is heated to the coating temperature and held there for the desired coating time. The retort is provided with a seal which permits escape of air during heat-up but excludes air when the retort is cooled.

Manuscript released by authors March 1964 for publication as an RTD Technical Documentary Report.

II. OUTLINE OF WORK PERFORMED UNDER THE CONTRACT

The purpose of the work performed under this contract was to optimize the W-2 coating, establish reliability and reproducibility and develop a basis for Air Force specifications.

This work was broken down by the sponsor into two phases: (1) investigation of the variables of the W-2 coating process and their effects on the obtained coatings; and (2) coating process optimization using the data obtained in Phase I.

A statistical approach was utilized in Phase I and the effects of all important variables was established before Phase II was initiated. Any attempt to investigate all the known variables and their interactions in Phase I would have led to a program too cumbersome to handle within the alloted time of the present contract. In order to carry out the provisions of the contract, it was necessary to limit the number of investigated variables. Battelle Memorial Institute was subcontracted by Chromalloy to design and later evaluate the results of the experiments on a statistical basis.

Battelle and Chromalloy compiled jointly a list of the variables to be investigated with two levels per variable. This list was approved by the Air Force. The only substrate material coated was arc-cast Mo-0.5Ti of .035" thickness. The variables and levels of each variable studied were:

A. Material Compound (Pack Mixture)

1.	Purity:	high	commercial
2.	Particle size:	325 mesh	60 mesh
3.	Age:	new	one month old
4.	Mixing:	good	poor

B. Substrate

1.	Surface Condition:	uncontaminated	contaminated
2.	Surface preparation:	etched	as rolled

C. Process

1.	Time	24 hours	two 12 hour cycles
2.	Temperature	1800°F.	1900°F.
3.	Retort	Mild steel insert in mild steel box	Molybdenum insert in mild steel box

The following evaluation studies were made:

A. Metallographic (2 case depths, as coated, oxidized).

B. Chemical Composition and Distribution (2 case depths, as coated, oxidized).

C. Oxidation studies (limited to a single 2700°F. test due to lack of time and funds).

III. PRELIMINARY EXPERIMENTS

A. Aim and Experimental Conditions

In order to enable Battelle to determine the number of specimens necessary to make each experiment meaningful from a statistical point of view and to determine the best technique for detecting coating failures, 80 specimens were prepared in four coating experiments. Half of these specimens were tested by Battelle, the other half by Chromalloy. The data obtained here also provided information as to what form the statistical analyses might take.

The experiments were run in pairs with Chromalloy's present W-2 coating conditions, 2 cycles of 12 hours each at 1900°F. The specimens were oxidation tested in slowly flowing air in the presence of MoO_3 at 2700°F.

B. Preparation of Specimens

Specimens for these experiments, of the size 1" X 1/2" X 0.035", were prepared in the following way:

1. Edges and corners were rounded by grinding and finished on silicon carbide paper,
2. Etched with 1:1, HNO_3: water for 1 1/2 minutes,
3. Washed thoroughly with water,
4. Liquid honed,
5. Washed with hot water, and
6. Washed with acetone

The specimens were packed in an inert molybdenum box, containing the W-2 powder mixture. The box was then inserted in a 5" x 6" x 11" stainless steel retort and the retort put into a furnace pre-heated to

1900°F. Five hours heating-up time was added to the 12 hours coating time. After the retort was furnace cooled and opened, the specimens were removed and cleaned. These specimens were given a second processing under the same conditions of the first processing, using a newly mixed W-2 pack.

C. Oxidation Test Results

1. Battelle Tests.

The W-2 coated Mo-0.5Ti specimens were oxidation tested by Battelle Memorial Institute and Chromalloy Corporation. The initial forty specimens were tested in a globar heated muffle furnace at 2700°F. at Battelle. The specimens were set on zirconia boats and placed in the 2700°F. muffle which had previously been contaminated with MoO_3. An air flow of 3.8 cubic feet per hour was maintained through the muffle.

After a two hour period at 2700°F. the specimens were removed for inspection, after which they were returned to the furnace for another two hour cycle. This procedure was continued until failure, defined as the first hole large enough to be visible to the naked eye. Life of a specimen was defined to be one half cycle less than the period at which failure was observed.

Results of the cyclic oxidation test at 2700°F. are summarized in Table 1. The maximum and minimum lives of specimens were 21 and 5 hours (10.5 and 2.5 cycles) respectively. Analysis of the data indicated that the test conditions were homogeneous for the 40 specimens. No correlation of specimen life with position in the furnace was found.

For oxidation behavior of the individual specimens see Second Quarterly Report, January, 1961.

Excellent reproducibility of the average life was found for the series of 35 specimens which originated from the same lot of substrate. Figure 1 shows how the average life varied with the number of specimens used to compute the average for the individual series. A sample size of 10 served well to define the average life for the individual series. In some cases, a sample size of 5 gave a good average life, whereas, in other cases, it did not. The average life settled down very well when a sample size of 20 was reached, and the addition of 1 to 15 additional specimens to the average of 20 specimens affected the average life very little.

Series 8531B (8 specimens with new lot of substrate) had an average life of 6.8 cycles versus the average life for the other 35 specimens of 5.5 cycles. Also, the spread or deviation of the lifetimes was less for Series 8531B than for the other series tested, with the exception of 8531A, which, because of its smaller size, is considered to be less reliable from the standpoint of deviations.

TABLE 1. OXIDATION LIFETIMES AND DEVIATIONS FOR INDIVIDUAL SERIES OF SPECIMENS AND COMBINATIONS OF SERIES

Series	Specimen Life, cycles Min.	Specimen Life, cycles Max.	Average Specimen Life,(a) cycles First Half of Series	Average Specimen Life,(a) cycles Second Half of Series	Average Specimen Life,(a) cycles Total Series	Median Specimen Life,(b) cycles	Deviation of a Single Point, cycles Av.(c)	Deviation of a Single Point, cycles Standard(d)	Deviation of the Mean or Median Life, cycles Av.(e)	Deviation of the Mean or Median Life, cycles Standard(f)
8521 (10 spls)	2.5	8.5	5.5	5.7	5.6	5.6	1.5	2.1	0.47	0.66
8522 (10 spls)	3.5	10.5	6.5	4.7	5.6	5.3	1.3	1.5	0.42	0.48
8532 (10 spls)	3.5	7.5	5.1	5.7	5.4	5.4	1.1	1.7	0.35	0.54
8531A (5 spls) (-11,-13,-15,-17,-19)	4.5	6.5	-	-	5.5	5.5	0.4	1.0	0.18	0.45
8531B (8 spls) (-1 through -7,-9)	5.5	8.5	-	-	6.8	6.6	0.6	0.8	0.23	0.28
8521 + 8522 (20 spls)	2.5	10.5	-	-	5.6	5.6	1.4	1.8	0.32	0.40
8532 (10 spls) + 8531 (5 spls)	3.5	7.5	-	-	5.4	5.5	0.9	1.4	0.23	0.36
Composite (35 spls)	2.5	10.5	-	-	5.5	5.5	1.1	1.6	0.35	0.27

See footnotes on following page

Footnotes to Table 1.

(a) Computed from $L_{av.} = \frac{\Sigma L_i}{n}$.

(b) Read from normal probability graph at 50 per cent cumulative probability.

(c) Computed from $a = \frac{\Sigma |L_{av.} - L_i|}{n}$.

(d) Read from normal probability graph at 17 per cent and 50 per cent cumulative probability. Standard deviation of a single point = σ .

(e) Computed from $a_{av.} = \frac{a}{\sqrt{n}}$.

(f) Computed from $\sigma_m = \frac{\sigma}{\sqrt{n}}$.

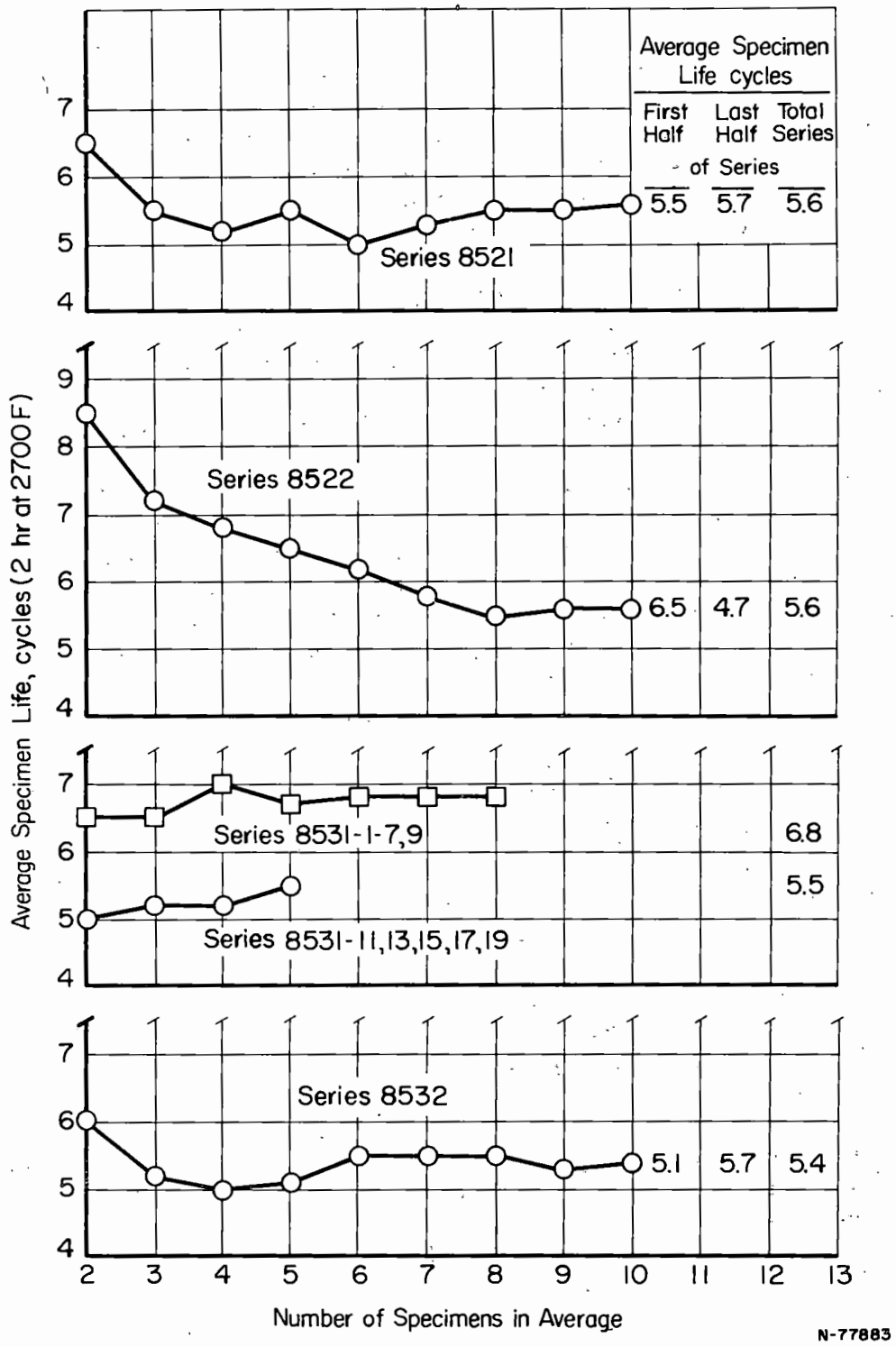


FIGURE 1. AVERAGE SPECIMEN LIFE FOR INDIVIDUAL SERIES VERSUS NUMBER OF SPECIMENS USED TO COMPUTE THE AVERAGE

Figures 2 and 3 show the distribution of lifetimes for the individual series and for composited series.

Table 2 correlates the failures observed with different areas of the specimens. For the 44 specimen composite, 45.5 per cent of the failures were observed on the large flat surfaces (closer to the edge than to the middle), and 54.5 per cent of the failures occurred on the edges. A relatively large (72.7 per cent) number of the total failures occurred near the rounded corners of the specimens.

The distribution of the edge failures (bottom section of Table 3) indicated that interaction of the zirconia boat with the coating was not the cause of this type of failure. Considering the distribution of surface failures, Series 8521 and 8532 suggest that interaction occurred, whereas Series 8522 and 8531 indicate that interaction did not occur.

Because visual inspection and probing of the specimens to determine failure appeared to allow considerable chance for error in ascertaining the exact time when failure occurred, it was desirable to weigh the specimens to try to determine lifetimes more exactly. When the initial 40 specimens were tested, a balance was set up in the hope that time would be available to weigh the specimens during the 1-hour periods out of the furnace. However, it was found that the time available permitted only the visual inspection which had been agreed upon.

2. Chromalloy Tests.

Thirty-five specimens of W-2 coated Mo-0.5Ti from the same groups as those tested by Battelle were oxidation tested by Chromalloy. The gas fired tube furnace used in the statistically designed experiment was used in this test (Figure 4).

Specimens were distributed among five tubes in order to provide similar conditions for the four sets of specimens. As was done with the Battelle tested group, the specimens were subjected to two hour cycles at 2700°F. After each cycle in the furnace the specimens were weighed and when weight losses were found, holes were probed for. In some cases, holes were found with very small weight losses. This was usually the case when the area where the hole was located looked suspicious. In some cases holes could not be found after large weight losses. This could be due to a self-healing property of the W-2 coating or a uniform bleeding of molybdenum or MoO_3 through the surface.

Results of the Chromalloy test are listed in Table 3. Specimens after failure are shown in Figure 5. The cycle at which failure was considered to have occurred is given. In some cases, the failure cycle was not considered to be the cycle at which the specimen was removed from test but actually the cycle in which the specimen began to lose weight at an accelerating or constant rate of ten milligrams per cycle or more. (See Section V-A) This technique has also been used in the statistically designed experiment.

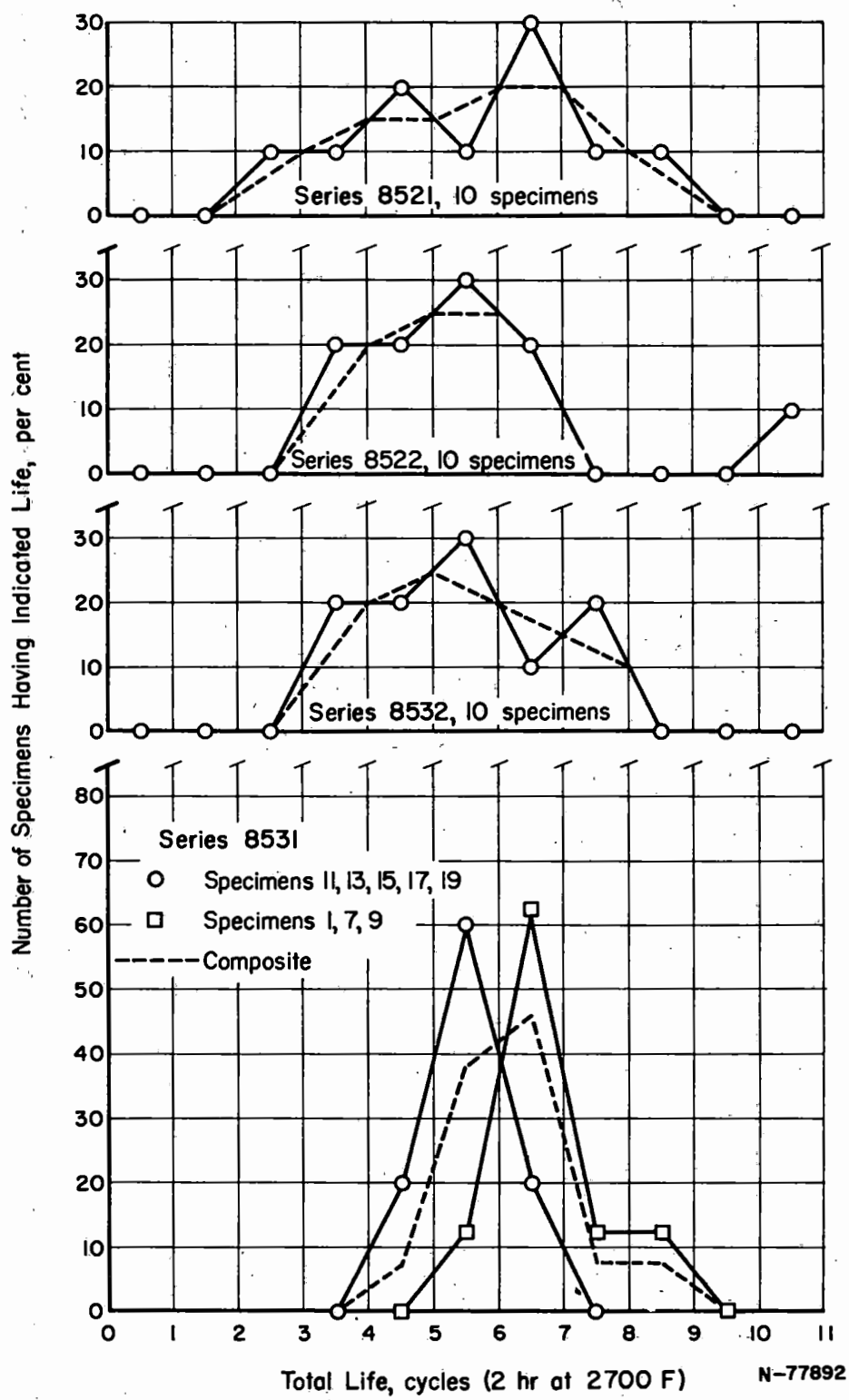


FIGURE 2. DISTRIBUTION OF LIFETIMES FOR INDIVIDUAL SERIES OF SPECIMENS

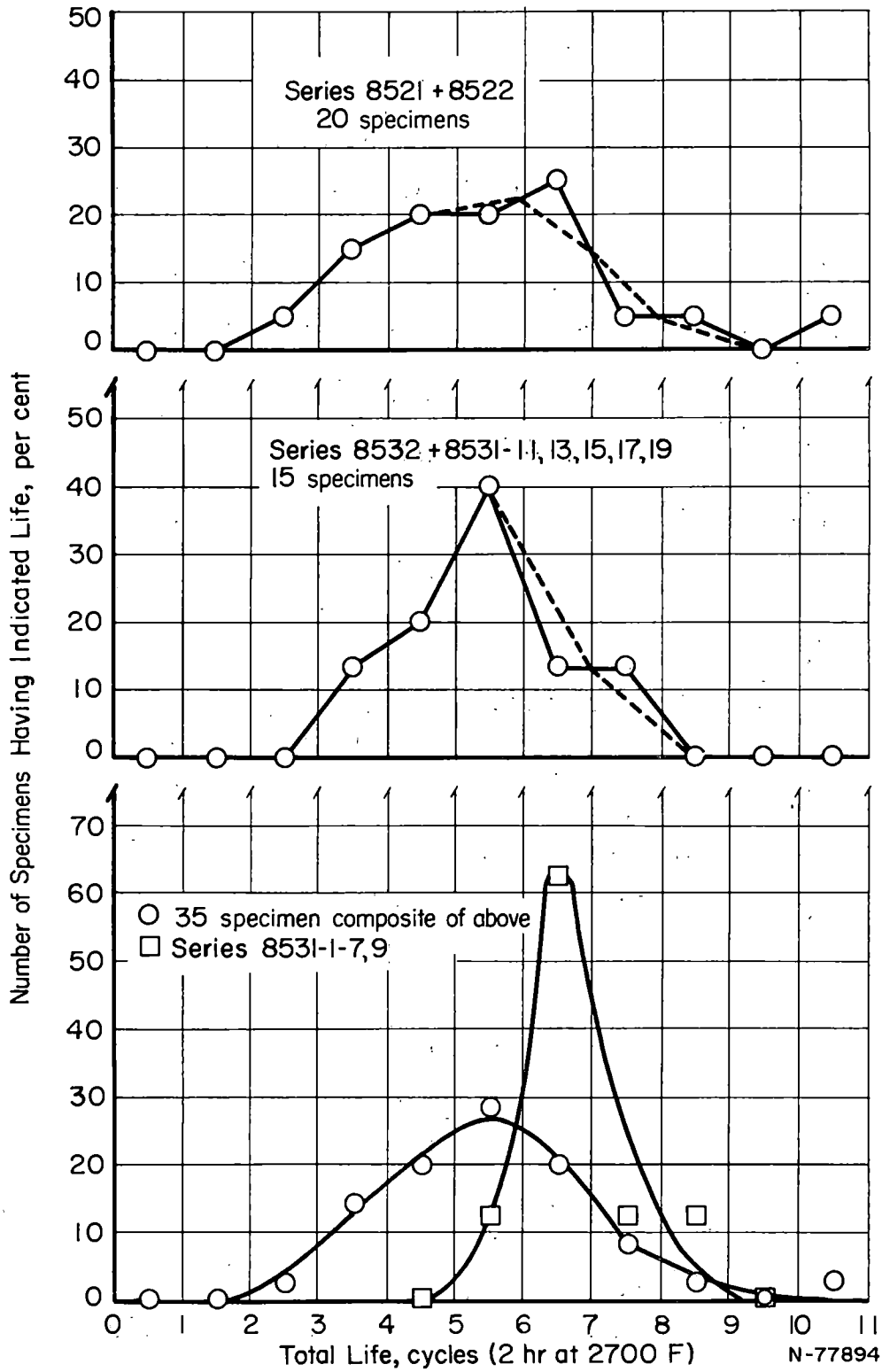
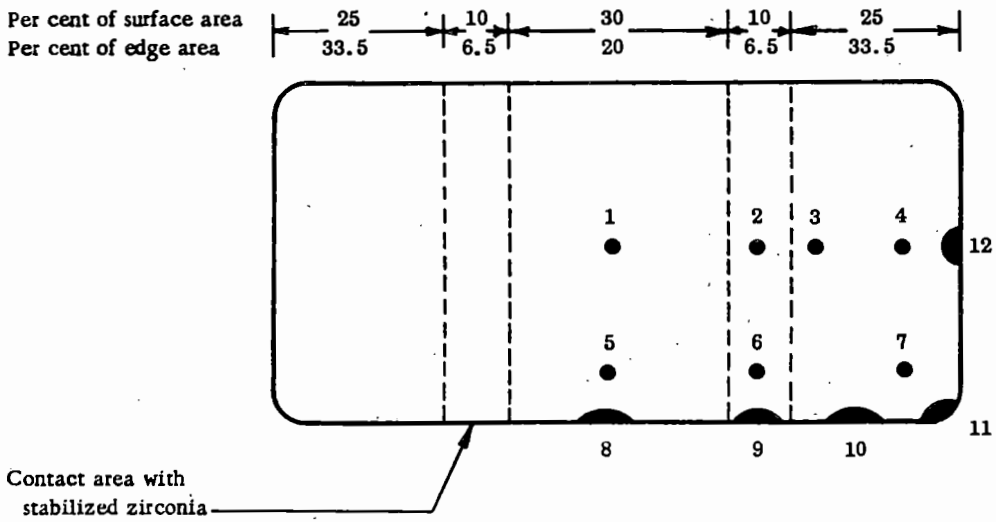


FIGURE 3. DISTRIBUTION OF LIFETIMES FOR COMPOSITED SERIES OF SPECIMENS

TABLE 2. CORRELATION OF LOCATION OF FAILURES IN W-2 COATED Mo-0.5Ti

Series	Failures at Indicated Location, per cent of specimens in series														
	1-4	5	6	7	8	9	10	11	12	5 + 8	6 + 9	7 + 10	5-7	8-12	7-12
8521 (10 spls)	0	0	30	50	0	0	10	0	10	0	30	60	80	20	70
8522 (10 spls)	0	40	10	20	0	0	10	20	0	40	10	30	70	30	50
8532 (10 spls)	0	0	10	20	10	0	20	30	10	10	10	40	30	70	90
8531A (5 spls)-11, -13, -15, -17, -19	0	0	0	20	0	0	40	40	0	0	0	60	20	80	100
8531B (9 spls, -1-9)	0	0	0	11	0	22	11	34	22	0	22	22	11	89	100
Composite (44 spls)	0	9.1	11.4	25.0	2.3	4.5	15.9	22.7	9.1	11.4	15.9	40.9	45.5	54.5	79.5



	Per Cent of Surface Area	Per Cent of Surface Failures in Series					
		8521	8522	8532	8531A	8531B	Composite
Boat contact areas	20	38	14	33	0	0	25
Center area	30	0	57	0	0	0	20
End areas	50	62	29	67	100	100	55

	Per Cent of Edge Area	Per Cent of Edge Failures in Series					
		8521	8522	8532	8531A	8531B	Composite
Boat contact areas	13	0	0	0	0	25	8
Center area	20	0	0	14	0	0	4
End areas	67	100	100	86	100	75	88

Table 3. Results of Oxidation Testing 35 Specimens of W-2 Coated Mo-0.5Ti at 2700°F in Chromalloy Tube Furnace

Specimen Number	Two Hour Cycles to Failure at 2700F	Weight Loss at Failure, Mg
8521-2	11	40.5
8521-4	3	11.5
8521-6	12	17.5
8521-8	6	15.5
8521-10	10	45.0
8521-14	15	87.5
8521-16	9	90.0
8521-18	6	15.0
8521-20	7	3.5
8521-22	4	0.5
8522-24	15	180.0
8522-26	6	18.5
8522-28	5	15.0
8522-30	6	18.0
8522-32	4e[a]	8.5
8522-34	6	6.0
8522-36	4	6.5
8522-38	11	24.0
8522-40	5	12.0
8531-12	6?[b]	40.5
8531-14	2e	18.0
8531-16	6?	95.5
8531-18	4e	16.5
8531-20	6?	7.0
8531-22	3e	11.0
8532-2	6?	46.0
8532-4	4	11.0
8532-6	1e	100.0
8532-8	6?	31.0
8532-10	6?	49.0
8532-12	2e	22.0
8532-14	1e	high
8532-16	6?	10.5
8532-18	1e	20.5
8532-20	4e	9.0

See footnotes on Table 4.

Figure 4. Tube Furnace Used for Oxidation Testing Specimens at 2700°F.

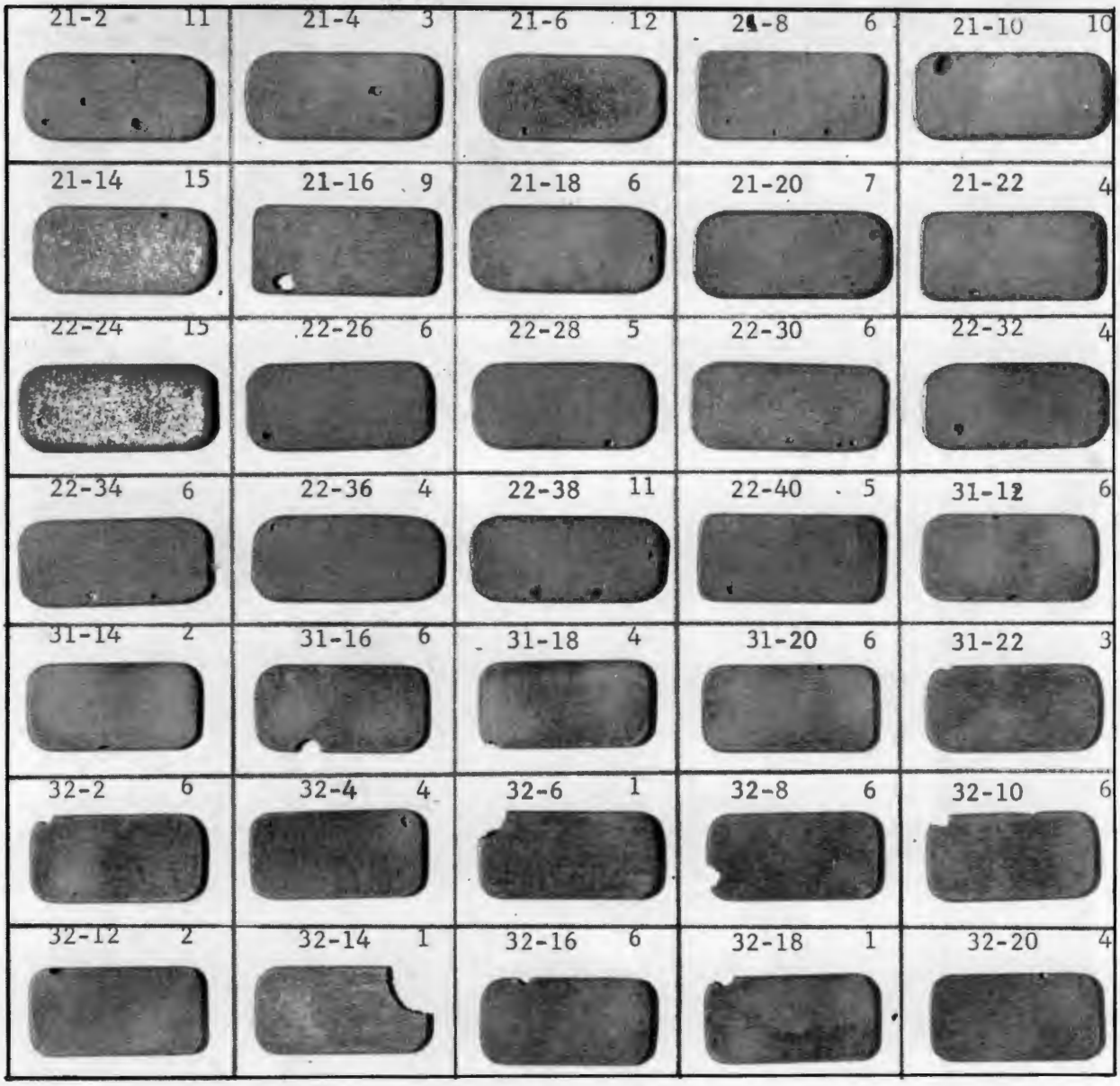


Figure 5. W-2 Coated Mo-0.5Ti After Oxidation Testing in Chromalloy's Tube Furnace at 2700°F.

TABLE 4. COMPARISON OF BATTELLE AND CHROMALLOY OXIDATION TESTS OF W-2 COATED Mo-0.5Ti AT 2700°F

Series	BATTELLE Specimen Life, Cycles		CHROMALLOY Specimen Life, Cycles		BATTELLE Average Total Series	CHROMALLOY Average Total Series
	Min.	Max.	Min.	Max.		
8521	2.5	8.5	2.5	10.5	5.6 (10 spls)	7.8 (10 spls)
8522	3.5	10.5	3.5	14.5	5.6 (10 spls)	6.4 (9 spls)
8532	3.5	7.5	0.5	5.5	5.4 (10 spls)	3.3 (10 spls)
8531A	4.5	6.5	1.5	5.5	5.5 (5 spls)	4.0 (6 spls)
8531B[d]	5.5	8.5	-	-	6.8 (8 spls)	-
8521 + 8522	2.5	10.5	2.5	14.5	5.6 (20 spls)	7.1 (19 spls)
8532 + 8531A	3.5	7.5	0.5	5.5	5.4 (15 spls)	3.5 (16 spls)
Composite[e]	2.5	10.5	0.5	14.5	5.5 (35 spls)	5.5 (35 spls)

(a) e next to failure cycle denotes edge failure.
(b) ? next to failure cycle denotes possible edge failure.
(c) Cycle at which specimen was considered to have failed. Failure cycle is 0.5 less by definition.
(d) Tested by BATTELLE only. Mo-0.5Ti was from a lot different from that of the other specimens.
(e) Does not include series 8531B.

3. Comparison of Battelle and Chromalloy Results

Table 4 correlates the results obtained by Battelle with those obtained by Chromalloy. One-half cycle was deducted from the Chromalloy failure cycles as had been done for the Battelle results.

It is immediately evident that there is much more scatter in the Chromalloy data than there is in the Battelle data. Groups 8521 and 8522 of the Chromalloy test have longer lives than the similar Battelle groups and groups 8531 and 8532 have noticeably shorter lives than the identical Battelle groups.

The longer lives of Chromalloy groups 8521 and 8522 may easily be due to less severe test conditions since the oxidation technique employed is very nearly static with air flow through the tubes due only to natural convection, whereas Battelle used an air flow of 3.8 cubic feet per hour. Also, Chromalloy specimens were slowly withdrawn from the furnace and Battelle rapidly removed specimens causing more severe thermal shock.

The reason for the shorter lives of Chromalloy groups 8531 and 8532 is easily explainable. Both Battelle and Chromalloy groups 8531 and 8532 had a much greater percentage of edge failures than did groups 8521 and 8522 (Table 5). However, Battelle did not use weighing as a technique for locating failures but looked for holes visible to the eye. Chromalloy found several edge failures after one or two cycles and had eliminated all definite edge failures by the fourth cycle. The first edge failure detected by Battelle was in the fourth cycle.

Table 5. Percentage Edge Failures in Oxidation Test Groups

Series	Battelle %	Chromalloy %
8521 + 8522	25	5
8531 + 8532	73	50-95*

It appears that weighing is a useful method for detecting failures and that edge preparation of specimens is important.

Based on the results from these preliminary studies, it was decided that each retort (representing an experiment) in the statistically designed program would contain 20 specimens, of which 1 would be retained for metallographic studies and the other 19 would be cyclically oxidized at 2700°F. It also was decided that weighing of the specimens after each cycle

* Some specimens were questionable as to whether or not edge failures were present.

of oxidation would be done to determine more exactly the time at which failure occurred.

IV. EXPERIMENTAL PROGRAM

A. Statistical Design

A statistical design was worked out with the benefit of several conferences involving both Battelle and Chromalloy personnel. The experimental work followed a fractional factorial design (Table 6.) which is a 1/8 replicate of a complete factorial based on 9 variables at 2 levels each.* To illustrate the coding (which differs from the reference), the first test unit requires a material compound which is commercially pure (A_1), 325-mesh particle size (B_1), aged 1 month (C_o), with good mixing (D_o), substrate with uncontaminated soundness (E_1) and surface preparation as rolled (F_1), processed for two 12-hour periods (G_o) at 1900°F. (H_1) in a mild steel retort (J_o). The order in which the units are listed has been properly randomized.

The above choice was based on the following considerations. A complete factorial experiment for 9 variables at 2 levels each requires 512 different test conditions (1 for each of the 512 ways in which 9 choices can be made from 9 pairs). However, by sacrificing information on higher-order interactions, economy can be achieved by running only a fraction of all possible test conditions. Thus, the amount of testing can be cut from 512 combinations to 64 combinations by sacrificing information on 6 of the 36 first-order (2 factor) interactions and all of the higher-order interactions. (An interaction is the effect of a variable on the effect of another variable or combination of variables.) This results in a balanced design with statistical tests of significance for the main effects of the 9 variables and for 30 first-order interactions. The choice here to limit interaction evaluation was later justified when even the more important first-order interactions were found to have little, if any, actual effect on the properties of the coating.

Selection of the 64 test conditions depended in part on existing knowledge of the relative importance of the variables. According to the basic design selected, first-order interactions, which are derived from the 6 possible pairings of 4 variables, were not measurable. Therefore, it was desirable to select the set of 64 test units so that the nonmeasurable first-order interactions involved the 4 variables which were least likely to interact pairwise. These were considered most likely to be the 4 variables having the least individual effects. At the beginning of the program, purity (A), age (C), and mixing (D), of the material compounds, and soundness (E) of the substrate, were thought to be the 4 variables of least importance.

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* National Bureau of Standards, Fractional Factorial Experiment Designs for Factors at Two Levels, NBS Applied Math. Series 48, 1957. (U.S. Government Printing Office, Washington 25, D.C.).

TABLE 6. EXPERIMENTAL DESIGN FOR W-2 CHROMALLIZING PROCESS

Material Compound

(A) Purity
- 0 - Extremely pure
- 1 - Commercially pure

(B) Particle size
- 0 - 60 mesh
- 1 - 325 mesh

(C) Age
- 0 - One month old
- 1 - New

(D) Mixing
- 0 - Good
- 1 - Poor

Substrate

(E) Soundness
- 0 - Contaminated
- 1 - Uncontaminated

(F) Surface Preparation
- 0 - Etched
- 1 - As rolled

Process

(G) Time
- 0 - 12, 12 hr. (2 cycle)
- 1 - 24 hrs.

(H) Temperature
- 0 - 1800 F
- 1 - 1900 F

(J) Retort Composition
- 0 - Mild Steel
- 1 - Mild Steel with Molybdenum insert

Unit	A	B	C	D	E	F	G	H	J
1	1	1	0	0	1	1	0	1	0
2	0	0	0	1	1	1	1	0	0
3	1	0	0	1	0	0	1	0	0
4	1	1	1	0	0	0	0	0	0
5	1	0	0	0	1	1	1	0	1
6	1	1	0	1	0	0	0	1	1
7	1	1	1	1	1	1	0	0	1
8	0	1	0	1	1	1	0	1	1
9	0	1	1	1	0	1	0	1	0
10	1	1	1	1	1	0	1	1	1
11	0	0	1	1	0	0	1	1	0
12	1	0	0	1	0	1	1	1	1
13	0	0	1	0	1	1	0	1	0
14	0	0	0	1	1	0	0	1	0
15	0	1	0	0	0	0	1	1	1
16	0	1	0	1	1	0	0	0	0
17	0	1	0	1	1	1	1	1	0
18	1	1	1	1	1	0	0	1	0
19	1	0	1	0	0	0	0	1	0
20	1	0	0	0	1	0	0	1	1
21	0	1	1	1	0	0	0	0	1
22	0	1	0	0	0	1	1	0	0
23	1	1	1	0	0	1	1	1	0
24	1	0	1	0	0	0	1	1	1
25	0	0	0	1	1	1	0	0	1
26	0	1	0	0	0	0	0	1	0
27	0	0	1	0	1	0	1	0	0
28	1	0	1	1	1	1	1	1	0
29	0	0	1	1	0	1	0	0	0
30	1	1	1	0	0	1	0	1	1
31	0	1	1	0	1	1	1	0	1
32	1	1	0	0	1	0	0	0	1
33	0	0	0	0	0	0	0	0	0
34	0	0	1	0	1	0	0	0	1
35	1	1	0	0	1	1	1	1	1
36	1	1	0	1	0	1	0	0	0
37	0	1	1	0	1	1	0	0	0
38	1	1	1	1	1	1	1	0	0
39	1	1	1	0	0	0	1	0	1
40	0	0	1	1	0	0	0	1	1
41	0	1	0	1	1	0	1	0	1
42	1	0	0	0	1	0	1	1	0
43	1	1	0	0	1	0	1	0	0
44	1	1	0	1	0	1	1	0	1
45	0	0	0	0	0	1	1	1	0
46	0	0	0	1	1	0	1	1	1
47	1	0	1	0	0	1	0	0	1
48	0	1	1	0	1	0	1	1	0
49	1	0	0	1	0	0	0	0	1
50	0	1	1	1	0	1	1	1	1
51	0	0	1	1	0	1	1	0	1
52	1	0	0	1	0	1	0	1	0
53	0	0	0	0	0	0	1	0	1
54	1	0	1	1	1	0	0	0	0
55	0	0	0	0	0	1	0	1	1
56	1	0	1	1	1	0	1	0	1
57	1	0	1	1	1	1	0	1	1
58	1	1	0	1	0	0	1	1	0
59	1	0	1	0	0	1	1	0	0
60	0	1	0	0	0	1	0	0	1
61	0	0	1	0	1	1	1	1	1
62	0	1	1	0	1	0	0	1	1
63	1	0	0	0	1	1	0	0	0
64	0	1	1	1	0	0	1	0	0

Therefore, the experimental program was designed to sacrifice information on pairwise interactions of these variables in order to insure information on interactions involving the other 5 variables.

B. Definitions of Investigated Variables

The nine variables whose influence was investigated on two levels were purity, particle size, age and mixing procedure of pack, soundness and surface preparation of work pieces, processing time and temperature and composition of retort. (See Table 6) A more detailed description of these variables follows:

1. Purity: The "extremely pure" materials had a minimum purity of 99.7%, the "commercially pure" materials of 98%.

2. Particle Size: The particle sizes of the "60 mesh" materials were in reality -60 +150 mesh and the sizes of the "325 mesh" materials were -230 mesh. These ranges of mesh size were used because of the difficulty and cost of obtaining powders of narrow mesh size ranges.

The purpose of the inclusion of mesh size as a variable was to determine whether or not the coarseness of the particles effects the type of coating produced. It is conceivable that coating reaction rates might be affected by the surface area of the coating elements and that finer powders might produce a greater cementation effect and/or a smoother coated surface.

3. Age: Age of the coating mixture was included as a variable since it is possible that upon standing in a poorly closed barrel the compound might pick up moisture, the energizer might decompose, or some other unknown reaction might occur. The "one month old mixtures" were all 5 weeks old and were aged in open jars.

4. Mixing: Since local segregation of coating elements might produce a coating of non-uniform composition and/or thickness, mixing was included as a variable. "Poor mixing" is a difficult term to define. In order to reproduce poor mixing in each preparation in which it was required, a standard technique was used. "Poor mixing" was produced by placing each element into a jar (same size jar used each time) in the same order, covering the jar, and turning it over twelve times. This produced a non-uniform, streaky mixture.

5. Substrate Soundness*. The two materials being used were both Mo-0.5Ti. "Uncontaminated" material was the normally produced commercial grade sheet supplied by General Electric Corp. The second material was purposely surface contaminated by eliminating processing steps that normally prevent contamination by air. It was supplied by Universal Cyclops.

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* For a detailed examination of substrate surface condition see the Third Quarterly Progress Report for this program, April, 1961.

6. Surface Preparation: Surface preparation is an important step in any coating operation. In order that a distinction may be made between the quality of coatings produced on a chemically clean surface and on the as rolled surface, a portion of the specimens was coated after washing in acetone to remove greases from the surface, and a second group was etched for 1.5 minutes in a 1:1 nitric acid-water solution, washed, liquid honed, rinsed, and finally also washed with acetone.

7. Time: Previous experience has indicated that "double processing" is better than processing specimens once for the same total time at temperature. Twelve hours at temperature produces most of the total coating since rate of coating is not linear and decreases with time. The total coating produced in one 24 hour process should be the same as that produced by two 12 hour processes. However, any cracks or weak spots formed in the coating during the first processing may be sealed or strengthened by the second one. The effect of similar case depth as supplied by one long or two shorter cycles is of interest. A fresh powder mixture was used in each processing.

8. Temperature: The depth of coating produced is a function of processing temperature. Most of the previous W-2 applications were made at 1800°F. and 1900°F., although other temperatures, higher and lower, were used. It is also possible that the composition of the coatings are temperature dependent, since the coating process involves chemical reactions whose equilibria are functions of temperature.

9. Retort Composition: The composition of the retort material could affect the composition and properties of the W-2 coating. This would occur by the transfer of retort elements to the W-2 coating through the coating reactions. Such a transfer could be harmful, beneficial, or inconsequential. Since mild steel would be a cheap retort material, it seemed worthwhile investigating as opposed to a more costly inert material as molybdenum.

In Figure 6 specimens are being packed in a mild steel box. The steel boxes are precoated with W-2 mixture before being used with specimens. The steel is attacked by the W-2 mixture as is evident from the appearance of the cover of the steel box.

Figure 6.
Steel box being packed with specimens.

C. Coating Preparations

All 64 sets of specimens were prepared as prescribed in Table 6. One furnace was used for all preparations in order to keep heating and cooling rates constant. Figures 7 and 8 show typical specimens representative of the 64 preparations. Clearly visible are marked differences between the surface appearances of the preparations.

Rough, spotty appearances as produced in many preparations, may be attributed, in most cases, to poorly mixed powders, coarse powders, or surface condition of pieces prior to coating.

D. Oxidation Test Furnace

The gas fired tube furnace used by Chromalloy Corporation for oxidation testing the 64 sets of specimens has six recrystallized alumina tubes. (Figure 4). Five tubes were used for the testing of specimens. The sixth tube was used exclusively as a sight tube for the "Rayotube" control instrument since evolution of MoO_3 from a failed sample in the control tube would result in poor temperature control. (The instrument would falsely detect a low temperature and thus keep the high flame on, resulting in an excessive temperature.)

Specimens were placed on zirconia boats since this material apparently does not react with the W-2 coating at 2700°F. Three specimens from each of two of the 64 sets of specimens prepared were placed on each boat.

In each furnace load of specimens there were six sets of specimens distributed throughout the five tubes as illustrated in Figure 9. This distribution was used in order that each set of specimens would encounter the same time-temperature pattern.

As was done with earlier specimens, a two hour period in the furnace was used. While one group of six sets of specimens was being weighed and examined, a second group was put into the furnace.

V. RESULTS OF OXIDATION TEST EXPERIMENTS

A. Definition of Failure.

While weighing was found to be useful for detecting failures, no definite failure point could be defined since weight changes did not establish any definite pattern. At times failures occurred suddenly with sharp weight losses. (Specimens 3-17 Table 7.) Sometimes failure was gradual with very small weight losses in each cycle followed either by a large final weight loss (Specimen 6-7) or continued small losses and the final appearance of a yellow oxide on the surface (Specimen 4-13). It was decided that either a large sudden weight loss, (hole must also be found by probing with tweezers), extrapolation of weight losses, back to the point where a specimen first began to lose at least ten milligrams per cycle, (Specimen 1-14) or the final appearance of an oxide where a hole could be found (after many small weight losses) would be the failure point.

B. Numerical Test Results and Analysis

Data obtained from the oxidation testing of the 64 sets of specimen are presented in Table 8. Lives as long as 38 cycles (76 hours) at 2700°F. were obtained. Failures that resulted from oxidation on specimen edges were thought to have particular significance and were given identification in Table 8.

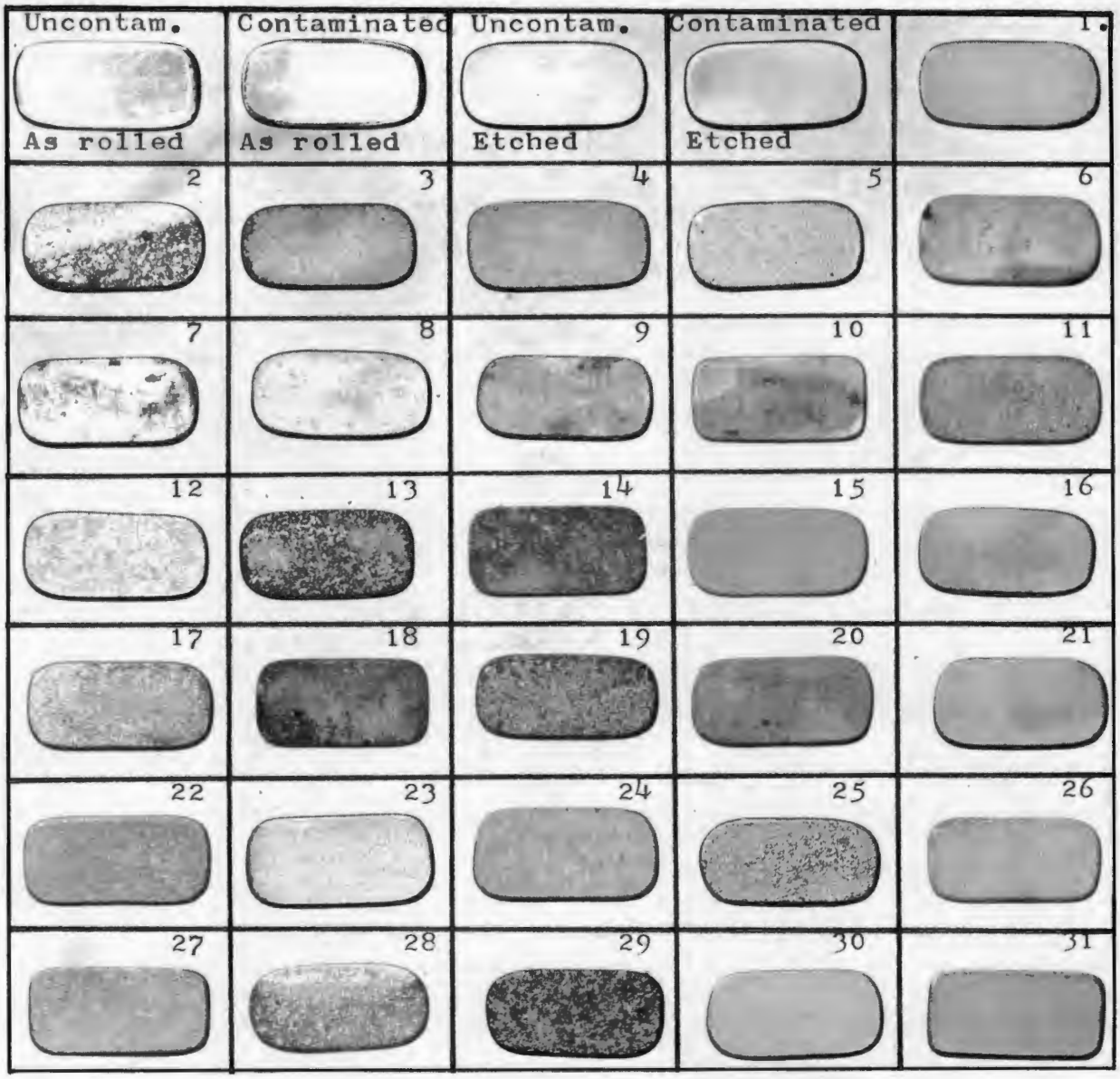

Figure 7. Typical W-2 Coated Mo-O.5Ti Specimens from Experiments One to Thirty-One.

The first four specimens are uncoated Mo-O.5Ti both in the as-received and etched and liquid honed conditions.

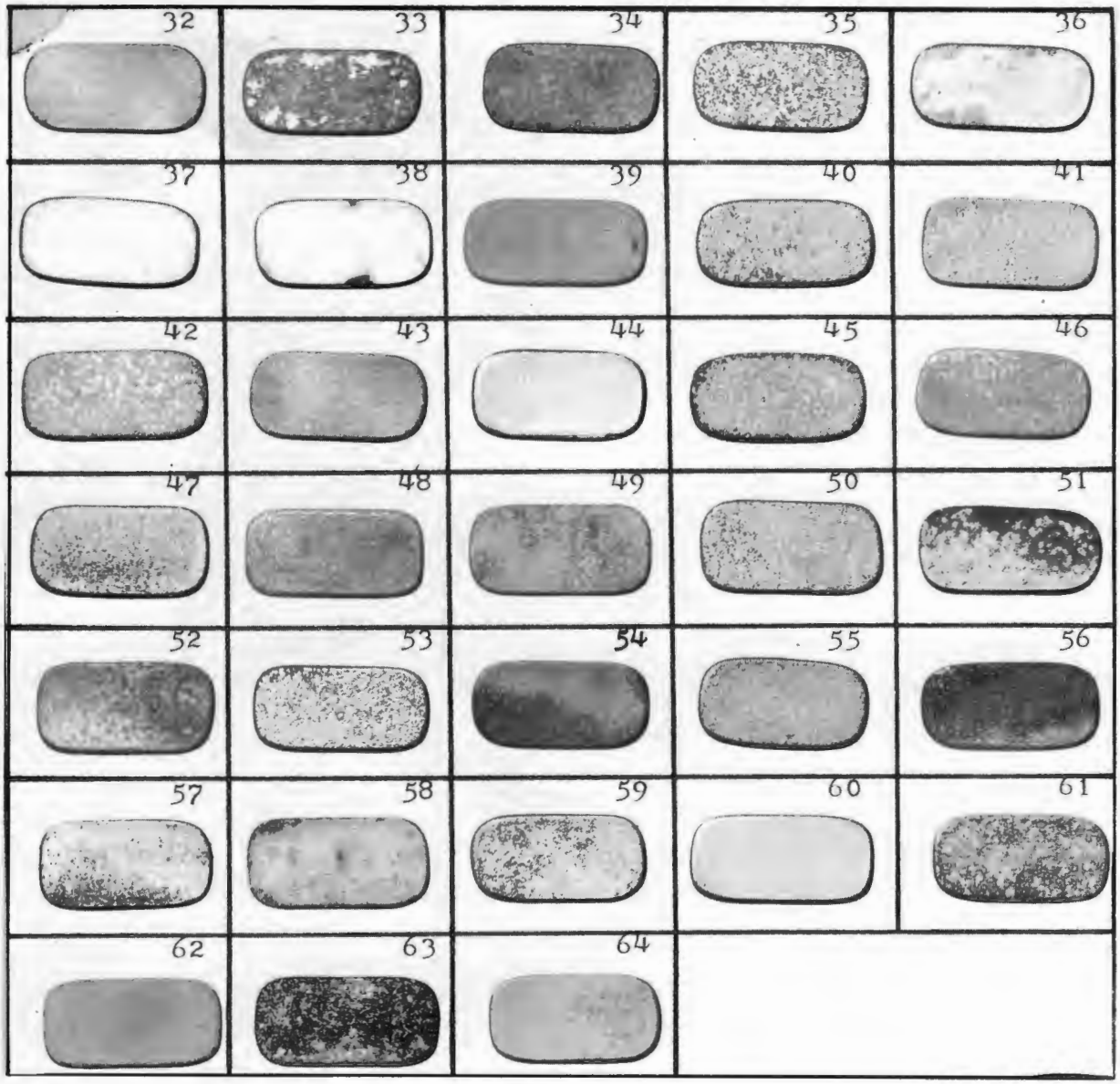

Figure 8. Typical W-2 Coated Mo-0.5Ti Specimens for Experiments Thirty-two to Sixty-four.

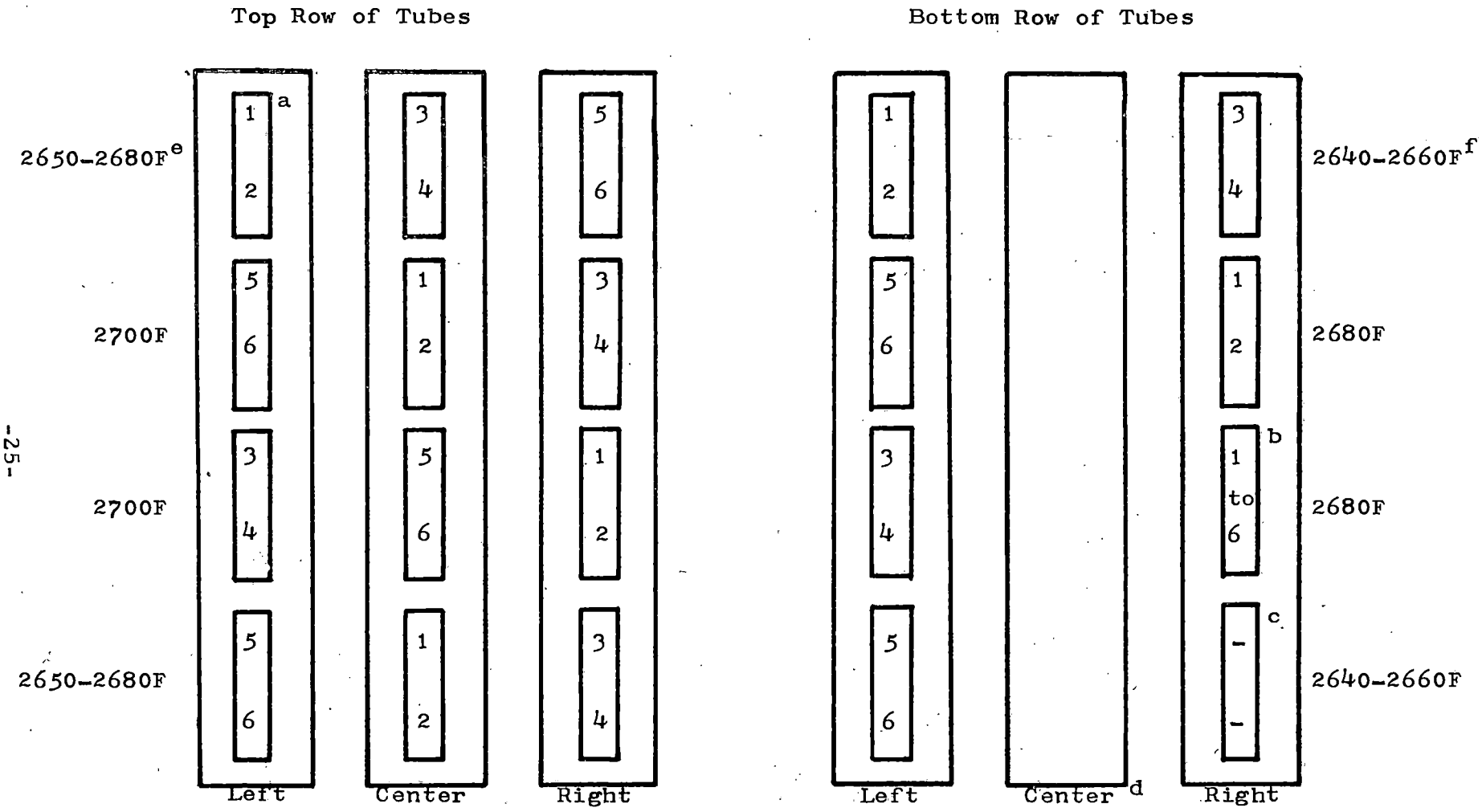

Figure 9. Temperature and Specimen Distribution in Furnace Tubes

a. Each boat has 6 specimens on it, 3 from each of two coating preparations.
b. This boat has one specimen from each of the six coating preparations in the furnace
c. Empty boat.
d. Empty tube used for temperature control only.
e. Temperature distribution for top row of tubes.
f. Temperature distribution for bottom row of tubes.

Table 7. **Weights of Specimens After Cycling at 2700°F.**

No. of Cycles *	Specimen Number				
	6-7	3-17	4-13	1-14	
0	2.4815	2.4125	2.6595	2.9785	
1	2.4825	2.4130	2.6605	2.9790	
2	2.4810	2.4130	2.6605	2.9785	
3	2.4816	2.4126	2.6605	2.9780	
4	2.4805	2.4110	2.6605	2.9785	
5	2.4810	2.4065	2.6605	2.9775	
6	2.4805	2.4050	2.6600	2.9775	
7	2.4810	2.3720	2.6600	2.9765	
8	2.4800		2.6600	2.9760	
9	2.4800		2.6600	2.9740	
10	2.4790		2.6595	2.9700	
11	2.4790		2.6595	2.9635	
12	2.4770		2.6590	2.9580	
13	2.4720		2.6580	2.9405	(failure point)
14	2.4725		2.6560	2.9040	
15	2.4635		2.6545		
16	2.4565		2.6475		
17	2.3690		2.6450		
18			2.6340		
19			2.6310		
20			2.6260		
21			2.6215		
22			2.6165		

* Two hours at 2700°F. per cycle

Table 8: Individual Specimen Test Lives for 64 Experiments

Unit	1	2	3	4	5	6	7	8	9	10	11
Spec. No.											
1	17	17	9	27	10	13	11	29	16	17	16
2	29	23	5	25	10	11	16	24	11	17	16
3	36	16	10	25	3e**	14	15	28	10	12	14
4	20	7	9	25	4	9	21	29	15	15	14
5	37	9	7	20	6	5e	10	6e	16	16	16
6	35	9	10	23	3	15	23	36	18	12	1?
7	20	10	11	26	10	17	20	20	19	14	16
8	38	9	7	23	3e	15	21	30	11	23	18
9	35	10	4	15	3e	17	1e	30	11	12	18
11	25	9	13	18	10	16	17	29	24	9	17
12	31	12	11	18	10	13	18	24	20	20	12
13	31	18	13	22	10	14	18	33	13	18	13
14	12e?*	16	10	25	9	8	13	13e?	9	23	13
15	30	22	11	17	9	10	6	11e	20	2e	13
16	30	11	8	21	9	13	16	25	18	22	15
17	33	14	8	18	9	14	14	20	17	2e?	11
18	33	13	6	17	8	9	16	15	17	5e?	11
19	36	15	4e	17	7	9	18	15	17	1e	14
20	15	15	10	-	8	11	20	25	14	10	18
Total	28.6	13.4	8.7	21.2	7.4	12.9	15.5	25.4	15.6	13.1	13.4

* e? denotes possibility of edge failure

** e denotes edge failure

Table 8: Individual Specimen Test Lives for 64 Experiments

Unit	12	13	14	15	16	17	18	19	20	21	22
Spec. No.											
1	14	20	21	18	23	4e	21	16	31	18	9
2	12	22	22	23	29	4e	25	19	33	21	8
3	13	9e	21	18	27	23	30	17	3e?	20	8
4	12	14	22	20	26	6e	32	20	20	21	9
5	14	32	22	20	21	21	36	19	18	17	10
6	14	28	24	18	22	13	28	20	8	11	12
7	11	31	15	20	22	19	25	20	22	11	8
8	12	28	18	21	7e	24	33	21	13e?	18	8
9	11	27	17	15	25	24	29	22	23	18	9
11	13	27	19	15	23	23	28	10e	24	13	13
12	13	27	21	17	18	26	7e	18	3e	21	9
13	12	18	22	18	13e	23	23	18	4	9	12
14	-	20	18	19	27	8e?	31	17	17	21	10
15	13	20	17	23	9e	19	27	17	19	20	12
16	8e?	20	18	19	28	22	31	20	12	20	9
17	12	24	23	17	25	18	28	16	20	17	12
18	14	24	21	17	30	18	30	16	1	17	12
19	13	23	20	17	20	11e?	27	17	21	15	12
20	15	35	18	18	4e	2e	26	18	4e	18	9
Total	12.4	23.6	19.9	18.6	20.9	16.2	27.2	17.9	15.6	17.1	10.1

Table 8: Individual Specimen Test Lives for 64 Experiments

Unit	23	24	25	26	27	28	29	30	31	32	33
Spec. No.											
1	19	14	9	32	7	25	10	24	6e	26	7
2	11	14	12	35	9	24	6	26	7e	26	9
3	11	12	12	31	9	27	6	22	9e	25	9
4	16	13	10	26	9e	22	8e	18	6e	26	9
5	16	14	12	25	9e	25	8	25	8e	15	9
6	16	14	12	25	10	24	8	12e	8e	16	8
7	16	13	11	29	7	24	8	25	11e	16	9
8	14	13	7	22	10	25	8	23	15e	23	8
9	16	12	9	23	10	23	8	27	12e	16	10
11	12	13	13	24	10	17	7	22	11	27	8
12	15	13	13	25	10	17	6	26	2e	26	8
13	15	13	12	24	11	18	7	17	9	17	9
14	15	14	16	19	7e	24	7	25	16	22	9
15	14	13	15	23	10	21	8	25	15	22	9
16	13	14	13	24	11	22	7	17	6e	7e	9
17	13	12	18	24	10	19	9	24	11	25	9
18	16	13	9	23	6e	17	9	20	17	25	10
19	15	12	17	17	11	15	9e	21	5	19	9
20	16	16	17	28	11	15	10	22	15	26	9
Total	14.7	13.2	12.5	25.2	9.3	21.2	7.9	22.2	10.0	21.3	8.8

Table 8: Individual Specimen Test Lives for 64 Experiments

Unit	34	35	36	37	38	39	40	41	42	43	44
Spec. No.											
1	21	7e	5	12	4	11	23	13	20	10e	5
2	20	19	5	10	3	11	23	12	20	20	5
3	22	18	4	11	4	12	19	5e	18	22	4e
4	24	18	5	1e	8e	12	25	11	22	21	5e
5	21	6e	15	14	4e?	12	23	12	23	21	5e
6	22	25-	5	16	5	12	23	13	22	9	5e
7	18	19	3e	17	9e	14	22	14	17	24	8
8	19	16	4e	18	6	14	18	12	22	17	4
9	22	26-	5	19	4e	11	18	7	18	23	6
11	22	17	3e	15	1e	14	18	11	-	23	9
12	23	17	5	14	5	17	19	14	-	20	7
13	21	17	4	16	5	15	17	14	-	23	7
14	22	23	-	14	8e	13	13	17	17	18	4e
15	13	23	5	18	3e?	13	14	17	15	21	5
16	24	19	6	19	8e	12	17	17	15	21	5
17	23	25-	6	15	2e	4	21	1e	21	19	7
18	23	25-	7	13	5	4	18	11	21	28	1e
19	24	28-	8	11	2e	4	20	15	21	-	1e
20	23	24-	6e	14	14	10	23	19	20	-	4e?
Total	21.4	19.6	5.1	14.0	5.3	11.3	19.7	12.4	19.5	20.0	5.1

Table 8: Individual Specimen Test Lives for 64 Experiments

Unit	45	46	47	48	49	50	51	52	53	54
Spec. No.										
1	9e?	21	15	20	18	12	2	21	11	26
2	12	14e	19	15	15	14	4	21	12	29
3	14	10e	11	18	15	17	4	20	6e	28
4	11	21	18	18	8e	23	6	22	13	32
5	14	21	19	18	7e	24	6	24	14	26
6	13	22	18	18	20	12	6	22	13	29
7	10	26	19	18	19	24	6	26	10	21
8	11	21	23	18	16	20	5	22	11	19
9	11	22	11	17	19	21	6	20	10	17
11	6e	23	9	19	17	27	5	22	17	29
12	-	22	9	18	16	10	5	21	15	23
13	-	20	11	18	20	17	5	29	12	26
14	11	23	17	15	8	15	7	22	17	29
15	13	10	15	12	7	17	7	22	13	26
16	13	23	24	18	13	15	7	22	15	27
17	10	20	11e	25	13	14	5	17	11	24
18	10	20	9	19	6e	10	5	14e	15	21
19	6	15e	11	2e	18	16	5	19	13	22
20	11	18	22	10	19	18	8	16	14	28
Total	10.9	19.6	15.3	14.4	14.4	17.2	5.5	21.2	12.7	25.4

Table 8: Individual Specimen Test Lives for 64 Experiments

Unit	55	56	57	58	59	60	61	62	63	64
Spec. No.										
1	24	1	-	9e	6	12	23	23	8e	6
2	22	1	10	9e	6	22	23	22	11	14
3	26	1	14	9e	8	7e	20	24	15	13
4	22	1	7	10	7	17	23	28	18	16
5	21	1	7	11	7	7e	24	24	17	16
6	20	1	10	9	7	18	18	24	19	18
7	22	1	12	4e	10	19	16	28	16	18
8	19	1	8	5	10	18	25	30	14	16
9	22	1	6	5e	10	11	24	25	16	15
11	23	1	13	6e	10	22	23	25	19	20
12	23	1	10	10e?	5	24	2e	24	15	7
13	17	1	5	10e?	8	19	23	22	16	17
14	23	1	5	4e	9	20	24	27	15	13
15	19	1	5	5e	9	18	21	26	20	13
16	22	1	5	8	9	18	21	16	17	10e
17	21	1	9	11	15	20	25	35	18	17
18	19	1	15	6e	14	20	23	24	20	20
19	19	1	6	11	13	20	23	33	15	17
20	21	1	6	15	12	18	25	24	10	8
Total	21.3	1.0	8.5	8.3	9.2	17.4	21.4	25.4	15.7	14.4

The first step in the numerical analysis was the computation of the arithmetic mean (m), standard deviation (s), m-2s, and m-4s from the individual lives for each experiment. Because the practical significance of edge failures was not known, these computations were carried out both with and without edge-failure data. The results are given in Table 9.

The primary objective of this program was to find a coating process which would maximize the average life of the coating and minimize the variability. However, the experimental results showed that in most cases these objectives were incompatible. Coatings that had long life usually were more variable in performance than those that had a short life. Figure 10. graphically displays this tendency. Experimental conditions that produced long average life were not those that produced the most consistent results. The arrows in the figure portray the effect of edge failures. Generally, excluding edge failures improved the record of a particular experiment. The sloping lines in the figure, labeled m-2s = 0 etc. are useful for graphically weighting the mean and standard deviation in the evaluation of various coating processes. The perpendicular distance of an experimental point from such a line is the appropriate measure of the performance of that experimental coating.

C. Statistical Tests of Significance

The results depicted in Figure 10, although informative, cannot be accepted at face value. These are experimental facts, truthfully represented, but future performance is what really counts. The coating processes represented here are virtually certain to produce different results in further trials. Furthermore, only 64 coating processes can be compared by looking at Figure 10. This is a small fraction of the number of processes for which information is desired. Full use of statistical techniques can supply valuable, additional information. Future results from similar coatings can be predicted, not merely for the 64 coating processes that were actually included in the experimental program but for the entire set of 512 coating processes which can be generated from combining in all possible ways the 9 experimental factors at 2 levels each. Before proceeding to this type of analysis, the effect of edge failures was examined. The central question was whether to include or to exclude edge failures in the statistical analysis. Their effect on the conclusions could not be completely foreseen.

The frequency with which edge failures occurred in the 64 experiments is shown by Table 10. Of the 64 experiments, 25 (39.0 per cent) had no specimens which failed via edges. As a means of deciding whether edge failures were objectionable in the analysis, their effect upon

TABLE 9. SUMMARY STATISTICS BY EXPERIMENT NUMBER

Experiment	Edge Failures Included (a)					Edge Failures Excluded (a)				
	m	m - 2s	m - 4s	s	n	m	m - 2s	m - 4s	s	n
1	28.6	12.5	-3.5	8.0	19	29.5	15.2	0.9	7.2	18
2	13.4	4.4	-4.7	4.5	19	13.4	4.4	-4.7	4.5	19
3	8.7	3.3	-2.1	2.7	19	9.0	4.0	-1.1	2.5	18
4	21.2	13.6	6.0	3.8	18	21.2	13.6	6.0	3.8	18
5	7.4	1.8	-3.8	2.8	19	8.3	3.8	-0.6	2.2	16
6	12.3	5.7	-0.9	3.3	19	12.7	6.9	1.2	2.9	18
7	15.5	4.5	-6.4	5.5	19	16.3	7.6	-1.0	4.3	18
8	23.3	7.0	-9.2	8.1	19	25.8	13.8	1.9	6.0	16
9	15.6	7.6	-0.4	4.0	19	15.6	7.6	-0.4	4.0	19
10	13.2	-0.8	-14.8	7.0	19	16.0	6.8	-2.3	4.6	15
11	13.2	3.5	-6.1	4.8	19	14.6	10.0	5.3	2.3	17
12	12.6	9.4	6.2	1.6	18	12.8	10.6	8.3	1.1	17
13	23.6	11.0	-1.7	6.3	19	24.4	13.7	2.9	5.4	18
14	19.9	15.1	10.3	2.4	19	19.9	15.1	10.3	2.4	19
15	18.6	14.1	9.7	2.2	19	18.6	14.1	9.7	2.2	19
16	21.0	5.8	-9.4	7.6	19	24.4	17.4	10.5	3.5	15
17	16.2	0.3	-15.7	8.0	19	21.0	14.0	7.1	3.5	13
18	27.2	15.1	3.0	6.1	19	28.3	21.0	13.7	3.7	18
19	17.9	12.7	7.5	2.6	19	18.4	14.8	11.1	1.8	18
20	15.6	-3.7	-23.0	9.6	19	18.2	0.4	17.4	8.9	15
21	17.2	9.7	2.2	3.7	19	17.2	9.7	2.2	3.7	19
22	10.1	6.6	3.1	1.7	19	10.1	6.6	3.1	1.7	19
23	14.7	10.7	6.7	2.0	19	14.7	10.7	6.7	2.0	19
24	13.3	11.3	9.3	1.0	19	13.3	11.3	9.3	1.0	19
25	12.5	6.4	0.3	3.0	19	12.5	6.4	0.3	3.0	19
26	25.2	16.6	8.0	4.3	19	25.2	16.6	8.0	4.3	19
27	9.3	6.3	3.2	1.5	19	9.7	7.2	4.6	1.3	15
28	21.3	13.7	6.1	3.8	19	21.3	13.7	6.1	3.8	19
29	7.8	5.4	3.0	1.2	19	7.8	5.3	2.8	1.3	17
30	22.2	14.4	6.6	3.9	19	22.7	16.5	10.3	3.1	18
31	9.9	1.5	-7.0	4.2	19	12.4	4.2	-4.0	4.1	8
32	21.3	10.4	-0.6	5.5	19	22.1	13.4	4.7	4.4	18
33	8.8	7.4	5.9	0.7	19	8.8	7.4	5.9	0.7	19
34	21.4	16.2	11.0	2.6	19	21.4	16.2	11.0	2.6	19
35	19.6	7.8	-4.0	5.9	19	21.1	13.3	5.6	3.9	17

TABLE 9. (CONTINUED)

Experiment	Edge Failures Included					Edge Failures Excluded [a]				
	m	m - 2s	m - 4s	s	n	m	m - 2s	m - 4s	s	n
36	5.1	2.5	0.0	1.3	18	5.4	3.2	1.0	1.1	14
37	14.1	5.8	-2.5	4.1	19	14.8	9.3	3.8	2.8	18
38	5.3	-0.9	-7.0	3.1	19	5.7	-0.8	-7.3	3.2	9
39	11.3	4.0	-3.2	3.6	19	11.3	4.0	-3.2	3.6	19
40	19.7	13.1	6.6	3.3	19	19.7	13.1	6.6	3.3	19
41	12.4	3.7	-5.1	4.4	19	13.5	7.6	1.7	2.9	17
42	19.5	14.4	9.4	2.5	16	19.5	14.4	9.4	2.5	16
43	20.0	10.7	1.3	4.7	17	20.6	12.6	4.5	4.0	16
44	5.1	1.1	-3.0	2.0	19	6.2	3.1	0.0	1.5	11
45	10.9	6.2	1.5	2.3	17	11.3	7.3	3.2	2.0	15
46	19.6	10.9	2.2	4.4	19	20.8	14.0	7.3	3.4	16
47	15.3	5.3	-4.7	5.0	19	15.6	5.5	-4.6	5.0	18
48	16.6	7.3	-2.1	4.7	19	17.4	11.2	4.9	3.1	18
49	14.4	4.6	-5.1	4.9	19	15.8	7.9	0.1	3.9	16
50	17.2	7.3	-2.5	4.9	19	17.2	7.3	-2.5	4.9	19
51	5.5	2.8	0.1	1.3	19	5.5	2.8	0.1	1.3	19
52	21.2	14.5	7.8	3.3	19	21.6	15.7	9.8	2.9	18
53	12.7	7.5	2.2	2.6	19	13.1	8.8	4.6	2.1	18
54	25.4	17.5	9.5	4.0	19	25.4	17.5	9.5	4.0	19
55	21.3	17.0	12.8	2.1	19	21.3	17.0	12.8	2.1	19
56	1.0	1.0	-1.0	0.0	19	1.0	1.0	1.0	0.0	19
57	8.5	1.9	-4.7	3.3	18	8.5	1.9	-4.7	3.3	18
58	8.3	2.3	-3.6	3.0	19	10.0	4.2	-1.5	2.9	8
59	9.2	3.7	-1.8	2.8	19	9.2	3.7	-1.8	2.8	19
60	17.4	7.9	-1.6	4.8	19	18.6	12.1	5.7	3.2	17
61	21.4	10.9	0.4	5.3	19	22.4	17.6	12.7	2.4	18
62	25.5	17.1	8.7	4.2	19	25.5	17.1	8.7	4.2	19
63	15.7	9.2	-2.7	3.3	19	16.2	10.7	5.2	2.7	18
64	14.4	6.1	-2.1	4.1	19	14.7	6.4	-1.8	4.1	18

(a) m = arithmetic mean, number of cycles (2 hours per cycle at 2700 F) to failure;
s = standard deviation, number of cycles (2 hours per cycle at 2700 F) to failure;
n = number of specimens.

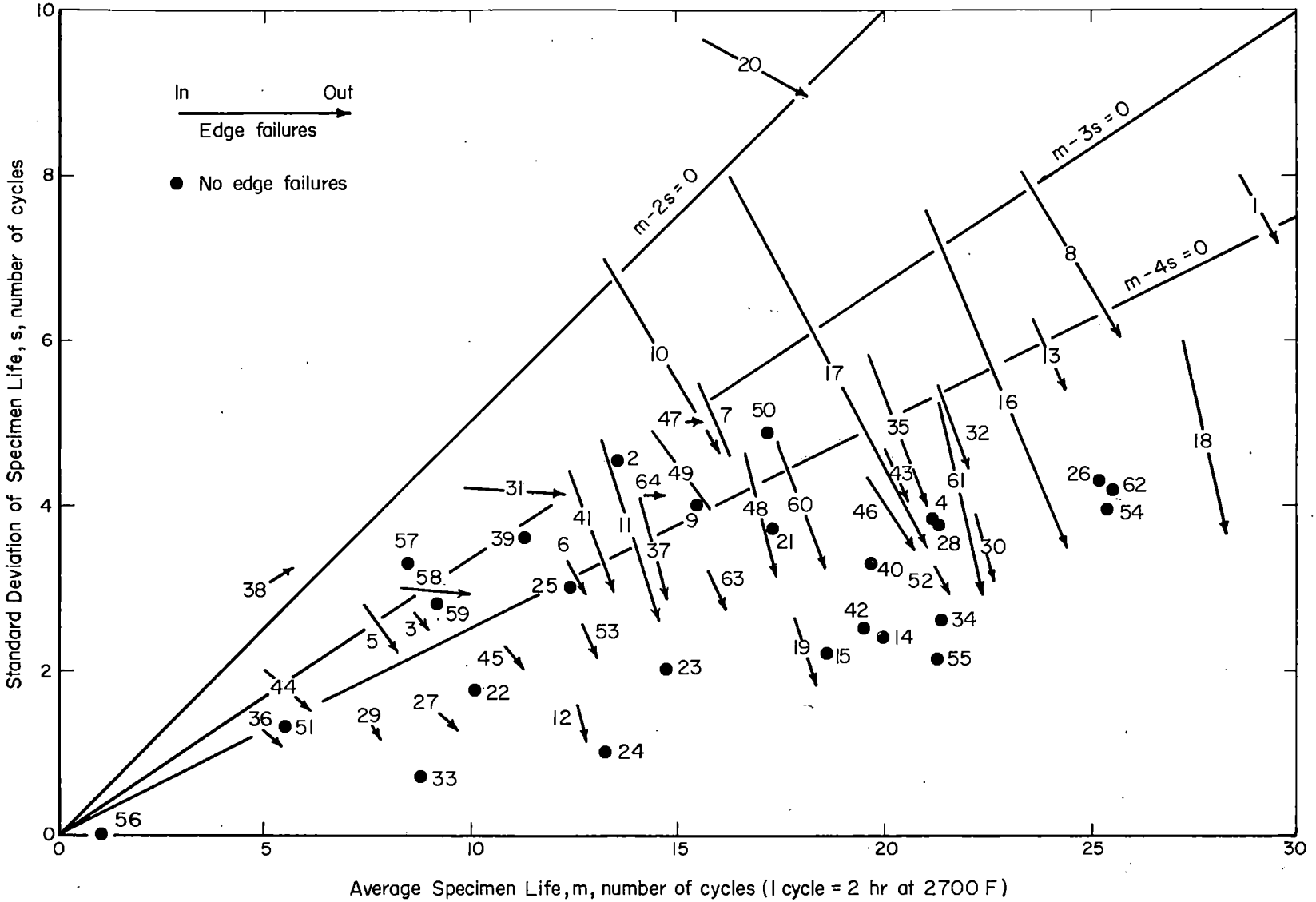

FIGURE 10. EXPERIMENTAL RESULTS FROM 64 SERIES OF SPECIMENS

Table 10. FREQUENCY OF OCCURRENCE OF EDGE FAILURES.

Number of Edge Failures in Experiment [a]	Number of Experiments [b] Having Indicated Number of Edge Failures			Experiment No.
	Number	Per Cent	Cumulative Per Cent	
0	25	39.0	39.0	-
1	19	29.6	68.6	-
2	6	9.4	78.0	-
3	4	6.2	84.2	-
4	5	7.8	92.0	-
5	0	0	92.0	-
6	1	1.6	93.6	17
7	0	0	93.6	-
8	1	1.6	95.2	44
9	0	0	95.2	-
10	1	1.6	96.8	38
11	2	3.2	100.0	38, 58

(a) Each experiment generally had 19 specimens.

(b) Statistical program had 64 experiments.

the statistical distribution of specimen lives was studied in two ways. Histograms constructed on an absolute scale seemed to indicate that the form of the statistical distribution of failure times depended on the percentage of edge failures. As the form of statistical distribution to be expected from this kind of data was not known, this histogram study did not furnish a basis for deciding whether or not edge failures should be included in the analysis.

The second way of examining the influence of edge failures was by use of statistical tests of significance. These results suggested that the frequency of edge failures was not appreciably affected by most of the experimental factors under study, Factor B being the most noteworthy exception. This means that it is not likely to matter whether or not edge failures are included in the statistical analysis.

The following criteria were used in the statistical analysis:

Edge Failures Included	Edge Failures Excluded
m	m
m-2s	m-2s
m-4s	m-4s
s	s

Here, m is the mean specimen life for an experimental group (consisting usually of 19 specimens), and s is the standard deviation of specimen lives for an experimental group. An interaction analysis was carried out for only one criterion (m, edges included). Only two interactions (AJ and FH) among those measurable were significant by ordinary standards. Another interaction (EJ) almost reached this level of significance. Tabulated below are the average number of cycles to failure (computed from 16 experiments per average) for the conditions reflecting these interactions.

	A_o	A_1		E_o	E_1		F_o	F_1
J_o	15.0	16.8	J_o	13.3	18.6	H_o	15.0	10.6
J_1	17.2	13.0	J_1	14.8	15.5	H_1	17.9	18.6

It will be seen later that this information helps to support the choice of an optimum coating process.

The performance of the experimental factors averaged over the entire experimental program is given in Table 11for all eight criteria. The significance of these results is shown in Table 12, which summarizes the statistical tests of significance. Economy in the analysis could be achieved by assuming that interaction effects in general are of little consequence and ignoring them in the subsequent analysis. For this reason, it was decided to combine all interaction effects with experimental error. This increased the degrees of freedom for experimental error from 18 to 54, thereby providing more sensitive significance tests for main effects. This procedure was extended to the analyses for all criteria.

The results shown in Table 11 are depicted graphically in Figure 11. Each arrow in this series of charts represents the performance of a particular experimental factor at a particular level averaged over 32 experimental groups of specimens. The tails of the two arrows in each chart are equally spaced from the point representing the average result ($m = 15.5$, $s = 3.2$) for the entire experiment, edge failures included (1186 specimens).

Similarly, the heads of the two arrows in each chart are equally spaced from the point representing the average result ($m = 16.2$, $s = 2.8$) for the entire experiment, edge failures excluded (1077 specimens). It is the distance from such a midpoint that represents the effect of a factor upon the grand average. Figure 11 is not only a record of past performance; it is also a prediction of the future performance of each experimental factor.

Table 13 is a concise summary of the findings in this section. It presents the distilled essence of Tables 11 and 12. These results will be presented in other ways in the next section.

D. Selection of Optimum Coating Process

The main justification for statistical analysis was the need for an objective method of selecting a coating process. This method is supplied by the analysis of arithmetic means and statistical tests of significance described in the preceding section. Since several standards of comparison were used in this analysis, interpretation of the results

TABLE 11. AVERAGE PERFORMANCE OF EXPERIMENTAL FACTORS FOR ENTIRE EXPERIMENTAL PROGRAM

Experimental Factor	$m^{(a)}$			$m - 2s^{(a)}$			$m - 4s^{(a)}$			$s^{(a)}$		
	Level 0	Level 1	Effect	Level 0	Level 1	Effect	Level 0	Level 1	Effect	Level 0	Level 1	Effect
					Edge Failures Included							
A	16.1	14.9	-1.2	8.4	7.3	-1.1	0.7	-0.3	-0.9	3.3	3.1	-0.2
B	14.6	16.4	1.8	8.3	7.4	-0.9	1.9	1.5	-0.4	2.6	4.1	1.5
C	15.6	15.5	-0.1	7.6	8.1	0.5	-0.4	0.7	1.1	3.4	3.1	-0.3
D	16.9	14.2	-2.7	9.3	6.4	-2.9	1.8	-1.4	-3.2	3.3	3.2	-0.1
E	14.0	17.0	3.0	8.1	7.6	-0.5	2.1	-1.8	-3.9	2.6	4.0	1.4
F	16.4	14.6	-1.8	8.8	6.9	-1.9	1.2	-0.8	-2.0	3.1	3.4	0.3
G	18.2	12.9	-5.3	9.7	6.0	-3.7	1.2	-0.8	-2.0	3.7	2.8	-0.9
H	12.8	18.2	5.4	6.1	9.6	3.5	-0.6	1.0	1.6	2.8	3.8	1.0
J	15.9	15.1	-0.8	8.5	7.2	-1.3	1.0	-0.6	-1.6	3.2	3.2	0.0
					Edge Failures Excluded							
A	16.8	15.6	-1.2	10.7	9.0	-1.7	4.5	2.5	-2.0	2.8	2.7	-0.1
B	15.0	17.4	2.4	9.5	10.2	0.7	3.9	3.1	-0.8	2.3	3.4	1.1
C	16.5	15.9	-0.6	10.1	9.6	-0.5	3.7	3.3	-0.4	2.8	2.7	-0.1
D	17.4	15.0	-2.4	11.0	8.7	-2.3	4.5	2.5	-2.0	2.8	2.7	-0.1
E	14.4	18.0	3.6	9.0	10.7	1.7	3.7	3.3	-0.4	2.4	3.2	0.8
F	17.1	15.3	-1.8	10.8	8.9	-1.9	4.5	2.5	-2.0	2.6	2.9	0.3
G	18.8	13.6	-5.2	11.6	8.1	-3.5	4.3	2.6	-1.7	3.2	2.3	-0.9
H	13.4	19.0	5.6	7.6	12.1	4.5	1.8	5.2	3.4	2.5	3.2	0.7
J	16.5	15.9	-0.6	10.4	9.2	-1.2	4.3	2.7	-1.6	2.8	2.8	0.0

(a) m = arithmetic mean, number of cycles (2 hours per cycle at 2700 F) to failure;
s = standard deviation, number of cycles (2 hours per cycle at 2700 F) to failure.

TABLE 12. RESULTS OF STATISTICAL TESTS OF SIGNIFICANCE

Experimental Factor	Degrees of Freedom	$m^{(a)}$ Variance	$m^{(a)}$ Significance	$m - 2s^{(a)}$ Variance	$m - 2s^{(a)}$ Significance	$m - 4s^{(a)}$ Variance	$m - 4s^{(a)}$ Significance	$s^{(a)}$ Variance	$s^{(a)}$ Significance
				Edge Failures Included					
A	1	22.33	72	18.38	NS[b]	14.25	NS	0.0196	NS
B	1	51.84	89	11.14	NS	191.13	97*	0.6642	99.6**
C	1	00.23	NS	3.95	NS	20.03	NS	0.0281	NS
D	1	114.49	98.2*	137.18	99.1**	159.39	95.3*	0.0023	NS
E	1	146.41	99.2**	2.68	NS	241.03	98.5*	0.4761	98.7*
F	1	53.66	90?	60.65	92?	67.65	81	0.0225	NS
G	1	450.50	>99.99***	213.53	99.86**	64.80	80	0.2280	92?
H	1	473.06	>99.99***	192.86	99.8**	37.82	NS	0.3164	96*
J	1	9.92	NS	23.89	73	43.23	71	0.0000	NS
Error	54	19.32		18.94		38.54		0.0723	
				Edge Failures Excluded					
A	1	25.88	75	44.06	89	66.83	87	0.0033	NS
B	1	88.13	96.4*	8.34	NS	11.73	NS	0.4624	98.9*
C	1	5.12	NS	3.29	NS	2.18	NS	0.0056	NS
D	1	93.36	96.9*	78.99	96.5*	64.40	86	0.0106	NS
E	1	217.93	99.87**	45.39	89	1.76	NS	0.2450	94?
F	1	52.74	89.5	59.87	94?	67.65	87	0.0203	NS
G	1	425.91	99.99***	188.03	99.86**	46.24	79	0.2970	96.3*
H	1	518.13	99.99***	325.35	>99.99***	178.22	98.5*	0.1936	90.8?
J	1	7.36	NS	22.44	74	42.58	77	0.0000	NS
Error	54	19.36		16.99		28.67		0.0663	

(a) m = arithmetic mean, number of cycles (2 hours per cycle at 2700 F) to failure;
s = standard deviation, number of cycles (2 hours per cycle at 2700 F) to failure.

(b) NS = definitely not significant statistically.

? 90 per cent $\leq$ statistical significance < 95 per cent.

* 95 per cent $\leq$ statistical significance < 99 per cent.

** 99 per cent $\leq$ statistical significance < 99.9 per cent.

*** 99.9 per cent $\leq$ statistical significance.

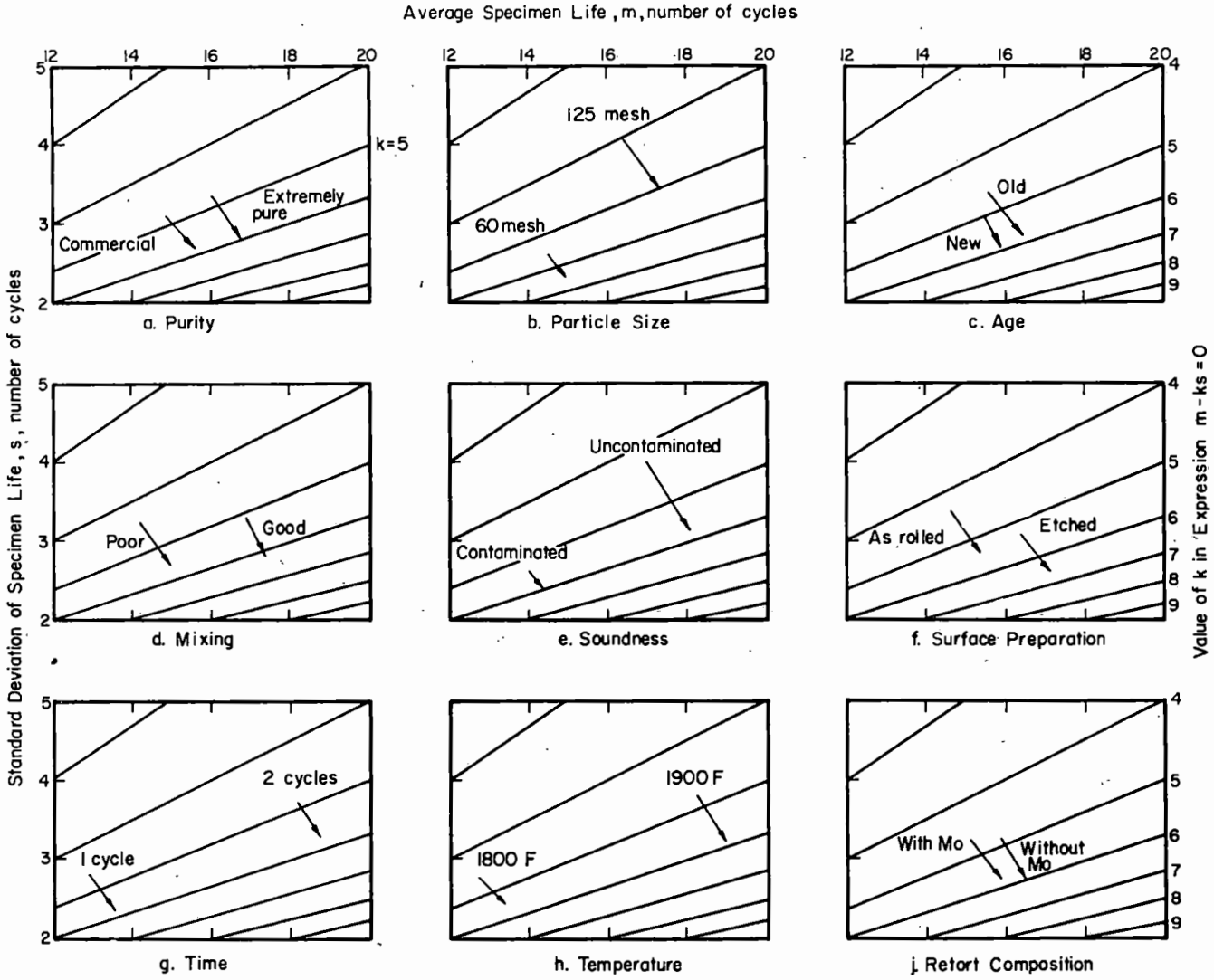

FIGURE 11. AVERAGE PERFORMANCE OF EXPERIMENTAL FACTORS FOR ENTIRE EXPERIMENTAL PROGRAM

Table 13. Preferred Levels of Experimental Factors By Decreasing Order of Their Statistical Significance.[a]

m	m-2s	m-4s	s
	Edge Failures Included		
H_1[b]	G_o[c]	E_o[d]	B_o[c]
G_o[b]	H_1[c]	B_o[d]	E_o[d]
E_1[c]	D_o[c]	D_o[d]	H_o[d]
D_o[d]	F_o ?[e]	F_o	G_1 ?[e]
F_o ?[e]	J_o	G_o	C_1
B_1	A_o	J_o	F_o
A_o.	B_o	H_1	A_1
J_o	C_1	C_1	D_1
C_o	E_o	A_o	$J_{o,1}$
	Edge Failures Excluded		
H_1[b]	H_1[b]	H_1[d]	B_o[d]
G_o[b]	G_o[c]	F_o	G_1
E_1[c]	D_o[d]	A_o	E_o ?[e]
D_o[d]	F_o?[e]	D_o	H_o ?
B_1[d]	E_1	G_o	F_o
F_o	A_o	J_o	D_1
A_o	J_o	B_o	C_1
J_o	B_1	C_o	A_1
C_o	C_o	E_o	$J_{o,1}$

(a) s = standard deviation, number of cycles (2 hr. per cycle at 2700F) to failure
(a) m = arithmetic mean, number of cycles (2 hour per cycle at 2700°F) to failure.
(b) 99.9 per cent $\leq$ statistical significance.
(c) 99 per cent $\leq$ statistical significance $<$ 99.9 per cent.
(d) 95 per cent $\leq$ statistical significance $<$ 99 per cent.
(e) ? 90 per cent $\leq$ statistical significance $<$ 95 per cent

requires the exercise of personal judgment. In order to simplify the task of surveying the many diverse results, the salient findings are summarized in condensed form in Table 11. In this table is shown the statistically preferred level * of each experimental factor for each of the eight criteria considered. A question mark follows the choice of level if that choice is not statistically significant at the 90 per cent level of certainty.

The following general observations can be made. With few exceptions, the choice of level is not affected by edge failures. Except for F and J, the statistically preferred levels for m and s are different. Excluding the criterion of minimum s, the preferred levels of A, D, F, G, H, and J were consistent for each factor. These consistent levels are boxed off in Table 11. Neither maximizing m nor minimizing s is of sole importance. The quantity m-ks must be maximized, where k is a finite, positive number. The size of k has not been specified but values between zero and 4 are of most interest.

Each experimental factor will now be considered in turn. Level 0 of factor A showed up slightly better than Level 1, but this finding is not statistically significant. Inasmuch as Level O is extremely pure powder, Level 1 is more economical, and this fact overshadows other considerations. Next consider Factor B, coarseness of powder. Table 14 shows that Level 1 (325-mesh powder) is favored for maximizing m, but Level O (60-mesh powder) is favored for maximizing m-4s. Level O is also favored (strongly) for minimizing s and was previously found to be associated with minimizing edge failures. Therefore this level is recommended for B. The analysis indicates no preference in the level of C (age of powder). Therefore Level 1 (new powder) or Level O (aged powder) may be used as operating convenience dictates. Level O (good mixing) is the obvious choice for D. Factor E, soundness of base metal performed inconsistently. From a practical standpoint, it seems unwarranted to intentionally contaminate commercial Mo-0.5Ti (Level O) before coating it unless a strong reason for doing so exists. Also, differences in lives of coated Mo-0.5Ti appeared in the preliminary experiments. This could be due to differences in degree of surface contamination. It would, therefore, appear wise to minimize such an affect in order to get consistent quality. Thus, Level 1 is recommended. Level O for F (surface etching), Level O for G (2 hour cycles), and Level 1 for H ($1900^{o}F.$) were confidently chosen. The analysis of Factor J (retort composition) favors Level O (mild steel) over Level 1 (mild steel with molybdenum insert) very slightly. No statistical significance is attached to this choice, but since Level O is a good choice economically, it is recommended. The complete coating process for producing an optimized

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* On the basis of maximum m, m-2s, m-4s, and minimum s.

TABLE 14 PREFERRED LEVELS OF EXPERIMENTAL FACTORS BASED ON DIFFERENT STATISTICAL CRITERIA[a]

Experimental Factor	Failures	m	m - 2s	m - 4s	s
A	Included	0?	0?	0?	1?
	Excluded	0?	0?	0?	1?
B	Included	1?	0?	0	0
	Excluded	1	1?	0?	0
C	Included	0?	1?	1?	1?
	Excluded	0?	0?	0?	1?
D	Included	0	0	0	1?
	Excluded	0	0	0?	1?
E	Included	1	0?	0	0
	Excluded	1	1?	0?	0
F	Included	0	0	0?	0?
	Excluded	0	0	0?	0?
G	Included	0	0	0?	1
	Excluded	0	0	0?	1
H	Included	1	1	1?	0
	Excluded	1	1	1	0
J	Included	0?	0?	0?	?
	Excluded	0?	0?	0?	?

(a) m = arithmetic mean, number of cycles (2 hours per cycle at 2700 F) to failure.
s = standard deviation, number of cycles (2 hours per cycle at 2700 F) to failure.
? = not statistically significant at the 90 per cent level.

W-2 coating on Mo-0.5Ti, based on maximum m-ks, statistical significance, and practical considerations is accordingly the following:

Factor	Level	Condition
A	1	Commercial-purity powder
B	O	-60 + 150 mesh particle size
C	O, 1	New or aged powder
D	O	Good mixing
E	1	Uncontaminated substrate
F	O	Etched and honed substrate
G	O	Dual processing (12 hours, 12 hours)
H	1	1900°F.
J	O	Steel retort

It is of interest to compare the statistical predictions for several selected coating processes with the experimental results (Table 15). First are considered the following three coating procedures recommended for maximizing m-ks:

$$D_o\ G_o\ H_1$$

$$D_o\ G_o\ H_1\ E_1\ F_o$$

$$D_o\ G_o\ H_1\ E_1\ F_o\ A_1\ B_o\ C_{o,1}\ J_o$$

Next are considered the following two coating procedures recommended for minimizing s:

$$B_o\ E_o\ G_1\ H_o$$

$$B_o\ E_o\ G_1\ H_o\ A_1\ C_{o,1}\ D_1\ F_o$$

TABLE 15. COMPLETED EXPERIMENTS WITH PREFERRED LEVELS OF PERTINENT VARIABLES FOR MAXIMUM (m – ks) AND MINIMUM s[a]

Experiment	Level of Indicated Variable									Edge Failures:	m, cycles[b]		s, cycles[b]		Cycle Number in Which First Failure Occurred		
	D	G	H	E	F	A	B	C	J		Incl.	Excl.	Incl.	Excl.	Edge	Surface	First Failure
Consideration of Maximum (m – ks)																	
1	0	0	1	1	1	1	1	0	0		28.6	29.5	8.0	7.2	12	15	12
13	|	|	|	1	1	0	0	1	0		23.6	24.4	6.3	5.4	9	14	9
19	|	|	|	0	0	1	0	1	0		17.9	18.4	2.6	1.8	10	16	10
20	|	|	|	1	0	1	0	0	1		15.6	18.2	9.6	8.9	3	1	1
26	|	|	|	0	0	0	1	0	0		25.2	25.2	4.3	4.3	–	17	17
30	|	|	|	0	1	1	1	1	1		22.2	22.7	3.9	3.1	12	17	12
55	|	|	|	0	1	0	0	0	1		21.3	21.3	2.1	2.1	–	17	17
62	|	|	|	1	0	0	1	1	1		25.5	25.5	4.2	4.2	–	16	16
										Average:	22.5	23.2	5.1	4.6			
Statistical Prediction	0	0	1	–	–	–	–	–	–		22.2	22.8	4.4	3.8			
1	0	0	1	1	1	1	1	0	0		28.6	29.5	8.0	7.2	12	15	12
13	|	|	|	|	1	0	0	1	0		23.6	24.4	6.3	5.4	9	14	19
20	|	|	|	|	0	1	0	0	1		15.6	18.2	9.6	8.9	3	1	1
62	|	|	|	|	0	0	1	1	1		25.5	25.5	4.2	4.2	–	16	16
										Average:	23.3	24.4	7.0	6.4			
20	0	0	1	1	0	1	0	0	1		15.6	18.2	9.6	8.9	3	1	1
62	0	0	1	1	0	0	1	1	1		25.5	25.5	4.2	4.2	–	16	16
										Average:	20.6	21.8	6.9	6.5			
Statistical Prediction	0	0	1	1	0	–	–	–	–		24.6	25.5	5.2	4.1			
Statistical Prediction	0	0	1	1	0	1	0	0	0		23.6	24.3	4.2	3.4			
Statistical Prediction	0	0	1	1	0	1	0	1	0		23.5	23.7	3.8	3.2			
Consideration of Minimum s																	
3	1	1	0	0	0	1	0	0	0		8.7	9.0	2.7	2.5	4	4	4
51	1	|	|	|	1	0	|	1	1		5.5	5.5	1.3	1.3	–	2	2
53	0	|	|	|	0	0	|	0	1		12.7	13.1	2.6	2.1	6	10	6
59	0	|	|	|	1	1	|	1	0		9.2	9.2	2.8	2.8	–	5	5
										Average:	9.0	9.2	2.4	2.2			
Statistical Prediction	–	1	0	1	–	–	0	–	–		7.8	7.8	1.6	1.5			
Statistical Prediction	1	1	0	0	0	1	0	0	0		7.2	7.5	1.5	1.4			
Statistical Prediction	1	1	0	0	0	1	0	1	0		7.1	6.9	1.4	1.3			

(a) s = standard deviation of a single point in an experiment usually containing 19 specimens.
m = mean life in an experiment.

(b) 1 cycle signifies 2 hours at 2700 F.

In each of the above cases, the factors are shown in order of their importance from left to right. Table 15 lists the completed experiments which were run with the preferred levels of the pertinent variables. The following points should be noted:

1. The statistically preferred variable levels to give minimum s also give a small m, and s is not sufficiently small to make $(m\text{-}ks)_{min.\,s} > (m\text{-}ks)_{max.\,m}$. Consequently the levels to use for achieving an optimized coating are those specified for maximizing m-ks.

2. Eight experiments have been run at the preferred levels of the major variables (D, G, H) for maximum m-ks. It appears that Experiment 20, having a low m and a high s, was controlled by factors extraneous to the statistical program which was conducted.

3. Excluding Experiment 20 from consideration, 7 experiments (133 specimens) indicate that a specimen life of 8 cycles (16 hours) at 2700°F. can be specified with a reasonable degree of confidence, based on controlling the major variables, D, G, and H, at the preferred levels.

E. Tolerance Limits

Data summarized by use of only the arithmetic mean and standard deviation furnish a good idea of the magnitude and fluctuation of the measurements and is adequate for many purposes. Usually needed, however, is the percentage of measurements between two limits, or the limit above which lie a certain percentage of the measurements. This type of information cannot be derived from the mean and standard deviation alone. The statistical distribution of the individual measurements must be completely specified. Such information may be derived from experience, from theoretical considerations, or from a distribution study of current data. In the present case, theory suggests the normal and extreme-value distributions as likely candidates to describe the life data of individual metal tabs.

Tabulated below are fractiles, corresponding to several integral values of k in the expression m-ks, derived from a plot of actual points and extreme value and normal distribution curves on probability graph paper. Each fractile represents the percentage of specimens failing before time m-ks. This tabulation demonstrates that the

Statistical Distribution	k				
	1	2	3	4	5
Normal	15.9	2.28	0.14	0.003	0.00005
Actual	16.8	4.00	0.59	0.080	0.00020
Extreme value	14.4	4.23	1.19	0.333	0.09130

distributions under comparison differ most in the tails. It is usually more practical to have such tables in a form showing k as a function of the fractile. This is done in the tabulation below, which lists values of k corresponding to three fractiles for each of the three distributions.

Statistical Distribution	Fractile, per cent		
	0.1	1.0	5.0
Normal	3.09	2.33	1.65
Actual	3.88	2.70	1.87
Extreme value	4.94	3.14	1.87

It is desirable to predict failure time in such a way that at least a given percentage of future observations can be expected to lie above a computed fractile with a specified degree of certainty. The computed fractile is called a "tolerance limit" and the degree of certainty is referred to as the "confidence coefficient." When the mean and standard deviation of the statistical population are unknown, as in the present case, the tolerance limit must be computed on the basis of the sample estimate m of the mean and the estimate s of the standard deviation. A lower tolerance limit is given by m-ks, where the factor k accounts for the experimental errors in m and s as well as for the population fractile. Values of k corresponding to various population fractiles, confidence coefficients, and sample sizes are given in a table by Owen.* However, this table is limited to the normal distribution. Including in the calculation the entire experiment of 1186 specimens, while keeping the assumption of an extreme-value distribution and including specimens with edge failures, leads to the following lower tolerance limits corresponding to a confidence coefficient of 99.9 per cent.

* Owen, D.B., Tables of Factors for One-Sided Tolerance Limits for a Normal Distribution, Sandia Corporation Monograph under AEC Contract AT-(29-1)-789 (April, 1958).

Proportion (per cent) of population above limit	99.9	99.0	95.0
Lower tolerance limit (no. of cycles to failure)	2.1	9.8	15.4

There is less than one chance in a thousand of being misled by accepting the tolerance limits produced by these calculations, provided the assumptions are right.

The preceding results are intended to be conservative. A lower tolerance limit is designed to underestimate the population percentage point to provide a margin of safety. If no margin of safety is wanted, but only a "best guess" on a population fractile, then the quantity m-ks should be used, where k is the quantity tabulated earlier in this section. Proceeding on this basis, and using k-values corresponding to the actual experimental results for all 1186 specimens (including those with edge failures), leads to the following expected fractiles.

Proportion (per cent) of population above limit	99.9	99.0	95.0
Expected fractile (no. of cycles to failure)	8.0	12.7	16.0

An attitude of extreme optimism could motivate the calculation of even higher estimates. Assuming a normal distribution of failure times and excluding specimens with edge failures leads to the following expected fractiles.

Proportion (per cent) of population above fractile	99.9	99.0	95.0
Expected fractile (no. of cycles to failure)	13.8	16.3	18.6

These figures may be regarded as predictions of future achievements, after the reasons for edge failures are learned and failures of this type are eliminated.

Other assumptions lead to other estimates. Tabulated below for easy comparison are tolerance limits in units of cycles to failure, corresponding to a confidence coefficient of 99.9 per cent, which represent various sets of assumptions.

Statistical Distribution	Proportion (per cent) of population above limit, including edge failures			Proportion (per cent) of population above limit, excluding edge failures		
	99.9	99.0	95.0	99.9	99.0	95.0
Extreme value	2.1	9.8	15.4	6.4	12.7	17.3
Actual	6.7	10.9	15.3	11.7	15.4	17.8
Normal	10.1	13.4	16.3	13.0	15.7	18.1

A similar tabulation of expected fractiles*, representing the same sets of assumptions, is given below.

Statistical Distribution	Proportion (per cent) of population above fractile, including edge failures			Proportion (per cent) of population above fractile, excluding edge failures		
	99.9	99.0	95.0	99.9	99.0	95.0
Extreme value	3.7	10.9	16.0	7.7	13.6	17.8
Actual	8.0	12.7	16.0	12.6	16.0	18.3
Normal	11.1	14.2	16.9	13.8	16.3	18.6

Clearly, the assumptions strongly influence the predictions of future performance.

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* Computed from the arithmetic mean and standard deviation predicted for A_1, B_o, $C_{o,1}$, D_o, E_1, F_o, G_o, H_1, J_o, where $C_{o,1}$ is the average of C_o and C_1. Including edge failures, this prediction (based on 1186 specimens) is $m = 23.5$, $s = 4.0$ cycles to failure; excluding edge failures, this prediction (based on 1077 specimens) is $m = 24.0$, $s = 3.3$ cycles to failure.

F. Preparation and Testing of Optimized Coating

In order to test the performance predictions for the optimized coatings, five sets of specimens were separately produced under the prescribed conditions. Figure 12 is a photograph of specimens from each of the five runs which shows the uniform appearance of the as-coated specimens.

The specimens were oxidation tested in the Chromalloy tube furnace at 2700°F. The first failure (an edge failure) occurred after 7 cycles (14 hours) at 2700°F. According to earlier predictions (assuming the extreme value type distribution is applicable), only one specimen in one hundred should fail before 9.8 cycles. Since this first failure was only one in forty-five specimens, it cannot be concluded that the prediction would not be fulfilled. Also, edge failures are found to be random and could occur even earlier. What is needed here is more uniform quality of edge preparation.

The mean lives and standard deviations obtained are presented in Table 16.

Table 16. Mean Lives, m and Standard Deviations, s in 2 Hour Cycles at 2700°F for Optimized W-2 Coatings

Experiment No.	Edge Failures, In or Out	m	s
8690	In	18.6	3.7
	Out	20.0	2.7
8692	In	29.7	2.1
	Out	29.7	2.1
8693	In	19.7	4.7
	Out	23.7	3.1
8696	In	24.8	3.4
	Out	25.6	2.9
8701	In	14.8	1.4
	Out	14.8	1.4
Average for five runs	In	21.1	3.1
	Out	23.8	2.4

There is considerable spread in the life data for the five preparations tested, as is evident from Table 16. However, it seems certain that a life of fron 29 to 60 hours at 2700°F. can be guaranteed with a minimum life of 11.6 hours at a 99.9 tolerance limit and 99.9 confidence coefficient.

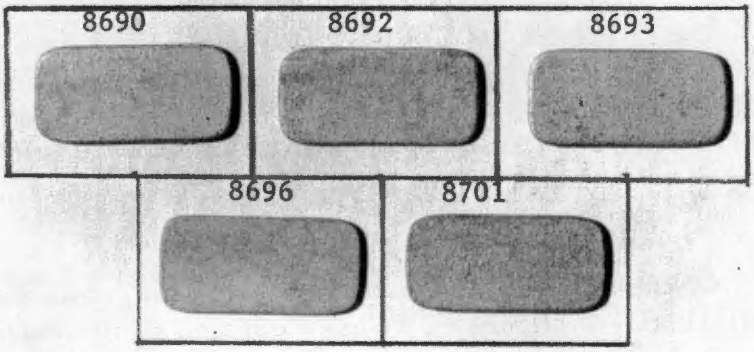

Figure 12. Appearance of 5 Optimized Coatings.

G. Discussion

Since the factors in the W-2 coating process which were primarily responsible for increasing the coating life in cyclic oxidation at 2700°F. also tended to reduce the reliability of the coating life, the quantity to be considered in optimization of the process is (m-ks, where m is the mean life of the coating, s is the standard deviation of the mean life, and k is a constant which depends on the statistical distribution which the life data follow and the degree of reliability desired. This factor is important since neither maximum coating life nor maximum reliability alone is of much practical usefulness.

Using the (m-ks) criterion, the major coating process variables were found to be time and temperature of processing and mixing of the powders used in the process. The variables of secondary importance were soundness of substrate and surface preparation. Minor importance was attached to the variables purity, particle size and age of the powder and retort composition.

Of the thirty measurable interactions, only two were found to be statistically significant. Consideration of the main effects of the variables indicated, however, that the interaction effects were of little practical importance.

Only particle size of the powder was found to be related to frequency of edge failures. The data indicates that the coarse powder (-60 + 150 mesh) was preferable for reducing edge failure occurrence. In general, identification of major process variables and their preferred levels for optimization were unaffected by the inclusion or exclusion of edge failures in the analysis.

Data for coating life in cyclic oxidation at 2700°F. followed a statistical distribution which was between the normal and extreme-value types. Excluding edge failures favored the normal distribution type, inclusion of edge failures favored the extreme-value type.

The type of distribution assumed by the data is important because reliability is strongly associated with the type of distribution followed. If a normal distribution was indicated by the data, greater reliability could be predicted. Since removal of edge failure data resulted in a more nearly normal distribution, it is evident that elimination of edge failures would increase coating reliability. This could be done by

improving edge preparation quality or, where feasible, keeping edges out of heat encountering zones.

Production of an optimized W-2 coating on Mo-0.5Ti should be carried out by using either a new or aged pack of commercial purity powder of -60, + 150 particle size. The powder should be well mixed. The Mo-0.5Ti to be coated should present a uniform quality uncontaminated surface. This material would be etched and honed. The work pieces should be "double processed" (2 times for 12 hours) at 1900°F. in a steel retort.

Statistical predictions for this coating indicate an average life of 23.5 cycles (47 hours) at 2700°F. and a standard deviation of 4.0 cycles (8 hours) at 2700°F. under the experimentally used conditions. With a confidence coefficient (certainty) of 99.9 per cent, 99.9, 99.0 and 95.0 per cent of the optimized coating lives should fall above 2.1, 9.8 and 15.4 two hour cycles at 2700°F.

Cyclic oxidation tests on five groups of optimized coatings were conducted. One of the forty-five specimens failed on the edge before the predicted 9.8 cycles. However, on so small a sample it cannot be stated that the prediction was not fulfilled.

One of the five optimized groups prepared and tested apparently did not fulfill the predictions. This group had an average life of 14.8 cycles, well below the lives of the other four groups. Reasons for this discrepancy are not apparent at this time. It is suspected, however, that there may have been some deviation from optimum conditions in preparing this coating. It is, however, certain that an average life of 29 to 60 hours at 2700°F. can be expected under the oxidizing conditions of this program.

VI. Characterization and Analysis of the W-2 Coating on Mo-0.5Ti

A. Procedure

At the beginning of the project it was planned that Battelle would do detailed identification, characterization, and evaluation studies on the optimized W-2 coating which would emerge from Chromalloy's program. As the program progressed, it became obvious that time limitations would not permit the carrying out of these studies on the final optimized coating. Therefore, it was decided that these studies should

be done on the specimens which were used by Battelle early in the program to aid in designing the experimental program. Because these specimens had the double-cycle processing (12 hours per cycle) at 1900°F. which subsequently was recommended from the statistical program, and because the pack and substrate compositions remained fixed for the program, the characterization and chemical analysis results obtained should be close to those which would have been obtained for the optimized conditions discussed earlier in this report.

B. Microscopic Study of Nature and Behavior of the W-2 Coating

1. Coating Zones

As prepared W-2 coated specimens had the same general appearance. Ordinary and polarized light revealed two differently textured zones with the outer zone occupying about fifteen per cent of the total coating thickness of 3.6 mils (Figures 13 and 14). This difference in texture could be the result of the double process used to coat the specimens.

Apparently, the coating texture was homogenized by recrystallization or grain growth during exposure to air at 2700°F. since the different texture was no longer observed in specimens exposed to these conditions for six hours. No specimens tested for shorter periods were available for study.

Based on appearance under polarized light, and election probe results (to be presented later), Zone A (Figure 15) appears to be remnant of the original coating remaining after oxidation.

The total coating thickness grows with exposure time at 2700°F., with Zone B increasing in depth, Zone A decreasing and Zone C and the oxide layer remaining constant (Table 17 and Figures 13, 15, 16).

2. Etching Characteristics

The procedure used for etching W-2 coated Mo-0.5Ti specimens was as follows:

(1) Swab with 30:10:5--lactic:nitric:hydrofluoric acid by volume. The nitric acid content of this etchant is critical; occasionally it has been responsible for etching out the narrow zone (Zone C) next to the Mo-0.5Ti substrate as well as overetching the substrate.

(2) Swab with Murakami's solution.

The as-prepared W-2 coating etched at a slower rate than the W-2 coating on specimens which had been oxidized. Zones A and B in oxidized specimens appeared to etch uniformly. Zone C next to the Mo-0.5Ti substrate was attacked rapidly by the Murakami etchant.

3. Thickness of Coating Zones and Substrate Versus Oxidation Time at 2700°F.

Table 17 gives the average thickness measurements made on Zones A and B on both the flat sides of each coated specimen and the substrate thickness. Figure 17 shows their variation with oxidation time.

Appreciable scatter is evident in some of the data, particularly those for Zone A for the 8531 series of specimens and the 8521 series after about 9 cycles (18 hours) at 2700°F. Measurements made on the edges show considerably more variation than those made on the flat portions of the tab specimens. Within a single as-coated specimen the substrate thickness was found to vary as much as 1.5 mils, and the difference between the maximum and minimum average substrate thickness for the four as-coated specimens was 2 mils.

Figure 17 shows:

(1) The thickness of the coated system (coating + substrate) remained approximately constant or increased slightly as oxidation time was increased.

(2) Substrate thickness decreased as oxidation time increased. After 22 hours of oxidation at 2700°F., the substrate thickness had decreased by 2.5 to 4.5 mils. During this same time the total coating thickness (oxide + A + B + C) increased by 4 mils.

(3) Zone B increased at the expense of Zone A and the substrate via interdiffusion with increasing oxidation time.

(4) The data for specimens 8531 - 4, 5, 6 and 9 (represented in Figure 17 by squares), which came from a different lot of Mo-0.5Ti substrate, agreed well with those for the other specimens except for Zone A. The data suggest that the original coating on specimens 8531-1 through 9 was about 1 mil less in thickness than the coating on the other specimens.

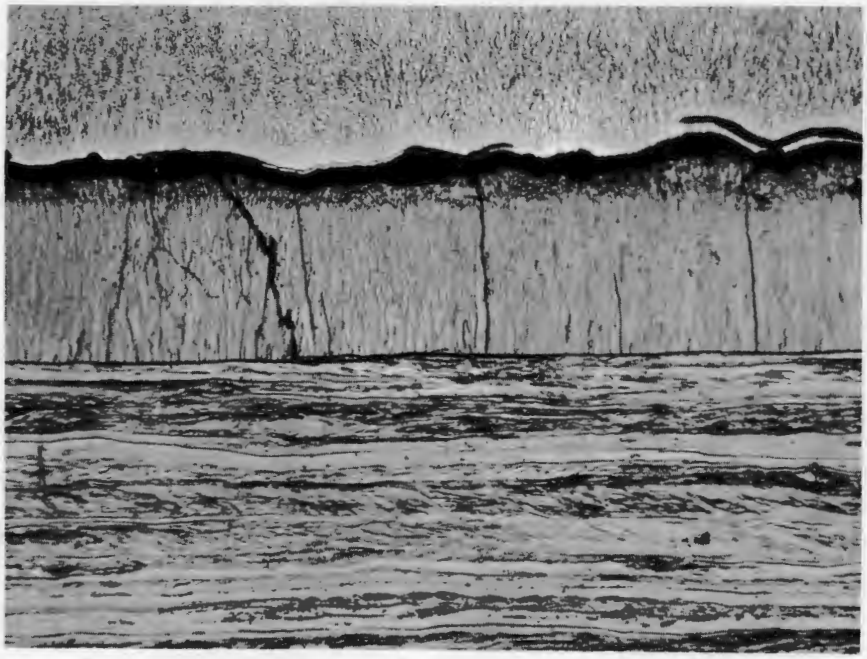

Figure 13. Mo-0.5Ti As coated with W-2
250 X

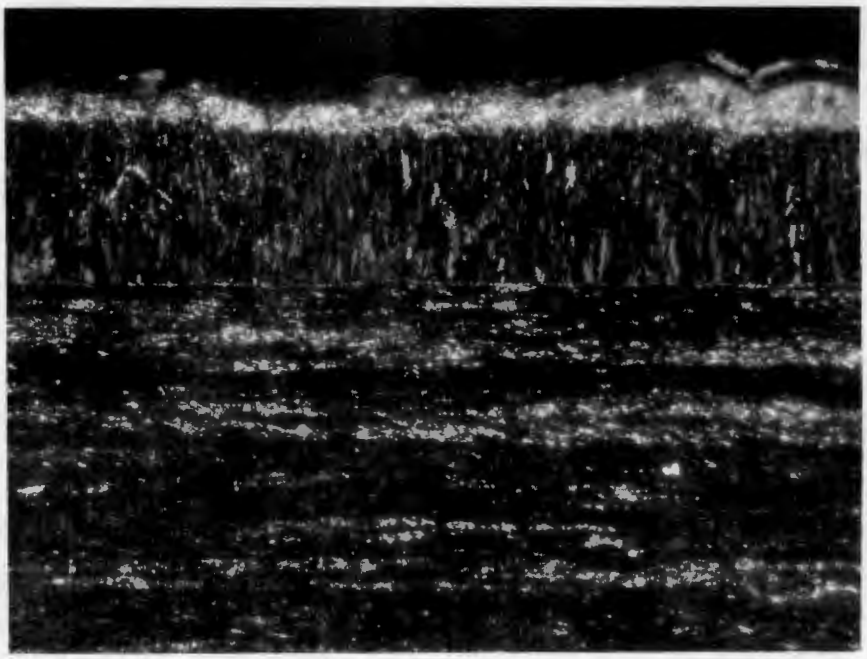

Figure 14. Mo-0.5Ti As coated with W-2
Under Polarized Light
250X

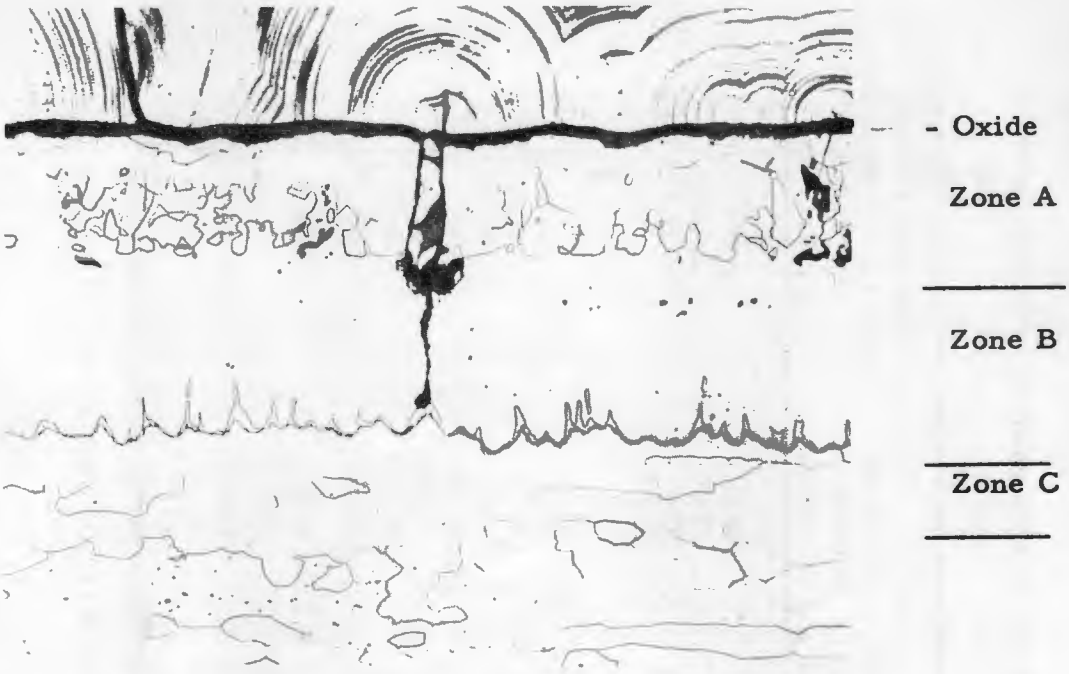

Figure 15. After 10 hours at 2700°F.
Mag. 250 X

Figure 16. After 22 hours at 2700°F.
Mag. 250 X

TABLE 17. AVERAGE THICKNESS OF COATING AND SUBSTRATE ON W-2 COATED Mo-0.5Ti TAB SPECIMENS

Specimen No.	Number of 2-Hr Oxidizing Cycles at 2700 F	Coating Thicknesses Measured on Flat Sides of Specimens, mils/side					Substrate Thickness, mils	Specimen (Total Coating + Substrate) Thickness, mils
		Oxide	A	B	C	A + B		
8521-21	As-Coated	-	3.5	-	-	3.5	34.1	41.1
8522-43	Ditto	-	3.7	-	-	3.7	33.6	41.0
8531-21	"	-	3.6	-	-	3.6	32.6	39.8
8532-23	"	-	3.4	-	-	3.4	32.1	38.9
8521-11	3	0.1-0.3	2.3	2.3	0.07-0.10*	4.6	30.7	40.5
-5	4	"	2.5	2.8	"	5.3	29.9	41.1
-3	5	"	2.1	3.2	"	5.3	30.5	41.7
-17	6	"	2.2	3.6	"	5.8	29.7	41.9
-9	7	"	2.6	3.8	"	6.4	31.0	44.4
-13	8	"	1.9	3.8	"	5.7	29.2	41.2
-1	9	"	2.4	4.4	"	6.8	29.7	43.9
8522-23	11	"	0.9	4.8	"	5.7	28.4	40.4
8531-5	6	"	1.0	3.6	"	4.6	31.0	40.8
-9	7	"	1.2	3.8	"	5.0	31.0	41.6
-6	8	"	1.0	4.2	"	5.2	29.4	40.4
-4	9	"	0.6	4.8	"	5.4	29.4	40.8

* Zone C protruded into Zone B with pips measuring as high as 1.3 mils and as wide as 0.8 mil.

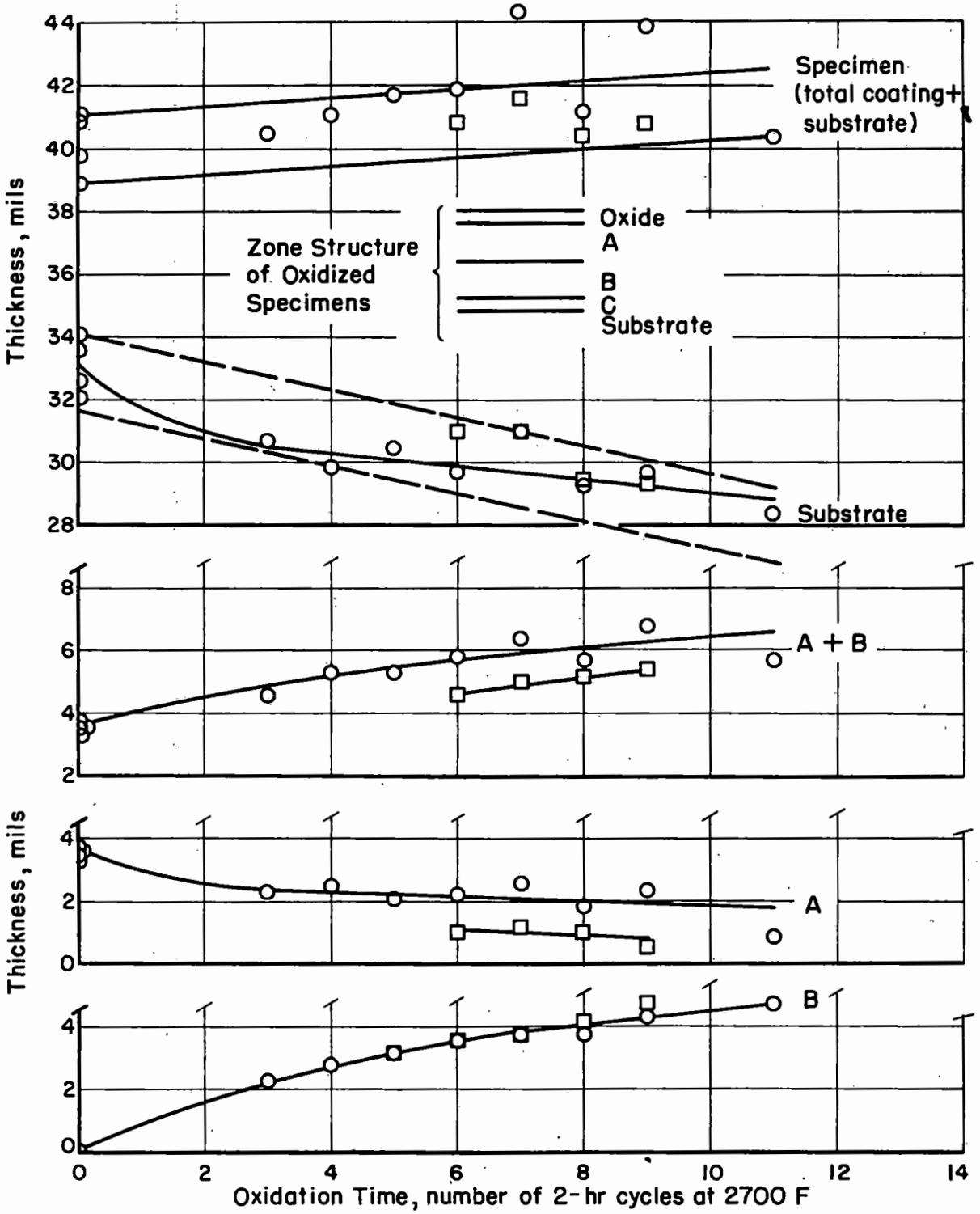

FIGURE 17. VARIATION OF THICKNESS OF SUBSTRATE AND COATING ZONES IN W-2 COATED Mo-0.5Ti VERSUS OXIDATION TIME AT 2700°F

4. Hardness of Coated Systems

Hardness traverses were made on the coatings and substrates of the as-coated and oxidized specimens. Traverses were made in the substrate under crack-free coating and where cracks existed in the coating.

No systematic variation of hardness with distance was observed for the coating or substrate in the as-coated condition. Except for three specimens, no systematic variation of hardness was found with distance in the oxidized specimens. Table 18 gives the extreme and average hardnesses obtained from the traverses, and Table 19 and Figure 18 give the data for the three specimens which showed hardness variation in the substrate under coating cracks. This variation probably was caused by a contamination reaction; the microstructures appeared normal in the areas of hardening.

The grand average hardness of Zone A in the as-coated condition was 1825 KHN; this dropped after three cycles (6 hours) of oxidation at 2700°F. to 1095 KHN, after which it remained constant (grand average hardness of Zone A for oxidized samples was 1080 KHN). Zone B was harder than Zone A (grand average of 1550 versus 1080 KHN).

As shown in Figure 18, the substrate hardness dropped from 375 KHN initial to about 235 KHN due to recrystallization within the first three cycles (6 hours) of oxidation, after which a small and constant rate of decrease occurred with increasing oxidation time.

5. Coating Cracks

Location and Geometry. The flat sides of the as-coated specimens had fairly regularly spaced hairline cracks which were perpendicular to the plane of the substrate and which measured $\leq$0.03-0.1 mil in width. Numerous larger cracks of varying geometry also were found; the maximum width of these cracks varied from 0.1 to 0.6 mil. Most of the cracks appeared to extend to the substrate of the as-coated specimens.

The edges of the as-coated specimens had hairline cracks and rather wide (on the outside) V-shaped cracks.

Cyclically oxidized specimens had wide cracks in Zone A, but these cracks narrowed into hairline cracks in Zone B, and frequently they terminated in Zone B or Zone C.

Crack Width. The width of 20 consecutive cracks, measured on the flat side of as-coated specimen 8521-21, was as follows:

TABLE 18. KNOOP HARDNESS OF COATING ZONES AND SUBSTRATE IN W-2 COATED Mo-0.5Ti

Specimen No.	No. of 2-Hr Oxidizing Cycles at 2700 F	Knoop Hardness Number, 100-g load											
		Zone A[a]			Zone B[a]			Under Crack-Free Coating			Under Coating Cracks		
		Max.	Min.	Av.[b]	Max.	Min.	Av.[b]	Max.	Min.	Av.[b]	Max.	Min.	Av.[b]
8521-21	As-coated	1895	1560	1725	—	—	—	415	345	385	—	—	—
8522-43	As-coated	2010	1670	1895	—	—	—	435	305	360	—	—	—
8531-21	As-coated	2010	1470	1845	—	—	—	455	355	390	—	—	—
8532-23	As-coated	2010	1670	1850	—	—	—	390	335	355	—	—	—
8521-11	3	1315	790	1095	1670	1010	1455	265	205	240	310	215	250
8521-5	4	1245	605	940	1315	1040	1205	265	240	250	240	205	225
8521-3	4	1435	1010	1230	1390	920	1180	275	220	240	280	220	240
8521-17	6	1355	1040	1205	1615	1315	1510	240	205	225	275	195	235
8521-9	7	1390	965	1180	2105	1775	1960	255	210	230	280	205	235
8521-13	8	1275	965	1145	2105	1670	1820	255	210	230	(345	210	250)[c]
8521-1	9	1275	840	1025	1950	1355	1715	235	200	220	(425	215	325)[c]
8522-23	11	1435	1125	1290	1830	1435	1645	285	215	240	(353	225	285)[c]
8531-5	6	1355	640	1000	1560	1010	1265	265	205	230	245	210	225
8531-9	7	1150	790	985	1775	1125	1545	270	215	240	250	205	230
8531-8	8	1315	515	1000	1775	1390	1610	225	215	220	240	205	225
8531-4	9	1040	500	850	1950	1520	1670	275	210	230	235	210	225

(a) See Table 2 for sketch of zonal structure.

(b) Averages computed on following data:

Area	No. of Readings	Method of Readings
Zone A, as-coated	5	Traverse
Zone A, oxidized	6	Random
Zone B	5-11	Traverse
Substrate	6	Traverse

(c) Traverse showed hardness variation with distance. See Table 6 for traverses. Recrystallization appeared to be same in areas of relatively high hardness as in areas of low hardness.

TABLE 19. KNOOP HARDNESS TRAVERSES FOR THREE OXIDIZED W-2 COATED Mo-0.5Ti SPECIMENS WHICH SHOWED HARDENING IN SUBSTRATE UNDER CRACK IN COATING

Distance from Edge of Substrate		Specimen No.:	Knoop Hardness Number, 100-g load		
cm X10^3	mils	Oxidation Cycles:	8521-13 8	8521-1 9	8522-23 11
2	0.8		343	423	353
5.5	2.2		295	363	353
9	3.5		225	374	302
16	6.3		241	347	269
23	9.1		222	295	244
30	11.8		222	250	227
37	14.6	(Center of Substrate)	210	215	236

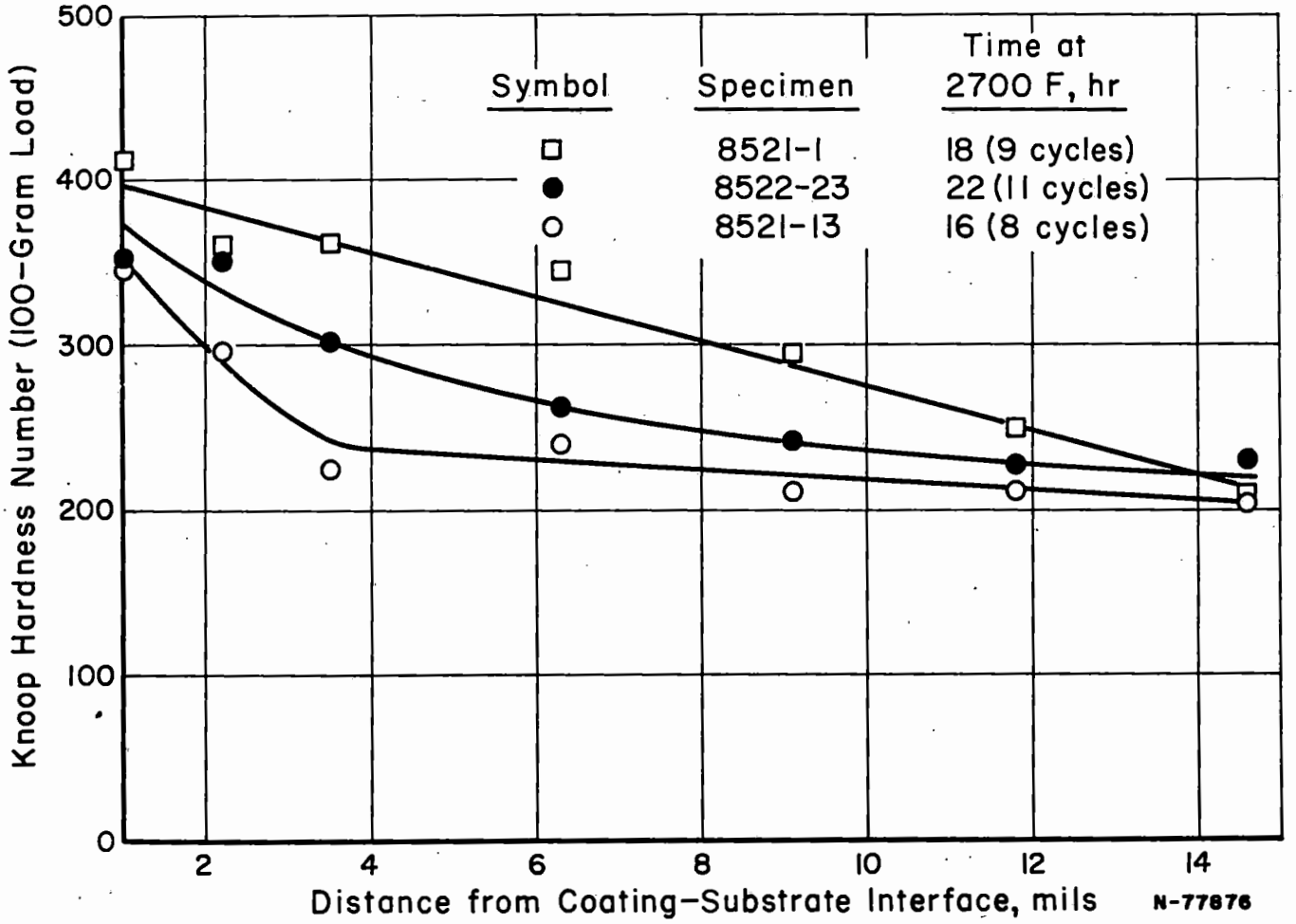

FIGURE 18. HARDNESS TRAVERSES FOR THREE OXIDIZED W-2 COATED Mo-0.5Ti SPECIMENS WHICH SHOWED HARDENING IN SUBSTRATE UNDER CRACK IN COATING

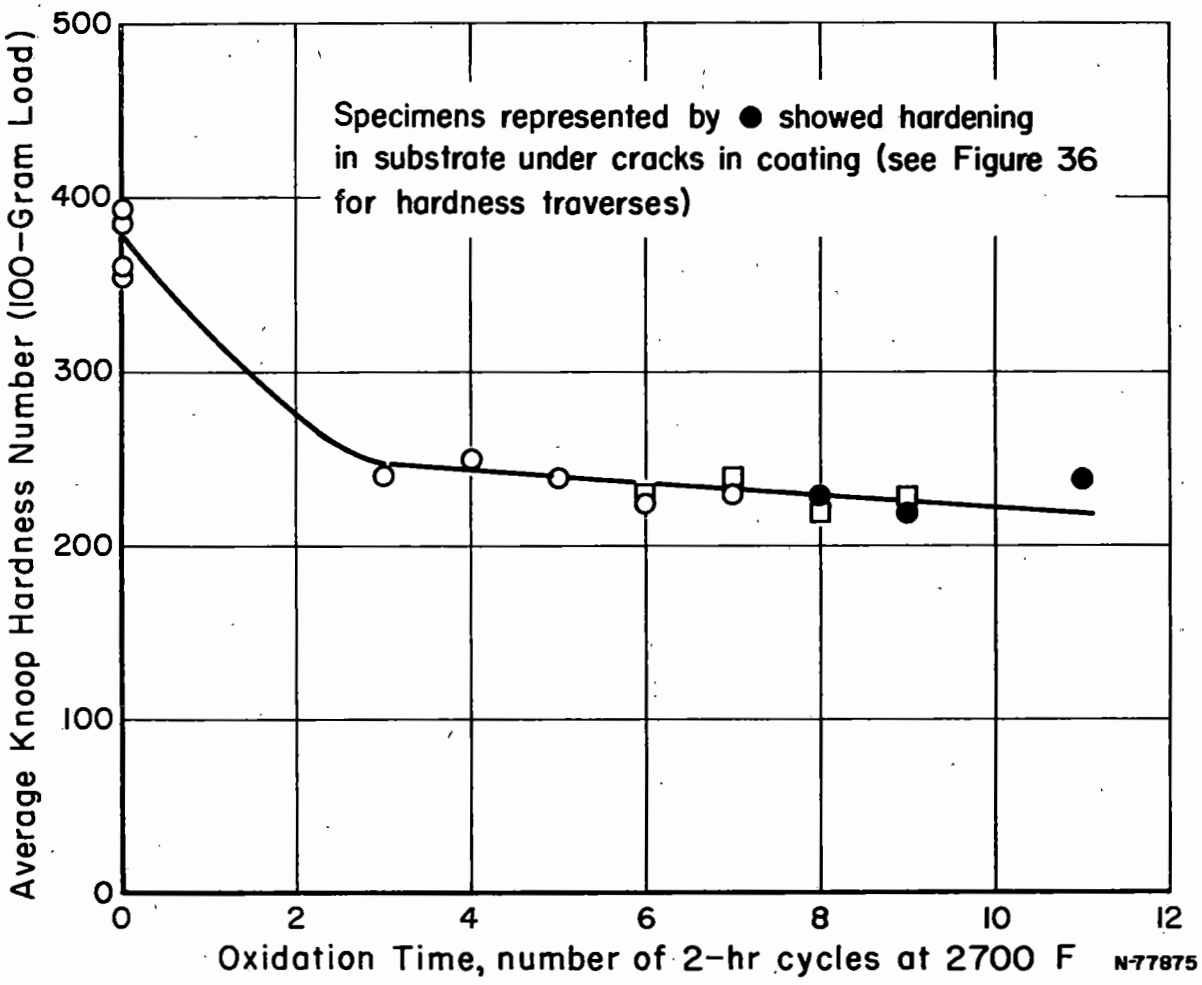

FIGURE 19. AVERAGE HARDNESS OF SUBSTRATE IN W-2 COATED Mo-0.5Ti VERSUS OXIDATION TIME AT 2700°F

<0.03, <0.03, <0.03, 0.03, 0.03, <0.03, <0.03, 0.03, 0.06, <0.03, 0.06, 0.03, <0.03, <0.03, <0.03, 0.03, <0.03, 0.1, <0.03, 0.3 mil.

Twenty-two of the larger cracks of variable geometry were found in the 2-inch perimeter of flat side on specimen 8521-211 maximum width measured for these cracks was as follows: 0.29, 0.36, 0.16, 0.19, 0.10, 0.29, 0.13, 0.26, 0.29, 0.36, 0.10, 0.30, 0.36, 0.39, 0.13, 0.10, 0.64, 0.19, 0.64, 0.30, 0.39, 0.10 mil. As-coated specimens 8522-43, 8531-21, and 8532-23 had 29, 20, and 24 of these cracks, respectively.

Table 20 contains data on crack widths found in specimens cyclically oxidized for various lengths of time at 2700°F. Figure 20 shows that the average crack width of both Zones A and B increased linearly with cyclic oxidation time, with the crack width of Zone A being a stronger function of time.

6. Crack Frequency

Tables 21 and 22 and Figure 21 summarize the information obtained on crack frequency of the flat sides and edges in Zone A of the as-coated and oxidized W-2 coated Mo-0.5Ti tabs and in Zone B of oxidized specimens.

The edge and flat-side crack frequencies in both Zones A and B appear to decrease slightly with increasing oxidation time.

The ratio of edge frequency to flat-side frequency for Zone A was between about 2 and 4, with no specific trend being noticeable with oxidation time due to scatter in the data. This ratio of frequencies for Zone B appeared to decrease slightly with increasing oxidation time. This could be due to self-healing properties in the W-2 coating. The ratio was significantly lower for Zone B than for Zone A.

Zone B, in general, had fewer cracks than did Zone A. On the edges, the difference in frequencies between the two zones was appreciable (Tables 21 and 22).

C. Chemical Analysis and Distribution of the W-2 Coating

The W-2 coating was analyzed as coated, and after oxidation for 10 hours and 22 hours at 2700°F. Analysis was done by spectrograph, X-ray diffraction, and electron probe.

Spectrographic analysis revealed molybdenum and silicon as the main constituents of the W-2 coating.

TABLE 20. WIDTH OF CRACKS IN COATING ON OXIDIZED W-2 COATED Mo-0.5Ti[a]

Specimen No.	No. of 2-Hr Oxidizing Cycles at 2700 F	Crack Width in Zone A,[b] mils				Crack Width in Zone B,[b] mils			
		Max.	Min.	Max.-Min. Difference	Av.	Max.	Min.	Max.-Min. Difference	Av.
8521-21	As-coated[c]	0.30	<0.03	~0.3	~0.04	—	—	—	—
8521-11	3	1.28	0.03	1.25	0.40	0.38	0.03	0.35	0.17
8521-5	4	1.82	0.06	1.76	0.45	0.32	0.06	0.26	0.13
8521-3	5	1.34	0.10	1.24	0.57	0.42	0.06	0.36	0.15
8521-17	6	3.58	0.29	3.29	0.96	0.58	0.06	0.52	0.19
8521-9	7	1.28	0.32	0.96	0.76	1.02	0.06	0.96	0.20
8521-13	8	1.22	0.35	0.87	0.75	0.96	0.06	0.90	0.28
8521-1	9	2.40	0.35	2.05	1.00	1.31	0.06	1.25	0.34
8522-23	11	1.92	0.64	1.28	1.21	0.35	0.06	0.29	0.16
8531-5	6	1.76	0.35	1.41	0.84	0.64	0.03	0.61	0.13
8531-9	7	1.42	0.32	1.10	0.87	0.58	0.03	0.55	0.17
8531-6	8	1.82	0.29	1.53	1.02	0.29	0.03	0.26	0.12
8531-4	9	1.73	0.58	1.15	0.93	0.61	0.03	0.58	0.15

(a) Twenty consecutive cracks were measured along flat sides of specimens.

(b) Zone structure of oxidized specimens:

Oxide

Zone A

Zone B

Zone C

Mo-0.5Ti Substrate

(c) As-coated specimens had only Zone A and substrate.

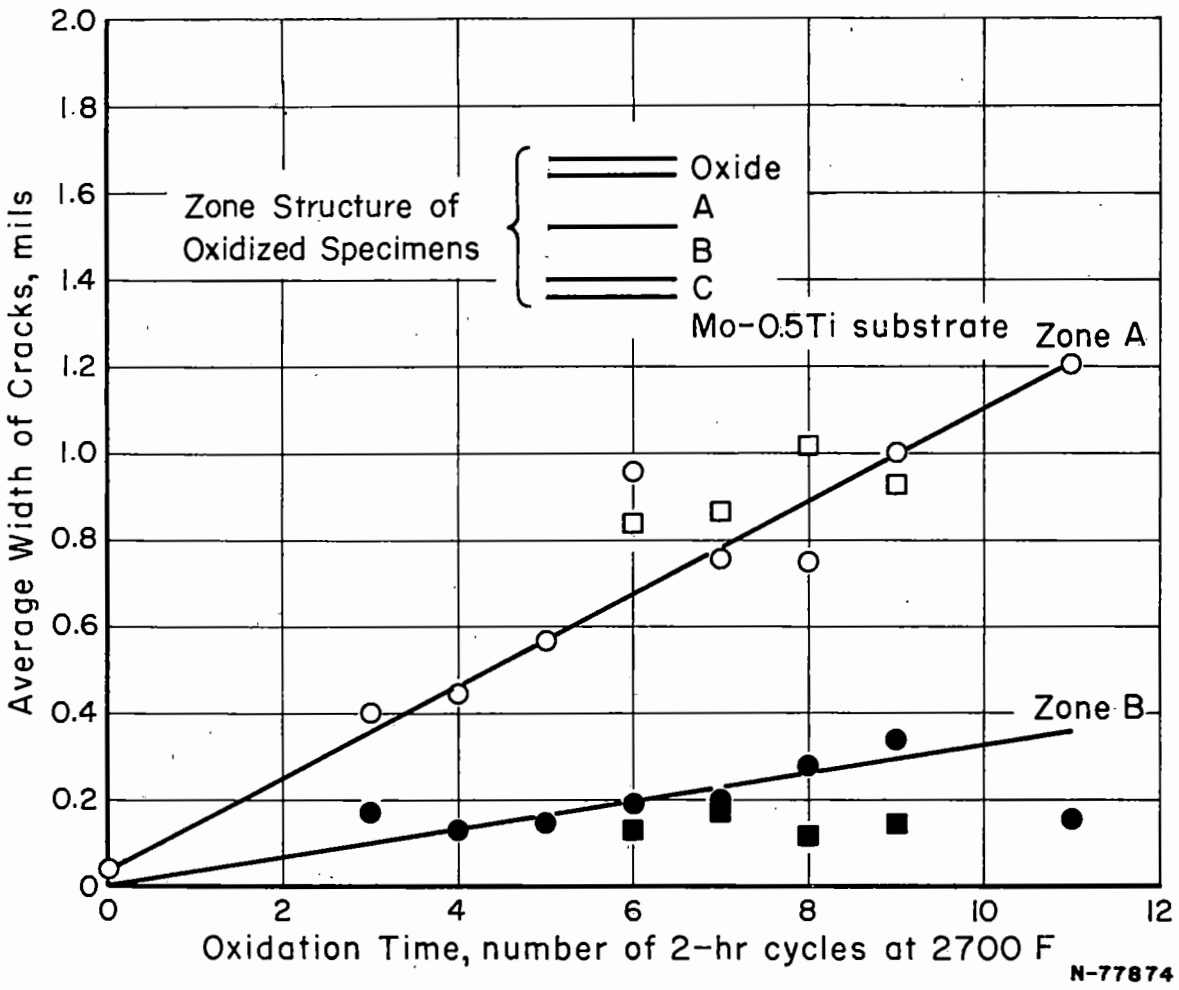

FIGURE 20. AVERAGE WIDTH OF CRACKS IN COATING ZONES IN W-2 COATED Mo-0.5Ti VERSUS OXIDATION TIME AT 2700°F

TABLE 21. CRACK FREQUENCY IN W-2 COATED Mo-0.5Ti TAB SPECIMEN

Specimen No.	Number of 2-Hr Oxidizing Cycles at 2700 F	Number of Cracks in Zone A per 100 Mils of Length		Ratio
		Flat Side	Edge	
8521-21	As-Coated	18	94	5.2
8522-43	Ditto	21	55	2.6
8531-21	"	16	62	3.9
8532-23	"	24	73	3.0
8521-11	3	14	55	3.9
-5	4	21	55	2.6
-3	5	18	55	3.1
-17	6	13	39	3.0
-9	7	16	31	1.9
-13	8	14	47	3.4
-1	9	13	23	1.8
8522-23	11	13	55	4.2
8531-5	6	16	55	3.4
-9	7	21	47	2.2
-6	8	18	47	2.6
-4	9	19	47	2.5

TABLE 22. CRACK FREQUENCY IN ZONE B[a] OF W-2 COATED Mo-0.5Ti TAB SPECIMENS

Specimen No.	No. of 2-Hr Oxidizing Cycles at 2700 F	No. of Cracks in Zone B per 100 mils of Length		Ratio
		Flat Side	Edge	
8521-11	3	14	23	1.6
8521-5	4	14	16	1.1
8521-3	5	17	23	1.4
8521-17	6	11	23	2.1
8521-9	7	14	16	1.1
8521-13	8	17	23	1.4
8521-1	9	11	8	0.7
8522-23	11	12	16	1.3
8531-5	6	16	16	1.0
8531-9	7	12	16	1.3
8531-6	8	11	8	0.7
8531-4	9	9	16	1.8

(a) See Table 2 for sketch of zonal structure.

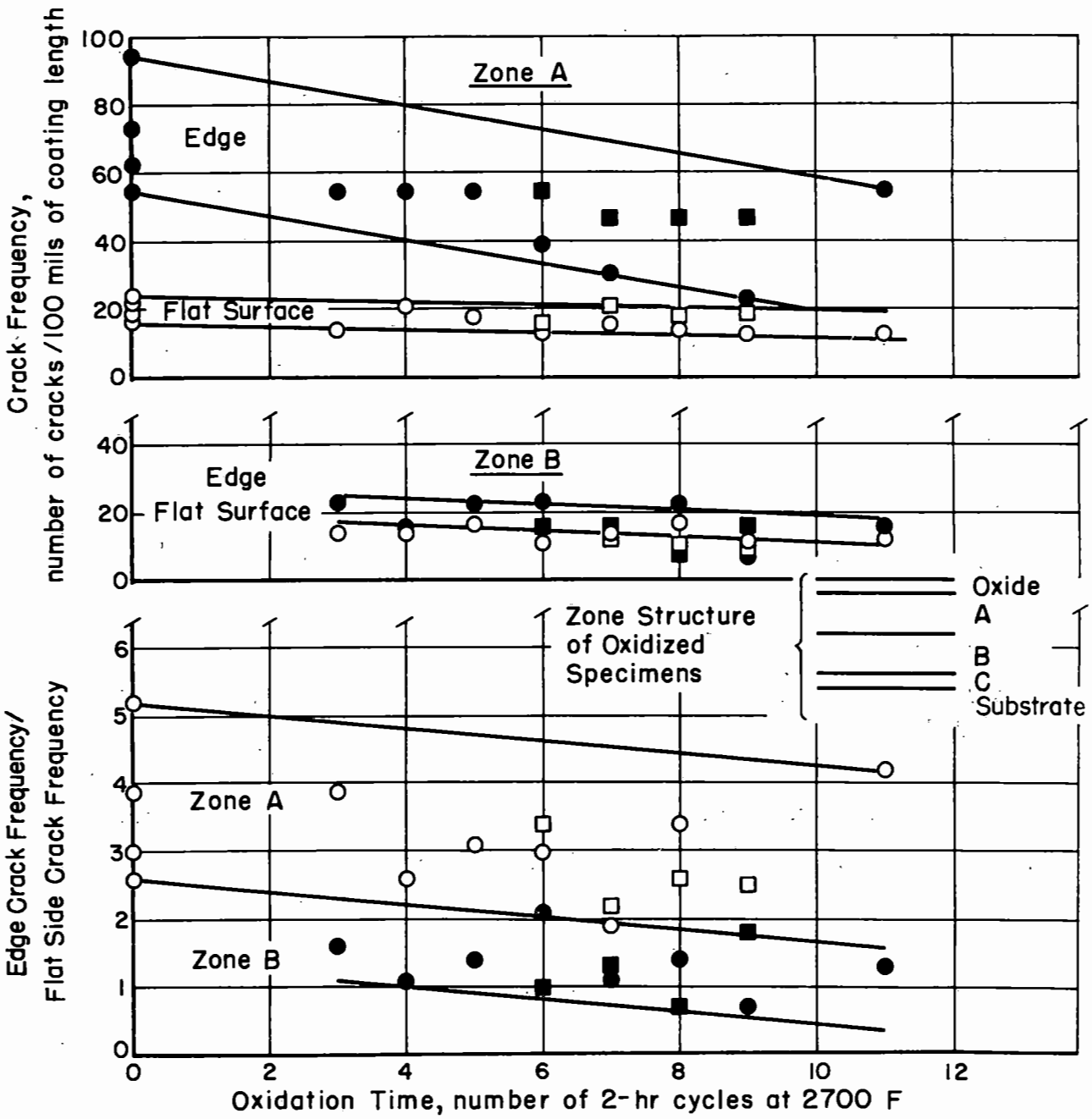

FIGURE 21. CRACK FREQUENCY AND CRACK-FREQUENCY RATIO FOR COATING ZONES ON EDGES AND FLAT SURFACES OF W-2 COATED Mo-0.5Ti VERSUS OXIDATION TIME AT 2700°F

Three specimens of W-2 coated Mo-0.5Ti were examined by electron-probe microanalysis and by X-ray diffraction to determine the nature of the coating material and its response to thermal cycling to 2700°F. The three specimens represented: (1) the as-coated alloy (8522-43), (2) the coated alloy (8521-3) after five thermal cycles (10 hours) to 2700°F., and (3) the coated alloy (8522-23) after 11 cycles (22 hours) to 2700°F.

By diffraction techniques, the coating material was found to be composed of binary compounds of molybdenum and silicon. Small amounts of other metals or metal silicides which are soluble in the coating material could not be detected by this technique. The variations in the concentrations of molybdenum and silicon, from the alloy interface to the free surface of the coating, was measured with the electron-probe microanalyzer. The results of the analysis of the three specimens are shown in Fig. 22. The origin of the distance scale used in Figure 22 was arbitrarily chosen to coincide with the visible coated interface. As the over-all thickness of the three specimens appears to be constant, the visible interface would appear to be a phase interface which is advancing into the alloy as a function of time. The origin of the distance scales in Figure 22, therefore, should not be considered as the original alloy-coating interface.

Analysis of the as-coated specimen (8522-43) with the micro-analyzer showed the coating material to be 64-65 w/o Mo, balance Si. There appeared to be a depletion of Mo, near the free surface of the coating; however, it cannot be ascertained whether this is an actual depletion or the result of a change in the bulk density of the coating material.

Analysis of the as-coated surface by X-ray diffraction showed the coating to be single phase. It was identified as $MoSi_2$ (63.1 w/o Mo), which is in close agreement with the microanalysis.

Microanalysis of Specimen 8521-3, which was cycled five times to 2700°F., showed a single-phase region about 75 microns (3.0 mils) wide, extending from the visible interface into the coating material. This material had a range of composition of 83-85 w/o Mo, balance Si. A second single-phase region of 62-64 w/o Mo was found to extend from the free surface of the coating inward about 50 microns (2.0 mils). This phase corresponded to the discontinuous grey phase, which was observed metallographically. X-ray diffraction analysis of the coated surface showed three phases, the most predominate of which was $MoSi_2$. The other two phases were quite faint, one being cristobalite (SiO_2) and the third being unidentifiable on the basis of diffraction data

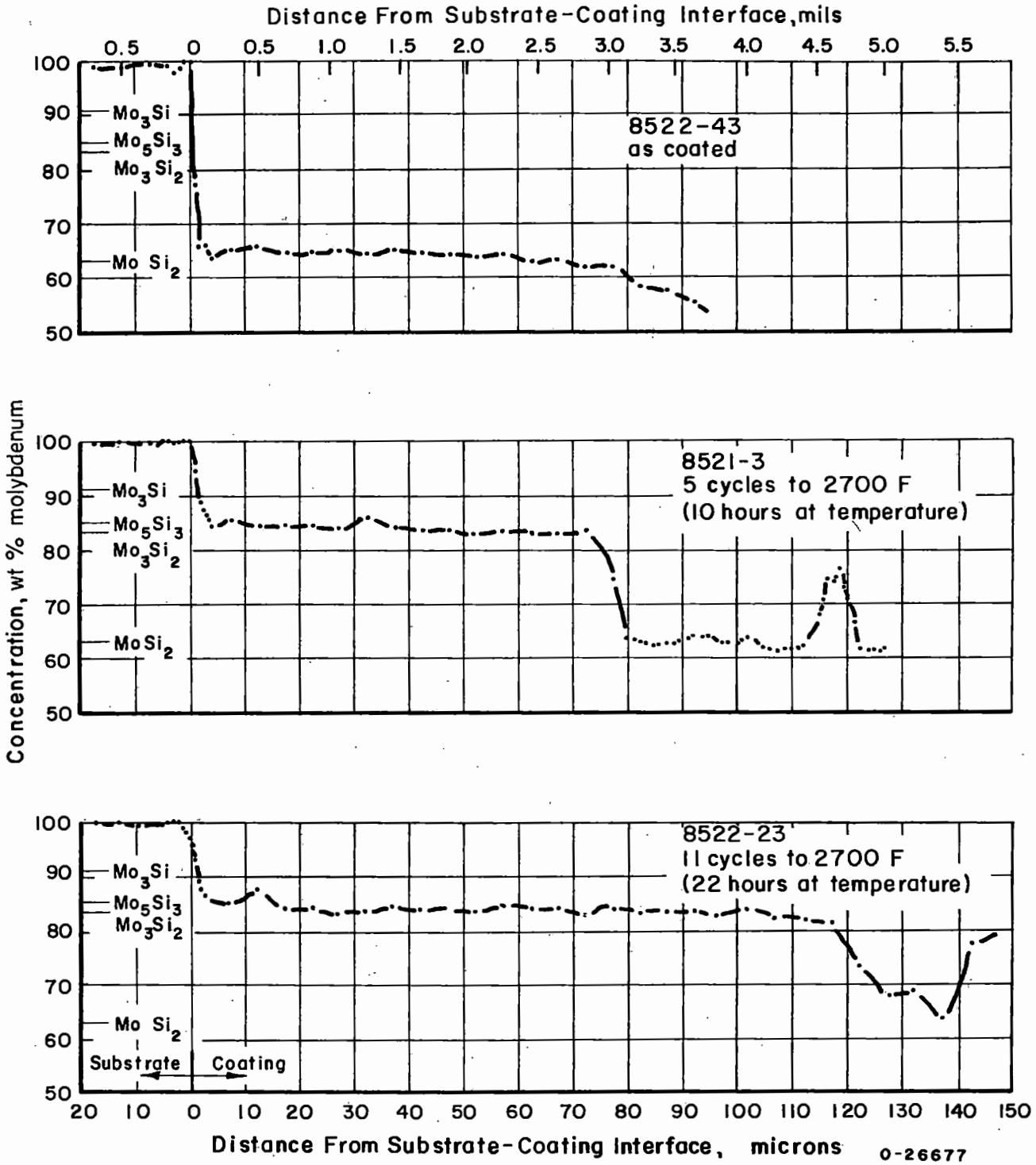

FIGURE 22. DISTRIBUTION OF MOLYBDENUM IN W-2 COATED Mo-0.5Ti

alone. The identification of this phase as Mo_5Si_3, on the basis of the microanalysis, would not be inconsistent with the diffraction data.

Microanalysis of Specimen 8522-23 (11 cycles) showed a single phase region of 85-83 w/o Mo extending about 120 microns (4.7 mils) into the coating material from the visible interface. A second phase of a lower contentration of Mo extended about 30 microns (1.2 mils) into the coating from the free surface. The variation in the concentration in this region (63-73 w/o) undoubtedly indicated a mixture of the two phases, $MoSi_2$ and Mo_5Si_3. The diffraction data from this specimen were similar to those obtained from Specimen 8521-3. The predominant phase was $MoSi_2$; however, the two additional phases, SiO_2 and Mo_5Si_3(?) were present in larger amounts than found in specimen 8521-3.

Metallographic examination of this specimen (8522-23) showed a narrow (approximately 0.1 mil) interface between the alloy and the coating material. This phase was too narrow, however, to be wholly resolved by the microanalyzer. Unless the interface phase were of considerably different composition than the adjacent phases, it would not be possible to differentiate between this phase and the adjacent concentration gradients. It would not be possible, for example, to note the presence of Mo_3Si at this interface unless the phase field were greater than 10 microns (0.4 mil) in width. No significant variation of the major constituents was detected in this region nor were there detectable amounts of other elements present.

No variations in composition were found to be associated with coating cracks. In Specimen 8522-23, small quantities of dissimilar material appeared to be associated with these cracks. No elements other than Si were detected in this material. Though this method of analysis is not sensitive to O_2, the analysis of Si in this material would not be inconsistent with that of SiO_2.

The growth and phase-change behavior of the coating by interdiffusion with the substrate, as depicted by these analyses, is in agreement with the metallographic observations presented earlier in this report.

D. Discussion

The W-2 coating on molybdenum alloys is basically $MoSi_2$ as prepared. Upon exposure at elevated temperatures, diffusion between coating and base metal occurs. The coating now has an outer zone

(remnant of original coating), an intermediate zone (probably Mo_5Si_3) which continues to grow at the expense of the outer zone, and an inner zone (not chemically identified). Total coating thickness appears to increase with exposure time. A glossy phase on the surface (SiO_2) is the phase to which the oxidation resistance is attributed.

Crack frequency in the W-2 coating apparently decreases slightly with exposure at 2700°F. and many cracks terminated in the Mo_5Si_3 phase.

This information and the fact that oxidation test specimens have displayed erratic weight loss trends in which losses decreased in magnitude indicate that W-2 coatings are self-healing.

Coating crack width increased with exposure and failure of the coated system may occur where the glossy phase can no longer fill in the crevice. There was hardening in the areas under coating cracks, indicating this was the area of oxygen penetration.

The pre-statistical program experiments indicated that identical coating applications to two different lots of Mo-0.5Ti resulted in different test lives. The two substrates tested in the statistical experiment also displayed different behavior. This could be due to either lot to lot variations in Mo-0.5Ti or surface contamination (both materials appeared to have contamination, but to different extents). Elimination of lot to lot variation of Mo-0.5Ti would, therefore, be desirable for producing a coated system of uniform quality.

VII. CONCLUSIONS

1. The statistical program conducted revealed that the critical variables and preferred level of each variable are processing time (two 12 hour processes), processing temperature (1900°F.) and mixing of powders (well mixed).

2. Variables of secondary importance and preferred levels are substrate soundness (uncontaminated) and surface preparation (etched and honed).

3. Optimized coatings produced using the levels indicated in 1, 2 and 5 should have a mean life of 47 hours at 2700°F. with a standard deviation from the mean of 8 hours.

4. The most conservative evaluation predicts 1 failure/1000 in less than 4.2 hours.

5. Retort composition and powder purity, age and mesh size were of minor importance statistically; so that steel retorts, commercial purity and -60 + 150 mesh size powder may be chosen for cost and convenience purposes.

6. W-2 coating has an oxidation resistant glassy phase which provides self-healing characteristics to the coating.

7. As prepared W-2 coating is essentially $MoSi_2$.

8. Upon exposure at 2700°F. the coating becomes a three phase structure by interdiffusion of coating and base metals.

9. Total coating thickness increases slightly with exposure time.