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Improved Silicon Carbide for Advanced Heat Engines

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FOREWORD

The planning of experiments, the processes of mixing, forming, sintering, and testing of SiC samples, and the analysis of data were performed by the Research Staff of the Ford Motor Company at the Scientific Laboratory, Dearborn, Michigan.

The principal investigator was Dr. Thomas J. Whalen and the program manager was Dr. Walter L. Winterbottom. Ms. N. Shaw of NASA Lewis Research Center is project manager. Contributions in the second year of the program were made by W. Trela, Dr. R. Govila, J. R. Baer, L. R. Reatherford, E. L. Cartwright, B. N. Juterbock, Dr. R. Williams, Dr. S. Shinozaki, V. Mindroiu and R. Elder.

NASA - FORD SECOND ANNUAL REPORT
FOR THE PERIOD FEBRUARY 15, 1986 TO FEBRUARY 14, 1987

TABLE OF CONTENTS

EXECUTIVE SUMMARY

This is the second annual technical report for the program entitled "Improved Silicon Carbide for Advanced Heat Engines" and includes work performed during the period February 16, 1986 to February 15, 1987. The program is conducted for the National Aeronautics and Space Administration (NASA) under contract number NAS3-24384.

The objective of the program is the development of high strength, high reliability silicon carbide parts with complex shapes suitable for use in advanced heat engines. The fabrication methods used are to be adaptable for mass production of such parts on an economically sound basis. Injection molding is the forming method selected for the program. This objective is to be accomplished in a two phase program: Phase I - achieve a 20% improvement in strength and a 100% increase in Weibull modulus of the baseline material; Phase II - produce a complex shaped part, a gas turbine rotor, for example, with the improved mechanical properties attained in Phase I.

Eight tasks are included in Phase I covering the characterization of the properties of a baseline material, the improvement of those properties and the fabrication of complex shaped parts. Activities during the first contract year concentrated on two of these areas: fabrication and characterization of the baseline material (Task I) and improvement of material and processes (Task VII). Activities during the second contract year included an MOR bar matrix study to improve mechanical properties (Task II), materials and process improvements (Task VII), and a Ford-funded task to mold a turbocharger rotor with an improved material (Task VIII).

Task I

The objective of Task I was the characterization of the Ford baseline starting materials (Ibiden beta SiC, carbon and boron sintering aids) and determination of the mechanical properties of test bars produced by the baseline process. The properties measured were the chemical composition, polyphase distribution, particle size distribution and surface area of the starting powders, specific gravity and packing density of the silicon carbide powder. The binder materials used in the molding mix were characterized by Thermal Gravimetric Analysis and Differential Scanning Calorimetry. MOR bars were individually formed by injection molding, dewaxed in vacuum, and sintered in vacuum. Machined test bars were measured for room temperature and elevated temperature strength. Determination of Weibull characteristic strength and modulus at room temperature, mean strength and stress rupture at elevated temperatures, fracture origins, microstructure and density was made on statistically significant sample sizes.

A group of 276 test bars were injection molded for the baseline study, and 122 were sintered and machined for testing.

A total of 48 MOR bars were tested for strength at room temperature, 1000^0 C, 1200^0 C and 1400^0 C . The results of these tests indicated that the baseline materials have a room temperature characteristic strength of 316 MPa (45.8 Ksi) with a Weibull modulus of 8. The mean strengths at room temperature, 1000^0 C, 1200^0C and 1400^0 C were 299 (43.3 Ksi), 285 MPa (41.4 Ksi), 298 MPa (43.2 Ksi) and 325 MPa (47.2 Ksi) respectively. The mean stress rupture life at 1400°C of five samples tested at 172 MPa (25 Ksi) stress was 62 hours and at 206 MPa (30 Ksi) stress was 14 hours.

Task II

The objective of Task II is improvement of the strength and reliability of the molded silicon carbide MOR test bars by performing a series of statistically-designed experiments to develop improved materials and processing parameters. The initial program goals were to attain a 20% improvement in MOR and 100% improvement in Weibull modulus over the baseline properties. Two groups of factorial-designed experiments were performed as a half-fraction of a 2^5 design which permitted evaluation of main effects and two-factor interactions. One group was vacuum sintered while the second group was argon sintered. The five variables which were evaluated at two levels each were Process A (fluid mixing) and Process B (modified fluid mixing with improvements), solids loading (55% and 60%), dewaxing process (argon and vacuum), sinter time and sinter temperature. For both argon-sintered and vacuum-sintered groups, Process B was significantly superior to Process A and, for the vacuum-sintered group, the shorter sintering time of 6 minutes was better than 12 minutes. The other variables did not significantly influence the strength, but some variables did influence the sintered density.

A group of 643 MOR bars were injection molded for the Task II study, and 256 were sintered and machined for testing.

The best group of 8 duplicate MOR bars from the vacuum sintered Matrix had a mean strength of 444 MPa (64.5 Ksi) and a standard deviation of 70 MPa (10.1 Ksi). The best group of 30 vacuum-sintered MOR bars had a mean strength of 423 MPa (61.4 Ksi) with a Weibull characteristic strength of 442 MPa (64.2 Ksi) and a Weibull modulus of 10.5. The best group of 28 argon-sintered MOR bars had a Weibull strength of 407 MPa (59.1 Ksi) and a Weibull modulus of 10.1 . The strength of the vacuum-sintered material is 40% greater and the Weibull modulus is 31% greater than those values measured for the baseline material in Task I.

Task VII

The objectives of Task VII are to improve the processing and properties of the SiC material. During the first year, a number of experimental matrix designs were carried out to facilitate selection of the baseline composi-

tion, the dewaxing and sintering processes and the injection molding parameters which would give fully dense materials with MOR strengths of at least 310 MPa (45 Ksi). Vacuum dewaxing and sintering and high-shear dry mixing processes were developed and utilized in producing a baseline material which met the minimum strength requirement. Concerted efforts to further reduce the flaw size and improve mechanical properties using hot-roll and high-shear milling methods were ineffective.

A fluid mixing process was initiated during the first year, and more fully developed during the second year, when it became obvious that materials prepared with the dry mixing process were strength-limited by a flaw size characteristic of the mixing process. Reductions in flaw size and improved properties have been achieved with this approach. The process has been scaled up, process controls have been added and statistical process control data have been collected. Five identical fluid-mixed batches were evaluated and it was shown that the process was reproducible.

Dewaxing cycle factors were evaluated in a statistically-designed 2^{5-2} fractional factorial experiment (Matrix 6) with 5 variables in 8 experimental runs. The five factors were gas type, pressure, temperature, hold time at temperature and heating rate. Pressure, temperature and a pressure-temperature interaction were noted as having a significant effect on the amount of wax removed in the cycle.

A vacuum-argon sintering cycle was developed from the results of Matrix 7, which was a statistically-designed series of experiments (2^{4-1}) evaluating four factors. Sintered densities up to 98% of theoretical and strengths up to 462 MPa (67Ksi) were attained under the best conditions of this matrix. Fractographic analysis of these materials showed that surface and sub-surface flaws, 25 to 100 micrometers in size were still the strength controlling factors in these materials.

TASK VIII

The objective of this task is to evaluate an improved, fluid-mixed, Process B molding material, developed for simple MOR bars, as a candidate material for molding a complex shape such as a turbocharger rotor. The plan was to use a 2^{5-1} factorial designed experiment to evaluate the five factors of injection pressure, die temperature, material temperature, flow rate, and time at pressure as they affect the density, volume and number of cracks in the rotor. The result of this experiment was that many factors influenced the density, volume and number of cracks in the molded rotor. Three conditions of the sixteen studied in the experiment were observed to yield crack-free rotors of acceptable density. It was concluded that the improved fluid-mixed, Process B material was acceptable for molding of complex parts, such as a turbocharger.

The effort under this task was performed at Ford expense in consideration of the Company's cost sharing requirement. This task is complete.

FUTURE PLANS

Strength improvements derived from Task VII processing advancements have led to a revised set of goals for injection-molded SiC upon which NASA and Ford have agreed. The revised Phase I goals are a Weibull characteristic strength of 710 MPa (80 Ksi) and a Weibull modulus of 16. A second iteration Task II matrix study should achieve this revised goal since the first iteration advanced us more than half way to the strength goal.

The program will focus on material strength and Weibull modulus improvements (reliability) in the coming year.

INTRODUCTION

This is the second annual technical report on "Improved Silicon Carbide for Advanced Heat Engines" submitted by the Ford Motor Company. The program is conducted for the National Aeronautics and Space Administration (NASA) under contract number NAS3-24384. The period February 16, 1986 to February 15, 1987 is covered by this report.

The objective of this program is to develop high strength, high reliability silicon carbide parts, having complex shapes suitable for use in advanced heat engines. The fabrication method is to be adaptable to mass production of such parts on an economically sound basis.

The original program schedule is shown in Figure 1. Two phases of development are shown which are to be completed in 60 months. Phase I contains the fabrication, evaluation and optimization of test bars, and is divided into four tasks:

Task I - Fabricate and characterize the baseline silicon carbide material

Task II - Improve silicon carbide MOR bars with process and material improvements by iterative, statistically designed experiments and show a 20% increase in strength and a 100% increase in Weibull modulus.

Task III - Characterize the improved process and material.

Task VII - Advance silicon carbide technology with statistically designed experiments and input these advances into Task I and Task II.

Task VIII - Form a turbocharger rotor from the best material and process available in the last quarter of 1986 to supplement the information developed during the other tasks with simpler shapes and to provide preliminary data for Tasks IV, V, and VI. Ford supports this task as a cost-sharing effort.

Task I of Phase I has been completed and is reported along with results from Task VII studies in the first annual report.

Phase II involves the fabrication, evaluation and optimization of a large shape that has potential application in a heat engine. This effort is divided into four tasks:

Task IV - Fabricate a large, complex part and characterize the product.

Task V - Use iterative, statistically designed studies to improve the properties of this large shape.

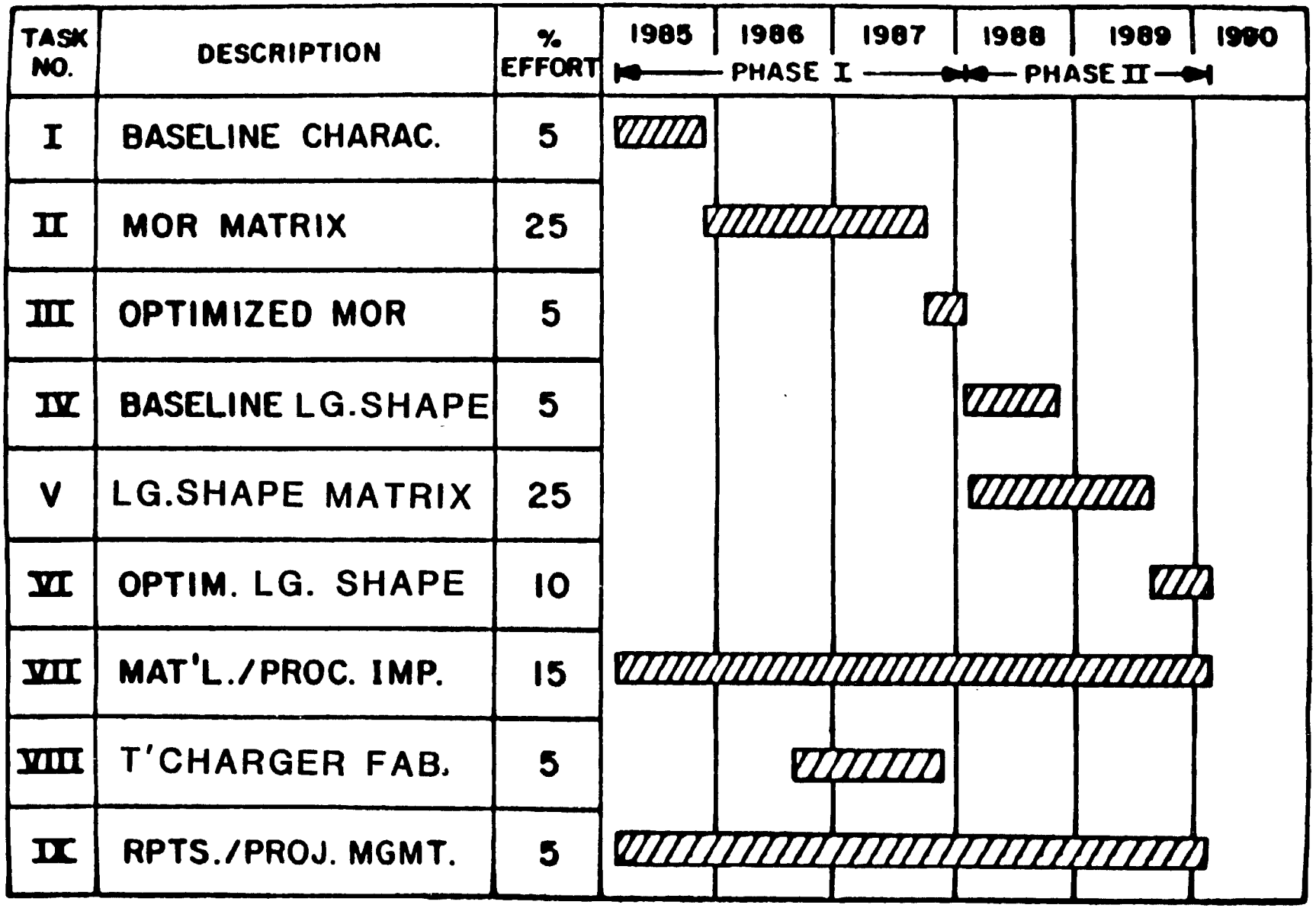

Figure 1: Timing Chart

Task VI - Fabricate and evaluate the large complex shape developed in Task V.

Task VII - Advance silicon carbide technology with statistically designed experiments and input these results into Tasks V and VI.

During the first year of the program, more than twenty material and processing variables were studied in statistically-designed experiments to determine their relative importance on the properties of the sintered material. Task I of Phase I was completed and reported in the first annual report. Variables related to powder processing in the mixing through dewaxing steps were placed under statistical process control.

Major efforts were given to Task II (MOR Matrix), Task VII (Material and Process Improvement) and Task VIII (Turbocharger Molding - Ford funded) in the second year of the program, which are reported in this document. The first iteration of the Task II matrix was completed along with four Task VII studies. One molding matrix in Task VIII was completed.

The program has been restructured to focus on attainment of greater reliability (higher Weibull modulus) at the expense of fewer Task II iterations for higher strength.

EXPERIMENTAL WORK

TASK II MOR BAR MATRIX STUDY

II.1 Matrix I Plan

The initial experiment in Task II was designed to compare the effect of five variables, each at two levels, on the strength and reliability of sintered SiC. The variables were selected so that the influence on sintered strength of agglomerate size in the green (and presumably the sintered) body and dewaxing/sintering processing could be evaluated. The experimental design was a half-fraction 2^5 design permitting evaluation of main effects and two-factor interactions. A summary of the experimental matrix is given in Figure 2 and in Table I. As a result of the Task VII, Matrix 7 (vacuum - argon sintering cycle study), it was decided to divide the Matrix 1 into Matrix 1A (vacuum sintered) and Matrix 1B (vacuum-argon sintered). A process flow chart is shown in Figure 3.

II.2 Preparation of Molding Mixes, Injection Molding, and Evaluation of Molded Bars

Process A is identical to the fluid mixing process used in producing the five replicate batches for the fluid mixing study described under Task VII. Process B represents a modified fluid mixing process that reduces agglomerate size relative to Process A. The process was selected on the basis of the results of the experimental matrix described under Task VII. Solids loading levels, dewaxing environment and argon sintering time and temperature were compared. Under Process A, a total of 466 bars of the five replicate batches, H - L, were molded at 55% and 60% solids loading with a yield of greater than 90 %. Spiral flow results for the two loadings were 8.3 inches (55%) and 2.0 inches (60%). The densities of the molded bars were determined and statistical process control charts were developed for the process. The SPC for the 60% solids loading, Figure 4, illustrates the small density differences observed between batches H and I and J - L.

The National Weather Service indicated that a wide range of temperature and relative humidity occurred in Detroit during the molding of the batches. The correlation between molded density and weight of water in the air during molding is shown in Figure 5. In the future, temperature and relative humidity will be recorded at the molder in order to determine whether this inverse relation persists between the water content in the air and molded density Moisture could affect molded density by either entering the wax binder or by altering the properties of the wax-silicon carbide interface.

II.3 Dewaxing and Sintering of Molded Bars

A dewaxing run of 25 bars from each of the 4H-L batches was carried out in vacuum with the standard dewaxing cycle (run #060686). An SPC chart based

1/2 FRACTION OF FULL 2^5 DESIGN
TEST BLOCKS WITHOUT SHADING ONLY

VARIABLE A FLUID MIX PROCESS
VARIABLE B SOLIDS LOADING
VARIABLE C DEWAX PROCESS
VARIABLE D SINTER TEMPERATURE
VARIABLE E SINTER TIME

		A_1				A_2			
		B_1		B_2		B_1		B_2	
		C_1	C_2	C_1	C_2	C_1	C_2	C_1	C_2
D_1	E_1	1			BC		AC	AB	
	E_2		CE	BE		AE			D
D_2	E_1		CD	BD		AD			E
	E_2	DE			A		B	C	

EVALUATE: { MAIN EFFECTS: A, B, C, D, E
INTERACTIONS: AB, AC, AD, AE, BC, BD, BE, CD, CE, DE

ASSUME THREE-FACTOR AND HIGHER ORDER INTERACTIONS ARE NEGLIGIBLE

Figure 2: Experimental Design

TABLE I

TASK II

MATRIX 1: Improve Strength by Reducing Agglomerate Size

Yield - Strength and Reproducibility

Design - 2_V^{5-1} - Main Effects & 2-Factor Interactions

	MATRIX 1A	MATRIX IB
Variables	A. Fluid Mix Process (Process A & Process B)	Fluid Mix Process (Process A & Process B)
	B. Solids Loading (55% & 60%)	Solids Loading (55% & 60%)
	C. Dewax Process (Vacuum & Argon)	Dewax Process (Vacuum & Argon)
	D. Vacuum Sinter Temp. (2080°C & 2110°C)	Argon Sintering Temp. (2120°C & 2135°C)
	E. Sinter Time (6 Min. & 12 Min.)	Argon Sintering Time (30 Min. & 60 Min.)

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TASK II MATRIX I

MATRIX VAR.	DESCRIPTION	
A	FLUID MIX PROCESS	
B	SOLIDS LOADING	
C	DEWAX PROCESS	
D	SINTER VAC / TEMP. ARGON	
1	2110°C / 2120°C	
	2080°C / 2135°C	
E	SINTER VAC / TIME ARGON	
	6 MIN / 12 MIN	
	12 MIN / 30 MIN	

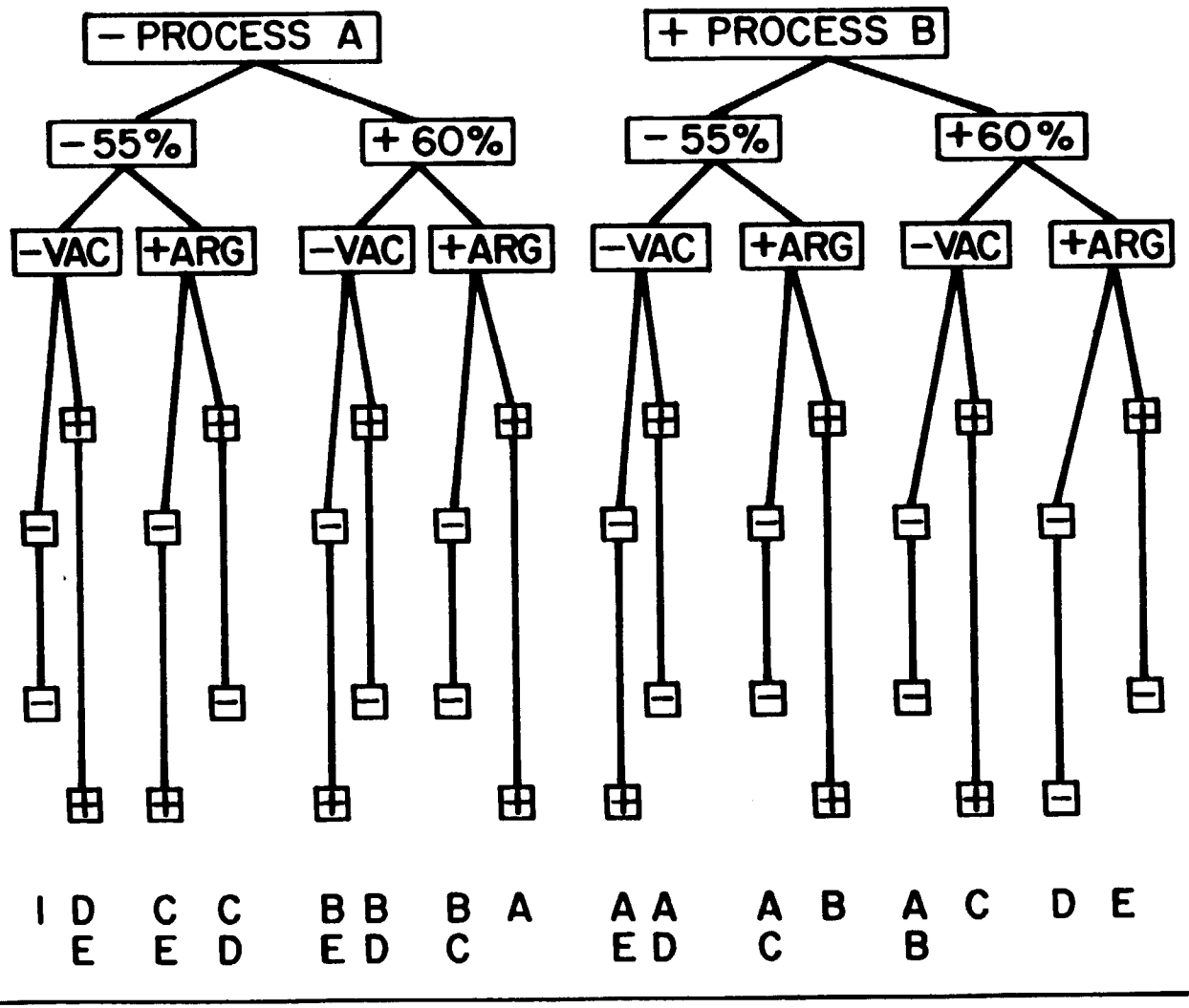

Figure 3: Process Flow Chart For Task II - Matrix 1

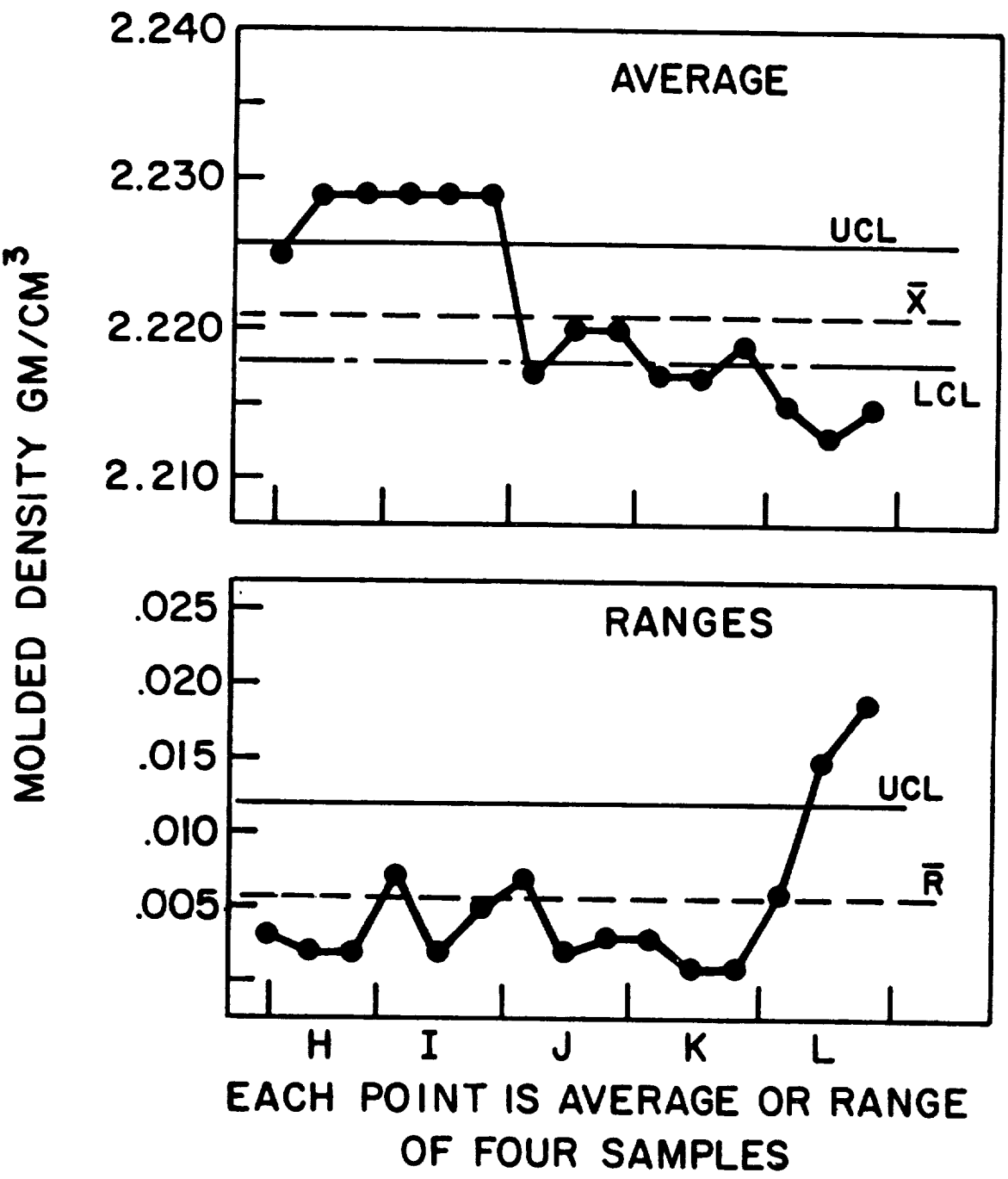

Figure 4: Statistical Process Control Chart
For Injection Molding Process

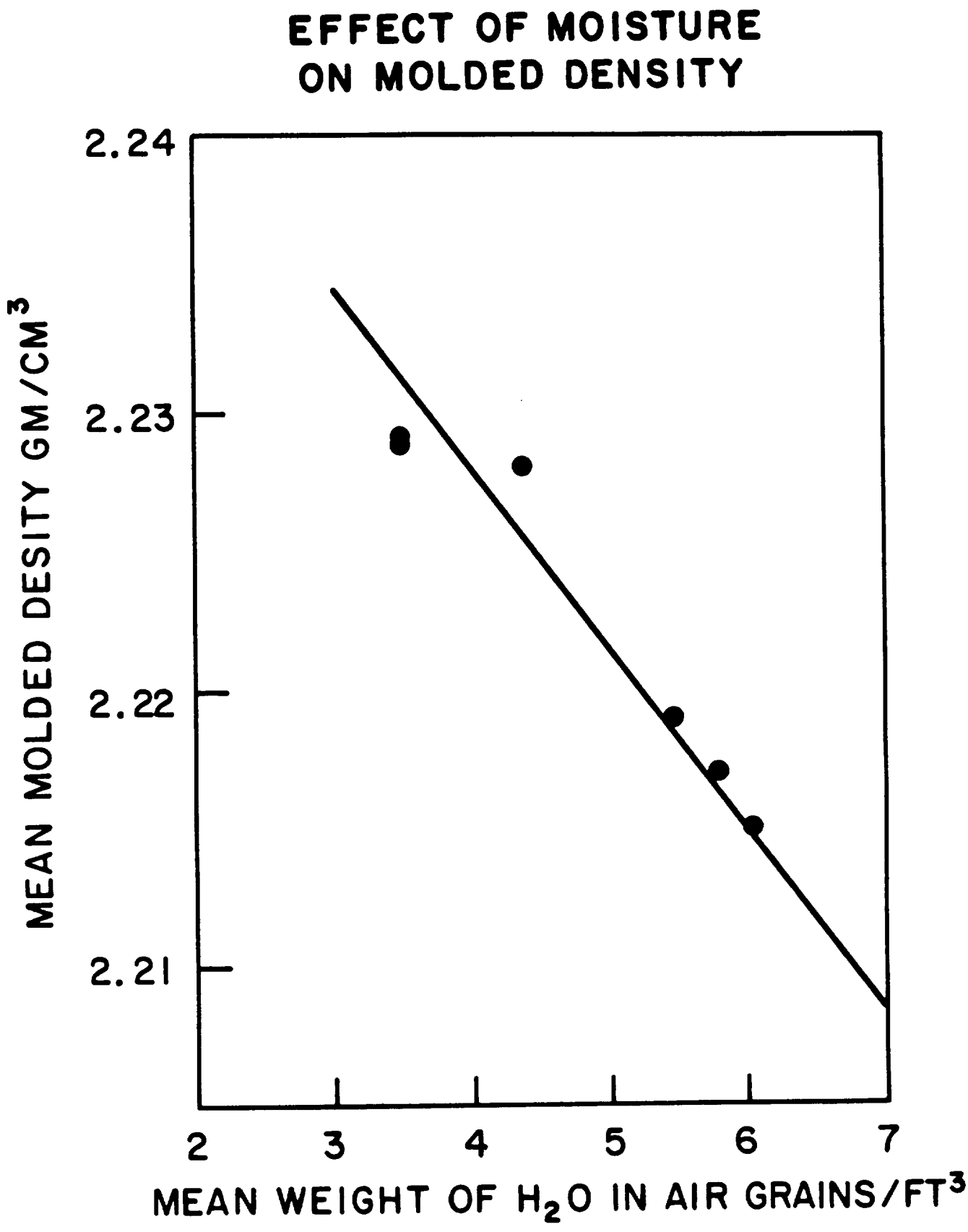

Figure 5: Molded Density As Related To Amount Of Water In Air

on weight loss, Figure 6, illustrates that the fluid mixing process is under control for all but the last batch. The molded density variation described above produces no measurable effect on the dewaxed weight loss.

A standardized procedure was developed to measure the weight of volatiles removed from fluid mixed material as a process control check. In the procedure, the specimens are heated to 1000°C in open ignition boats in a tube furnace under a flowing argon (4 SCFH) atmosphere. A slow heating rate is used to reach the highest temperature which is held for 17 hours. Samples of injection-molded bars and samples from the dried batches have been tested.

Some results of the standardized burn-out test are shown below for the molded bars from batches H - L. The average and sample standard deviation of triplicate samples for MOR bars from each batch vary by less than a standard deviation from the overall mean (15.75%).

Batches	H	I	J	K	L
MEAN (%)	15.71	15.76	15.71	15.75	15.84
Std. Dev. (%)	0.20	0.21	0.12	0.12	0.11

Linear shrinkage of the 4H-L bars after dewaxing was found to be small (0.4%) compared to the baseline, dry-mixed, 4G material (3.89%). Shrinkage measured for the length of the bar is most accurate, and these values for the five replicate batches were 0.4% with a standard deviation of 0.1%. No significant differences between batches were found.

Dewaxing of Matrix 1 Bars

Dewaxing was carried out in vacuum and argon atmospheres, and a summary of the results are given in Table II. The average burnout as a percentage of the added volatiles was 95.3% in vacuum and 96.1% in argon. Eight bars of 4G baseline composition were included in each run as internal standards and yielded acceptable burnout values of 92.5% and 94.0% for vacuum and argon, respectively. The Matrix 1 dewaxing results are as expected, with larger weight losses and shrinkages encountered in materials with higher wax contents (lower solids loading). The difference in the shrinkage between Process A and Process B for the 55% loading may be attributable to either or both of two factors:

1. Mix 4BLD, Process A at 55%, received more mixing (greater total amount of shear) since it was derived from the 5BAT mix with more wax added and mixed. Previous experience with 4G mixes was that dewaxing shrinkages increased with added shear mixing.
2. Mix 4BLD was reduced to the 55% loading level by adding wax. Mix 4Q was mixed at 55% level by dissolving the proper amount of wax into the fluid and no wax was added prior to molding.

Sintering of Matrix 1 Bars

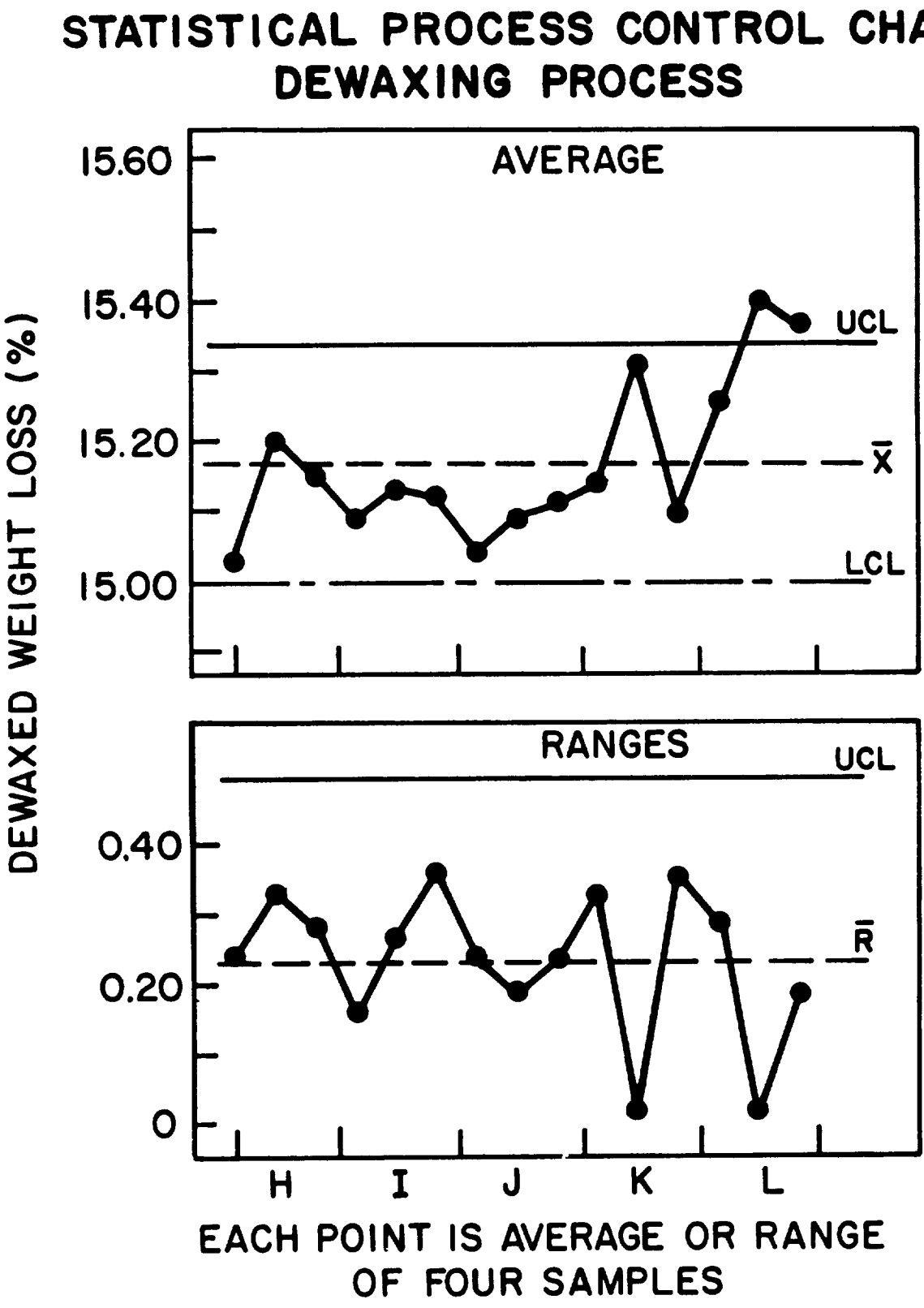

Figure 6: Statistical Process Control Chart For Dewaxing Process

TABLE II

DEWAXING RESULTS TASK II MATRIX 1

	Process A		Process B	
Batch No.	5 BAT	4 BLD	4M	4Q
Solids Loading (%)	60	55	60	55
Burn-Out (%)				
Argon Dewax	96.29 (2.8)*	95.82 (2.5)	95.93 (2.1)	96.25 (2.4)
Vacuum Dewax	95.47 (1.0)	95.10 (1.0)	94.74 (1.1)	95.73 (1.1)
Weight Loss (%)				
Argon Dewax	15.16 (0.4)	18.00 (0.5)	15.43 (0.3)	18.38 (0.5)
Vacuum Dewax	15.03 (0.2)	17.87 (0.2)	15.26 (0.2)	18.27 (0.2)
Linear Shrinkage (%)				
Argon Dewax	0.22 (0.05)	2.14 (0.12)	0.20 (0.05)	0.50 (0.07)
Vacuum Dewax	0.09 (0.07)	2.41 (0.14)	0.09 (0.05)	0.30 (0.07)

* Each group is the mean of 32 bars with standard deviation in parenthesis.

It was decided to divide the Matrix 1 MOR bars into two groups and sinter one group in the standard vacuum cycle (Brew Furnace) and the second group in the newly-developed vacuum-argon sintering cycle (Astro Furnace). Eight sintering runs were planned:
Matrix 1A - Table III

4 in vacuum..... 2 at 2080^0 C for 6 and 12 minutes
..... 2 at 2100^0 C for 6 and 12 minutes

Matrix 1B - Table VII

4 in vacuum-argon.... 2 at 2120^0 C for 30 and 60 minutes
..... 2 at 2135^0 C for 30 and 60 minutes

Each run contained four groups of 8 duplicate samples and two 4G baseline standard bars as internal standards for density control.

Vacuum Sintering

The Matrix 1A study for vacuum-sintered MOR bars (Table I) lists five variables for the 16 experiments summarized in Table III. The density data for as-sintered and machined bars which are given in Table IV illustrates that removal of the outer surface layer by machining the bars results in increased density. This increase in density becomes larger with higher sintering temperature and longer sintering time.

In the as-sintered condition, the densities were in the range of 93 to 95% of theoretical, whereas in the machined condition the densities ranged from 96 to 98% for all the batches. In all cases, the highest densities were obtained with the 4M batch (Fluid Mixing Process B at 60% solids loading). The density increase is attributed to removal of the porous carbon-rich layer from the surface of vacuum-sintered bars.

The mean densities of the machined MOR bars are listed as yields in Table V together with the mean effects found in the study. The circled effects are those which are considered significant for improving density. The conclusions for machined bars are listed at the bottom of the table:

- Process B is better than Process A
- 2110^oC is better than 2080^oC
- Strong interactions exist between Process (variable A in the Table) and solids loading (variable B in the Table) and between sinter time (variable E) and temperature (variable D)

Extreme value statistics were used to gain further insight on the effects of the treatments on the maximum values of the MOR strength. In measuring the results of certain physical phenomena such as floods, droughts, winds, temperatures, etc., it can be appreciated that under certain circumstances one is more interested in extreme values than in averages. It is the extreme earthquake or flood, not the average earthquake or flood, that is more damaging. So too in our program, since we are attempting to reach new, high values of strength first, and then

TABLE III

TASK II
MATRIX 1A

SUMMARY OF EXPERIMENTS IN MATRIX 1A

EXPT. NO.	VAR.	PROCESS A	LOADING B	DEWAX C	SINTER TEMP D	SINTER TIME E
1		A	55	VAC	2080°c	12 min.
2		B	55	VAC	2080	6
3		A	60	VAC	2080	6
4		B	60	VAC	2080	12
5		A	55	AR	2080	6
6		B	55	AR	2080	12
7		A	60	AR	2080	12
8		B	60	AR	2080	6
9		A	55	VAC	2110	6
10		B	55	VAC	2110	12
11		A	60	VAC	2110	12
12		B	60	VAC	2110	6
13		A	55	AR	2110	12
14		B	55	AR	2110	6
15		A	60	AR	2110	6
16		B	60	AR	2110	12

Vacuum Sinter Runs

V-34 2080°c 6 min - Expts. #2, #3, #5, #8
V-36 2080°c 12 min - Expts. #1, #4, #6, #7
V-35 2110°c 5 min - Expts. #9, #12, #14, #15
V-37 2110°c 12 min - Expts. #10, #11, #13, #16

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TABLE IV

DENSITIES OF SINTERED AND MACHINED MOR BARS

IN TASK II - MATRIX 1

VACUUM SINTERED

EXPT. NO.	SINTER NO.	DESCRIPTION	MEAN SINTERED DENSITY (% T.D.)	MEAN MACHINED DENSITY (% T.D.)	DENSITY INCREASE (%T.D.)
3	V-34	5 BAT	93.60 (0.29)*	95.94 (0.37)	2.34
5	2080°C-6 MIN	5 BLD	93.35 (0.21)	95.91 (0.30)	2.56
8		4 M	95.01 (0.17)	97.25 (0.28)	2.24
2		4 Q	93.72 (0.17)	96.39 (0.27)	2.67
				Ave.	2.45
15	V-35	5 BAT	93.63 (0.32)	97.13 (0.28	3.50
9	2110°C-6 MIN	4 BLD	93.97 (0.29)	97.81 (0.08)	3.84
12		4 M	94.42 (0.48)	97.95 (0.09)	3.53
14		4 Q	93.31 (0.44)	97.12 (0.09)	3.81
				Ave.	3.67
7	V-36	5 BAT	93.17 (0.38)	96.24 (0.41)	3.07
1	2070°C-12 MIN	4 BLD	93.57 (0.27)	97.22 (0.52)	3.65
4		4 M	94.65 (0.17)	97.52 (0.28)	2.87
6		4 Q	93.29 (0.22)	96.70 (0.30)	3.41
				Ave.	3.25
11	V-37	5 BAT	93.22 (0.45)	97.20 (0.11)	3.98
13	2110°C-12 MIN	4 BLD	93.11 (0.42)	97.17 (0.13)	4.06
16		4 M	93.94 (0.53)	97.57 (0.09)	3.63
10		4 Q	92.93 (0.54)	97.06 (0.11)	4.13
				Ave.	3.95

* Each group is the mean of 8 bars. Number in parenthesis is the standard deviation.

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TABLE V

TASK II
MATRIX 1A

MEAN DENSITIES OF MACHINED MOR BARS

YIELDS AND EFFECTS (%T.D.)

VACUUM SINTERED

EXPT. NO.	EFFECTS	MEANS	
		YIELD	EFFECTS
1	(AVE.)	96.22	(97.01)
2	A	96.39	.37 .10*
3	B	95.94	.18
4	AB	97.52	.58
5	C	95.91	-.25
6	AC	96.70	.18
7	BC	96.24	.14
8	ABC,DE	97.25	-.40
9	D	97.81	.73
10	AD	97.06	-.27
11	BD	97.20	.00
12	ABD,CE	97.95	-.08
13	CD	97.17	-.01
14	ACD,BE	97.12	-.08
15	BCD,AE	97.13	-.11
16	E	97.57	.14

*Estimated Standard Error

VARIABLE	-	+
A	Process A	Process B
B	55% Solids	60% Solids
C	Vac Dewax	Argon Dewax
D	2080°C	2110°C
E	6 Min.	12 Min.

CONCLUSIONS:

Vacuum Sintered:
- Process B Better Than Process A - Highly Signif.
- 2110°C Sinter Temp. Better Than 2080°C - Highly Signif.
- Strong Interactions Between Process and Solids Loading and Between Sinter Temp. and Time
- Vacuum Dewaxing Probably Better Than Argon Dewaxing

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reliability next, we must be aware of the effects of our variables on the highest values of strength. In this way we can estimate the potential strength and utility of this material in a quantitative manner.
As a first approach at extreme value analysis we have used the highest values as yields in the matrix, and made no assumptions as to the distribution of the extreme values (which can be shown mathematically to follow a limiting distribution of the Gumbel form).

The mean and highest value strengths for machined MOR bars in the Matrix 1A study are presented as yields in Table VI together with the calculated mean effects. The circled effects are considered significant as determined by their magnitude compared to the estimated standard error of the experiments. The conclusions derived from the analysis are listed at the bottom of the Table:

- Process B produces stronger material than Process A
- The lower sintering temperature (2080^0 C) produces significantly stronger bars than does the higher temperature (2110^0 C).
- Strong solids loading - dewaxing process and solids loading-sintering temperature interactions are noted in the effects from the extreme value statistics.

The highest strengths were achieved in experiments #6 and #8 where a mean strengths of 65 Ksi and highest-value strengths of 74.1 Ksi 83.4 Ksi were achieved. The characteristics of the two experiments were (Table VI):

- Experiment #6 - Fluid Mix Process B; 55% solids loading; dewaxed in Argon; and sintered at 2080^0 C for 12 minutes.
- Experiment #8 - Fluid Mix Process B; 60 % solids loading; argon dewaxed; and sintered at 2080^0 C for 6 minutes.

It should be noted that Process B and sintering temperature significantly influence both machined-bar density and strength. Sintering temperature, however, shows an inverse relationship since higher temperature favors higher density and lower temperature favors higher strength. The high temperature effect on strength may be related to excessive grain growth which is known to adversely affect strength. The interactions between process and solids loading noted in the density matrix are not found in the strength matrix.

Matrix 1B:

Argon Sintering

A new sintering cycle was developed which involves the heating of the materials to approximately 1500^0 C in a technical vacuum and then introducing argon at atmospheric pressure for the remaining part of the cycle. Satisfactory densities for bars of 4G and 5 Batch compositions were attained with this new cycle when sintered at 2125^0 C. The four groups of Matrix 1 bars, cited above, were sintered in this new vacuum-argon cycle.

TABLE VI

TASK II
MATRIX 1A

MEAN AND HIGHEST VALUE STRENGTHS OF MACHINED MOR BARS

YIELDS AND EFFECTS (ksi)

EXPT. NO.	EFFECTS	MEANS**		HIGHEST VALUE**	
		YIELD	EFFECTS	YIELD	EFFECTS
1	(AVE.)	56.8	(57.4)	64.4	(67.2)
2	A	63.0	4.9±1.0*	70.2	7.5±0.8*
3	B	54.3	-1.3	63.6	1.0
4	AB	58.2	-1.5	72.3	1.1
5	C	52.1	3.0	60.1	2.2
6	AC	64.6	1.1	74.1	3.1
7	BC	60.8	2.5	70.9	3.9
8	ABC,DE	64.5	-0.6	83.4	0.1
9	D	54.1	-3.9	67.4	-5.3
10	AD	57.3	-1.6	68.4	-2.7
11	BD	50.7	-1.6	60.3	-4.4
12	ABD,CE	52.7	1.3	62.5	0.8
13	CD	56.1	0.5	62.3	-2.3
14	ACD,BE	60.0	-0.4	67.0	0.1
15	BCD,AE	54.1	-1.4	58.7	-0.8
16	E	58.5	-0.6	69.9	1.2

*Estimated Standard Error
**From Group of 8 Samples

VARIABLE	-	+
A	Process A	Process B
B	55% Solids	60% Solids
C	Vac Dewax	Argon Dewax
D	2080°C	2110°C
E	6 Min.	12 Min.

CONCLUSIONS:

Vacuum Sintered:
- Process B Better Than Process A - Highly Signif.
- 2080° Sinter Temp. Better Than 2110°C - Highly Signif.
- Highest Value Statistics Indicate Strong Solids Loading - Dewax and Solids Loading - Sintering Temperature Interactions

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The Matrix 1B study for argon-sintered MOR bars includes five variables and evaluations of the main effects and the two-factor interactions for the 16 experiments summarized in Table VII.

The mean densities of the sintered MOR bars are shown as yields in percent of theoretical density in Table VIII. The average mean density achieved was 91.84%. Both the medians and means were determined and showed close agreement between these two measures of central tendency of the data. The effects (Table VIII) show that only two variables are significant. The B variable, solids loading, has an effect on sintered density; the 60% solids loading yielding higher sintered-density bars than the 55% loading. A strong process-solids loading interaction is indicated by the large AB effect.

The yields and effects of mean and highest value strengths for machined MOR bars for Matrix 1B study are presented in Table IX. The main effects which are circled are considered significant as determined by the magnitude of effects compared to the estimated standard error of the experiments. The conclusions as derived from the analysis are the following:

- Process B produces significantly stronger bars than does Process A (Variable A)
- Significant two-factor interactions (solids loading-dewaxing process and sintering temperature-sintering time) are observed.
- Vacuum dewaxing is preferred from the mean strengths data and only suggested in the highest value strength analysis.
- The variables of solids loading (B), temperature of sintering (D) and time of sintering (E) had no significant effects

The highest level of strength was achieved in experiment #8 in which a mean strength of 420 MPa (61 Ksi) and a highest value strength of 475 MPa (69 Ksi) were observed. The conditions of experiment #8 were:

Fluid Mix Process B
60% Solids Loading
Argon Dewax
2135^{0}C Sinter Temperature
30 Minutes Sinter Time

II.4 Analysis of Data and Process/Property/Microstructure Relationships

The experimental samples were selected from the same population for Matrix 1A and Matrix 1B, and the variables A, B, and C used were identical in each matrix. The MOR bars in Matrix 1A were sintered in vacuum at two temperatures and two times which were selected on the basis of past sintering experience.

Density

A comparison of the effects of the experiments on the mean densities of bars from the two matrices is shown in Table X. The average mean density

TABLE VII

TASK II
MATRIX 1B

SUMMARY OF EXPERIMENTS IN MATRIX 1B

EXPT. NO.	VAR.	PROCESS A	LOADING B	DEWAX C	SINTER TEMP D	SINTER TIME E
1		A	55	VAC	2135°c	60 min.
2		B	55	VAC	2135	30
3		A	60	VAC	2135	30
4		B	60	VAC	2135	60
5		A	55	AR	2135	30
6		B	55	AR	2135	60
7		A	60	AR	2135	60
8		B	60	AR	2135	30
9		A	55	VAC	2120	30
10		B	55	VAC	2120	60
11		A	60	VAC	2120	60
12		B	60	VAC	2120	30
13		A	55	AR	2120	60
14		B	55	AR	2120	30
15		A	60	AR	2120	30
16		B	60	AR	2120	60

Vacuum - Argon Sinter Runs

LA-9 2135°c 30 min. - Expts. #2, #3, #5, #8
LA-8 2135°c 60 min. - Expts. #1, #4, #6, #7
LA-6 2120°c 30 min. - Expts. #9, #12, #14, #15
LA-7 2120°c 60 min. - Expts. #10, #11, #13, #16

TABLE VIII

TASK II
MATRIX 1B

MEAN DENSITIES OF MACHINED MOR BARS

YIELDS AND EFFECTS (%T.D.)

ARGON SINTERED

EXPT. NO.	EFFECTS	MEANS**	
		Yield	Effects
1	(AVE)	93.00	(91.84)**
2	A	90.87	0.28 ± .12*
3	B	91.74	0.71
4	AB	92.93	1.15
5	C	91.93	-0.12
6	AC	90.82	0.22
7	BC	91.97	0.07
8	ABC,DE	92.45	-0.32
9	D	92.23	-0.24
10	AD	90.41	0.12
11	BD	91.82	0.09
12	ABD,CE	92.59	0.07
13	CD	91.65	0.04
14	ACD,BE	90.99	0.14
15	BCD,AE	91.51	-0.13
16	E	92.57	0.11

*Estimated Standard Error

VARIABLE	-	+
A	Process A	Process B
B	55% Solids	60% Solids
C	Vac Dewax	Argon Dewax
D	2135°C	2120°C
E	30 Min.	60 Min.

**Means of 8 bars

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TABLE IX

TASK II
MATRIX 1A

MEAN AND HIGHEST VALUE STRENGTHS OF MACHINED MOR BARS

YIELDS AND EFFECTS (ksi)

EXPT. NO.	EFFECTS	MEANS		HIGHEST VALUE	
		YIELD	EFFECTS	YIELD	EFFECTS
1	(AVE.)	50.4	(52.05)**	58.2	(60.0)
2	A	56.9	6.0±1.5*	63.6	6.4±0.6*
3	B	49.7	0.8	55.8	0.9
4	AB	55.8	1.9	58.4	0.4
5	C	49.1	-2.9	57.8	-1.2
6	AC	50.8	2.1	61.5	1.9
7	BC	45.6	2.3	54.0	3.5
8	ABC,DE	60.7	2.8	68.9	3.2
9	D	52.9	-0.6	59.3	0.4
10	AD	56.0	-1.3	68.6	-0.2
11	BD	52.3	-0.4	60.0	-0.1
12	ABD,CE	52.3	-1.3	60.9	-1.7
13	CD	46.2	-0.8	52.7	-2.8
14	ACD,BE	51.1	1.1	58.5	-0.8
15	BCD,AE	46.1	0.2	56.3	0.8
16	E	56.9	-0.6	65.1	-0.3

*Estimated Standard Error
**Means or Highest Values of 8 Bars

VARIABLE	-	+
A	Process A	Process B
B	55% Solids	60% Solids
C	Vac Dewax	Argon Dewax
D	2135°C	2120°C
E	30 Min.	60 Min.

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TABLE X

TASK II
MATRIX 1

COMPARISON OF VACUUM SINTERED AND ARGON-SINTERED
MEAN DENSITIES
OF MACHINED MOR BARS

EFFECTS (%T.D.)

EFFECTS	1A VACUUM SINTERED MEANS	1B ARGON SINTERED MEANS
(AVE.)	97.01	91.84
A	.37±.10*	-.28±.12*
B	.18	.71
AB	.58	1.15
C	-.25	-.12
AC	.18	.22
BC	.14	.07
ABC,DE	-.40	-.32
D	.73	-.24
AD	-.27	.12
BD	.00	.09
ABD,CE	-.08	-.07
CD	-.01	.04
ACD,BE	-.08	.14
BCD,AE	-.11	-.15
E	.14	.11

*Estimated Standard Error

VARIABLE	-	+
A	Process A	Process B
B	55% Solids	60% Solids
C	Vac Dewax	Argon Dewax
D Vac	2080°C	2110°C
Vac-Argon	2135°C	2120°C
E Vac	6 Min.	12 Min.
Vac-Argon	30 Min.	60 Min.

CONCLUSIONS:

Vacuum Sintered:
- Process B Better Than Process A - Highly Signif.
- 2110°C Sinter Temp. Better Than 2080°C - Highly Signif.
- Strong Interactions Between Process and Solids Loading

Vacuum-Argon Sintered:
- 60% Solids Loading Better Than 55% - Signif.
- Strong Process - Solids Loading Interaction

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of the vacuum-sintered material (97%) is much greater than for the argon-sintered material (91%). The results in Table X indicate the following:

For the vacuum-sintered bars
- Process B better than Process A
- 2110^0 C Sinter Temperature better than 2080^0 C
- Strong Interactions between Process and Solids Loading

For the argon-sintered bars
- 60% Solids Loading better than 55% Solids Loading
- Strong Process-Solids Loading Interaction

The large density difference between the bars from the two matrices (97% vs. 91%) make it difficult to make significant comparisons. The data from the vacuum-sintered matrix are probably more meaningful since the level of density was close to full density. The superiority of Process B over Process A is believed to be an important effect which becomes of even greater importance in determining the strengths of the bars as discussed below. Temperature has a strong effect on the vacuum-sintered densities, and will be an important parameter in optimizing the vacuum sintering process.

Strength

A comparison of the average of the means of the sixteen experiments indicates that the vacuum-sintered bars were stronger (392 MPa (57 Ksi) vs.359 MPa (52 Ksi)) than those sintered in argon. The average of the highest value data reflects the same improvement (462 MPa (67 Ksi) vs. 413 MPa (60 Ksi)). The following conclusions were drawn from the results summarized in Table XI:

For the vacuum-sintered bars
- Process B is better than Process A
- 2080^0 C Sinter Temperature is better than 2110^0 C
- Solids Loading, Dewax Conditions and Sinter Time have no significant effect
- Two-factor interactions of Solids Loading-Dewax Process and Solids Loading-Sintering Temperature are noted in the highest value data

For the argon-sintered bars
- Process B is better than Process A
- Two two-factor interactions are observed
- Vacuum Dewaxing is preferred from the mean strength data and only suggested from the highest value data
- Solids Loading, and Sinter Temperature and Time have no significant effect

From these results it seems clear that, within the range of these experiments, Process B is better than Process A for both sintering conditions, and Solids Loading, and Sinter Time have no significant effect on MOR strength. The importance of sinter temperature in the vacuum-sintered bars again suggests the influence of grain growth at the higher sintering temperature.

TABLE XI

TASK II
MATRIX 1

COMPARISON OF VACUUM SINTERED AND ARGON-SINTERED
MEAN AND HIGHEST VALUE STRENGTHS
OF MACHINED MOR BARS

	EFFECTS (ksi)			
	1A VACUUM SINTERED		1B ARGON SINTERED	
EFFECTS	MEANS	HIGHEST VALUE	MEANS	HIGHEST VALUE
(AVE.)	(57.4)	67.2	52.05	60.0
A	4.9±1.0*	7.5±0.8*	6.0±0.5*	6.4±0.6*
B	-1.3	1.0	0.8	0.9
AB	-1.5	1.1	1.9	0.4
C	3.0	2.2	-2.9	-1.2
AC	1.1	3.1	2.1	1.9
BC	2.5	3.9	2.3	3.5
ABC,DE	-0.6	0.1	2.8	3.2
D	-3.9	-5.3	-0.6	0.4
AD	-1.6	-2.7	-1.3	-0.2
BD	-1.6	-4.4	-0.4	-0.1
ABD,CE	1.3	0.8	-1.3	-1.7
CD	0.5	-2.3	-0.8	-2.8
ACD,BE	-0.4	-0.1	1.1	-0.8
BCD,AE	-1.4	-0.8	0.2	0.8
E	-0.6	1.2	-0.6	-0.3

*Estimated Standard Error

VARIABLE	-	+
A	Process A	Process B
B	55% Solids	60% Solids
C	Vac Dewax	Argon Dewax
D Vac	2080°C	2110°C
Vac-Argon	2135°C	2120°C
E Vac	6 Min.	12 Min.
Vac-Argon	30 Min.	60 Min.

CONCLUSIONS:

Vacuum Sintered:
- Process B Better Than Process A - Highly Signif.
- 2080°C Sinter Temp. Better Than 2110°C - Highly Signif.
- Solids Loading - Dewax and Solids Loading - Sintering Temperature Interactions Noted From Extreme Value Statistics

Vacuum-Argon Sintered:
- Process B Better Than Process A - Highly Signif.
- Vacuum Dewax Process Better Than Argon Dewax Process
- Solids Loading - Dewax Process and Sintering Temperature Interactions Noted

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The samples with the greatest mean strengths in Matrix 1A (Vacuum sintered) were from experiments #6 (445 MPa (64.6 Ksi)) and #8 (444 MPa (64.5 Ksi)) and in Matrix 1B (Argon sintered) from experiment #8 (418 MPa (60.7 Ksi)). All three of these experiments included Process B and Argon Dewaxing. Experiment #6 had 55% solids loading whereas experiment #8 had 60%. The machined-bar density (97% for vacuum sintered, 92% for argon sintered) seems to have only a minor effect on the strength. The similarity in strength levels despite the variation in processing and density suggests that flaws introduced in processing are the controlling factors for strength. The sintering conditions (time, temperature, atmosphere) at this strength level have only a minor effect. Microstructure and fracture origin studies are important at this point in the development program to delineate processing areas requiring further improvement.

An overall summary of the strength data in the program to date is listed in Table XII.

Matrix 1 MOR Bar Yields

The MOR bars formed and processed during the Task II Matrix 1 study have been evaluated for yields following each of the processing steps:

- Molding
- Dewaxing
- Sintering
- Machining

The results are summarized in Table XIII. The yield from each of the processing steps is greater than 90%, and the overall process yield is 86.4%.

Fractographic Analysis

Fracture surfaces of MOR test bars from the two matrices, 1A (vacuum sintered) and 1B (vacuum-argon sintered) were evaluated in the optical and scanning electron microscopes to determine the fracture origins. Samples were chosen on the basis of finding two matching surfaces on the same MOR bar and determining from fracture surface markings that the fracture origin could be identified.

A summary of this investigation for the Task II Matrix 1 samples is given in Table XIV. The matrix number, sample number, fracture strength of that particular sample and the analysis of the fracture origin are presented. In general, flaws larger than 100 micrometers yield strengths of less than 40 Ksi, flaws less than 50 micrometers lead to strengths of up to 70 Ksi. The position of the flaws in the bar also has a strong effect on the measured strength as the bars are tested in transverse bending which stresses the bar with a stress gradient from zero at the central axis to a maximum stress at the upper and lower surfaces. Inspection of Table XIV shows that the origins are primarily voids. Both surface and subsurface

TABLE XII

SUMMARY OF
SIC STRENGTH DATA
Room Temperature

	n	Mean (ksi)	Std. Dev. (ksi)	θ (ksi)	m
BASELINE	30	43.3	5.7	45.8	8.0
FLUID MIXED					
5 Batches					
2080°C	22	54.0	8.2	57.1	8.7
2110°C	20	51.7	8.4	55.2	6.7
TASK II MATRIX 1A					
Best Group (4M-60-A-2080)	8	64.5	10.1		
All 4Q	31	61.4	6.6	64.2	10.5
All 4M	32	58.6	10.2	62.9	6.0
MATRIX 1B					
Vac-Argon Sinter (Density 90-93%)					
Best Group #8 (4M-60-A-2135)-30)	7	60.7	4.5		
All 4Q	31	51.8	11.8	57.1	7.9
All 4M	28	56.3	6.3	59.1	10.1

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TABLE XIII

TASK II
MATRIX 1

PROCESSING YIELDS

PROCESS	MOR BARS	SINGLE PROCESS YIELD (%)	CUMULATIVE YIELD (%)
Molding	772	90.3	90.3
Dewaxing	256	99.2	89.6
Sintering	254	99.6	89.2
Machining	253	96.8	86.4

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TABLE XIV

FRACTURE SURFACE INVESTIGATION

MATRIX & SINTERING TREATMENT	SPECIMEN NUMBER	MOR STRENGTH (KSI)	REFERENCE FIG. NO.	REMARKS
IA VACUUM	V34, 5BAT #2126	38.9	Fig. 7	Surface flaw, 125 microns wide, 100 microns deep.
	V34, 4M #2260	66.5	Fig. 8	Sub-surface flaw, 25-30 microns wide, 25 microns deep or long.
	V34, 5BAT #1949	56.2		Surface flaw 40-50 microns wide, 30-35 microns deep.
	V34, 5BAT #2061	59.9		Surface flaw, 30 microns wide, 35 microns deep.
	V34, 4M #2321	52.7		Surface flaw, 30-35 microns wide and 80 microns long.
IB VACUUM/ ARGON	LA6, 5BAT #2057	47.5	Fig. 9	Surface flaw, 50 microns wide, 15-20 microns deep.
	LA6, 4BLD #2406	51.2	Fig. 9 & Fig. 10	Sub-surface flaw, 35 microns wide and 90 microns long.
	LA6, 4BLD #2399	47.6	Fig. 9 & Fig. 11	Sub-surface flaw, 35 microns wide and 90 microns long.
	LA6, 5BAT #2013	56.3		Surface crack in the vicinity of a long grain.
	LA6, 4M #2280	40.9		Surface flaw . . . possibly a large grain.

voids are found. A few cracks were also noted in these bars and they appear to be near large grains of SiC. As strengths begin to approach 70 Ksi in the program, the importance of grain growth as a source of fracture is expected to increase.

A typical fracture surface for vacuum sintered material is revealed in the SEM photograph of specimen #2126 (5 batch), shown in Figure 7. Failure in this bar initiated at a large surface pore about 125 micrometers wide and 100 micrometers deep. Note the large area of fine porosity surrounding the failure site in Figure 7b. Away from the site, Figure 7c, the fracture surface has a uniform microstructure and the failure mode appears to be transgranular.

A typical fracture surface for a specimen from batch 4M (#2260) is shown in Figure 8. Failure originated at a subsurface pore with a diameter of about 25 micrometers wide. The overall microstructure (especially related to fine porosity distribution in the matrix) Figure 8c, may be slightly better in this material (Process B) compared to 5 Batch (Process A). In addition, the size of voids which initiated failure decreased significantly and apparently resulted in higher fracture strength. This may be attributable to the longer fluid mixing time which provided a more uniform material.

Fracture surfaces of material sintered in the vacuum-argon, 1B matrix (LA6 5 Batch and 4 Blend) are shown in Figure 9. Figure 9a (#2057) clearly shows the fracture origin at the surface, while in Figure 9b (#2406) a subsurface flaw is revealed. A surface connected fracture origin is seen in Figure 9c (#2399). Away from the fracture origin, the microstructure appears to have a rather uniform, fine porosity comparable to vacuum sintered material.

The general mode of room temperature fracture for all of these samples appears to be transgranular. In most cases the fracture origin is a porous region. Figure 10 shows that the failure initiation site was rich in boron, probably due to an agglomerate in the mix. No significant iron was found. Figure 11 shows that some pores have mo detectable contamination and probably were voids after molding or dewaxing.

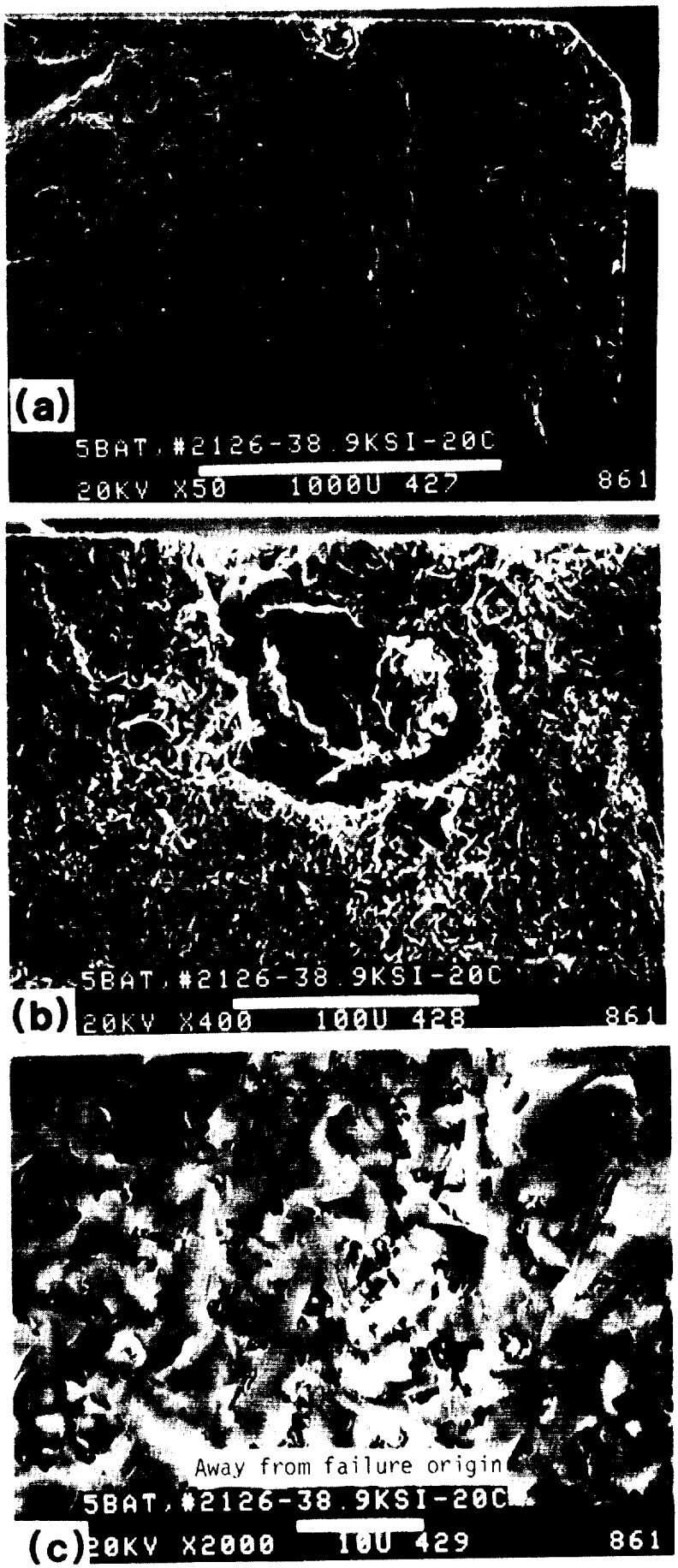

Figure 7

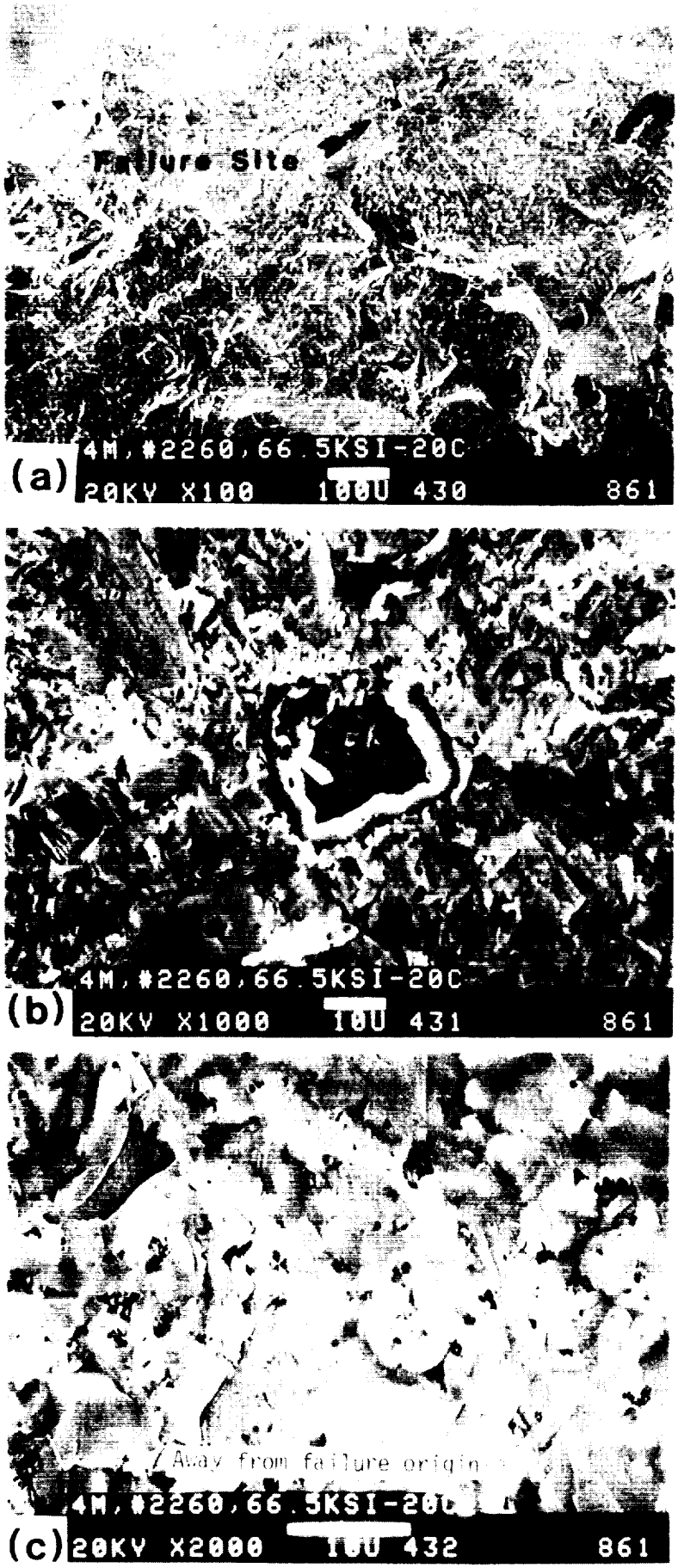

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Figure 8

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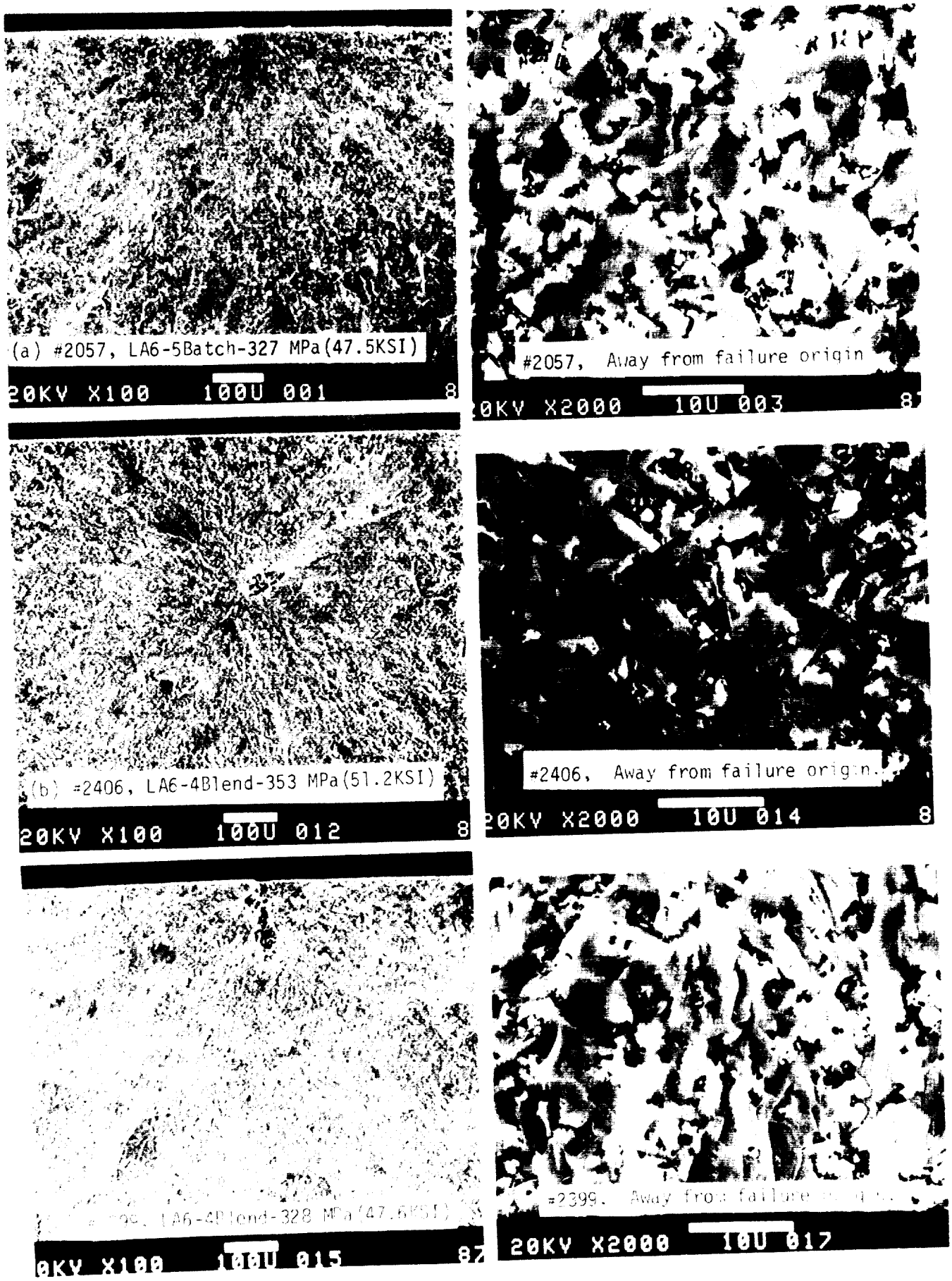

Figure 9

Figure 10

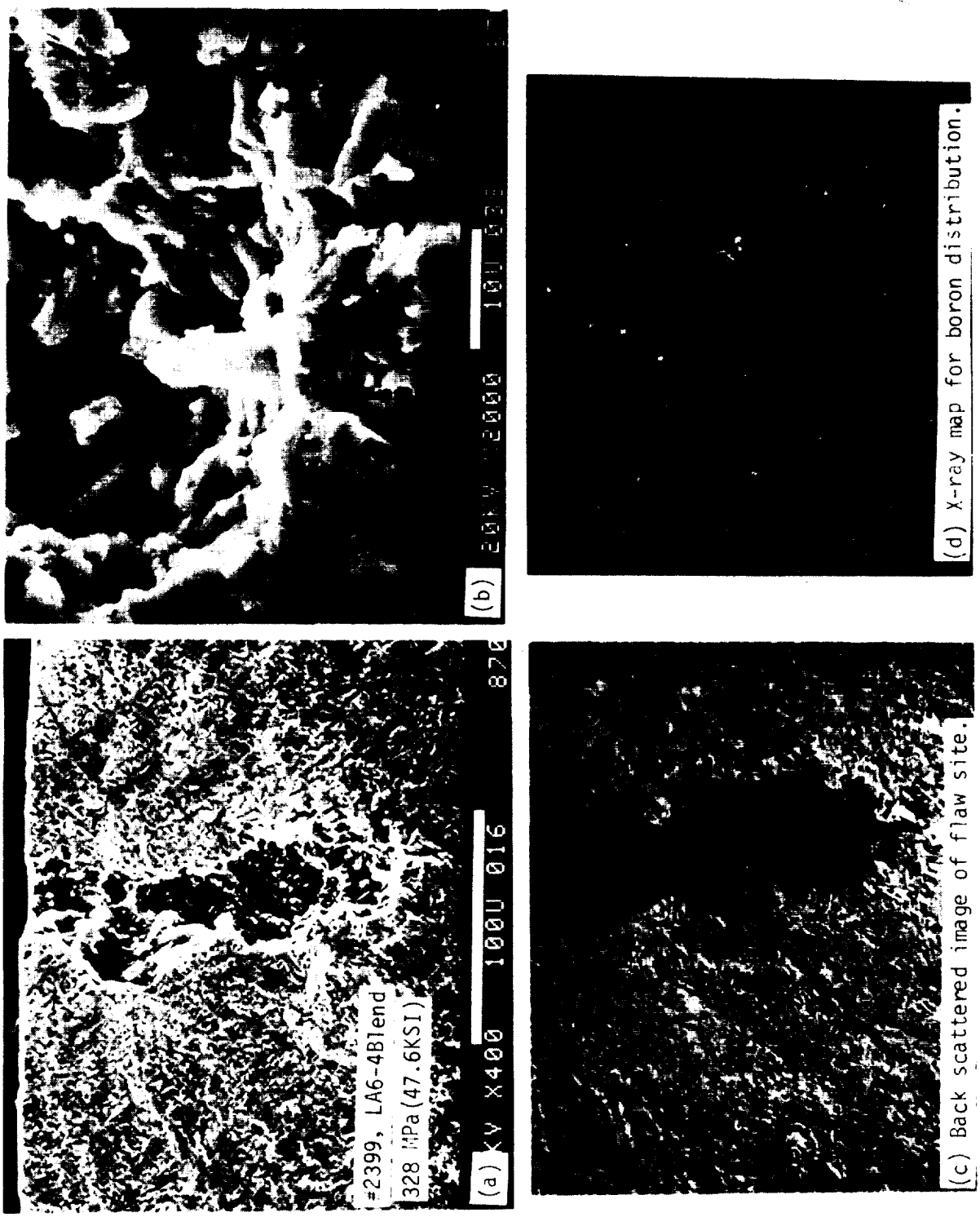

Figure 11

Task VII - MATERIALS AND PROCESSING IMPROVEMENTS

VII.1 Objectives

This task is aimed at exploring new ideas for materials and processing improvements which, if significant, can be incorporated into the Task II work plans.

As detailed in the first annual report, the Task I base line material, NASA4G(55), was prepared using a high shear dry mixing process. This process resulted in base line MOR bars having 95-96 percent of theoretical density and an average strength of 299 MPa (43.3 Ksi). Fractography identified failure origins as voids which originated in inhomogeneities in the molding mixture. No fracture origins could be attributed to molding, dewaxing, sintering or machining.

Preliminary results from Task VII, Matrix 3 during the first year of the program indicated that a fluid mixing process could substantially reduce the size and frequency of mix inhomogeneities. Sintered, machined MOR bars from that material resulted in a strength increase to 413 MPa (60 Ksi). Consequently, during the second year of the program, the primary emphasis in Task VII was on molding mix preparation using the fluid mixing process. Experiments were also conducted to investigate dewaxing and sintering cycle factors. There were four major studies completed during the second year:

1. Fluid Mixing Process Reproducibility

2. Fluid Mixing Process Improvement

3. Matrix 6 - Dewaxing Cycle Factors

4. Matrix 7 - Vacuum-Argon Sintering Cycle Factors

The Fluid Mixing Process Reproducibility study was undertaken to confirm the results of Matrix 3 and to demonstrate that this procedure could produce mixes which were under statistical process control.

The Fluid Mixing Process Improvement study investigated several important parameters identified during the reproducibility study. The mix quality was improved and evaluated in Task II, Matrix 1.

Matrix 6 investigated the influence of atmosphere, temperature and temperature ramp rates on dewaxing. The results indicated that although these factors influenced the binder removal percentage, no effect was observed on sintering results.

Matrix 7 studied the effects of several sintering cycle parameters on the density and strength of test bars made from four different materials. Optimum cycle parameters were determined for future use in Task II, Matrix 2.

VII.2.1 Fluid Mixing Process Reproducibility

The initial fluid mix batch (NASA 4E) clearly indicated the potential superiority of this process for mix preparation. A broad outline of this process is presented in Figure 12. A critical review of the actual procedures used in the preparation of batch 4E indicated that the process was not amenable to good statistical process control. Consequently a revised procedure was established, shown in Figure 13, and identified as Process A. Several process parameters were identified for recording in-process data, and five replicate batches were produced.

The five batches in this study are identified as NASA4H, I, J, K and L. In-process data consisted of milling times, temperatures, milling speeds, and mix viscosities and weight losses. Material samples were removed at 24 hour intervals during the ball milling, and at the end of the drying, mixing and waxing stages. The end product material was checked for viscosity and spiral flow on the injection molding machine.

Summary of results

Ball milling Times, temperatures and speeds were maintained at the nominal levels. The viscosities of all five batches were consistent. A decrease in the slurry viscosity was observed when the binders and additional solvent were added.

Stir drying weight losses The stir drying operation was performed over a two day period with the mix temperature held at approximately 100 C for about 7 hours the first day then allowing it to cool to room temperature overnight. The batch was reheated the next day for 7 additional hours of stir drying.

Weight-loss results are similar for four of the batches and are listed in Table XV. Batch 4I, however, had a significantly higher weight loss during the second day. The difference was due to a deliberate change in air flow over the batch, but did not noticeably affect the quality of this mix. The large change in the observed evaporation rate demonstrated that the stir drying process could be accelerated significantly.

Pan drying weight losses The pan drying process was carried out over a period of 100 - 200 hours at 50° C in an air circulating oven. Each mix was held in the oven until no weight loss was measured over a 24 hour period. Nominally this process step took 100 hours. Two batches took approximately 150 hours. One of these had higher residual solvent after stir drying, while the other was involved in an inadvertent oven shutdown. Neither of these process variations resulted in a noticeable affect on the mix quality.

Mixing and waxing The mixing and waxing steps were performed in a double planetary mixer at a temperature of 145 C. The pan dried material (formulated to yield a 62 volume percent solids loading) was stirred until

FIGURE 12

Injection Molded SiC Process Flow Sheet
Incorporating the Fluid Mixing Process

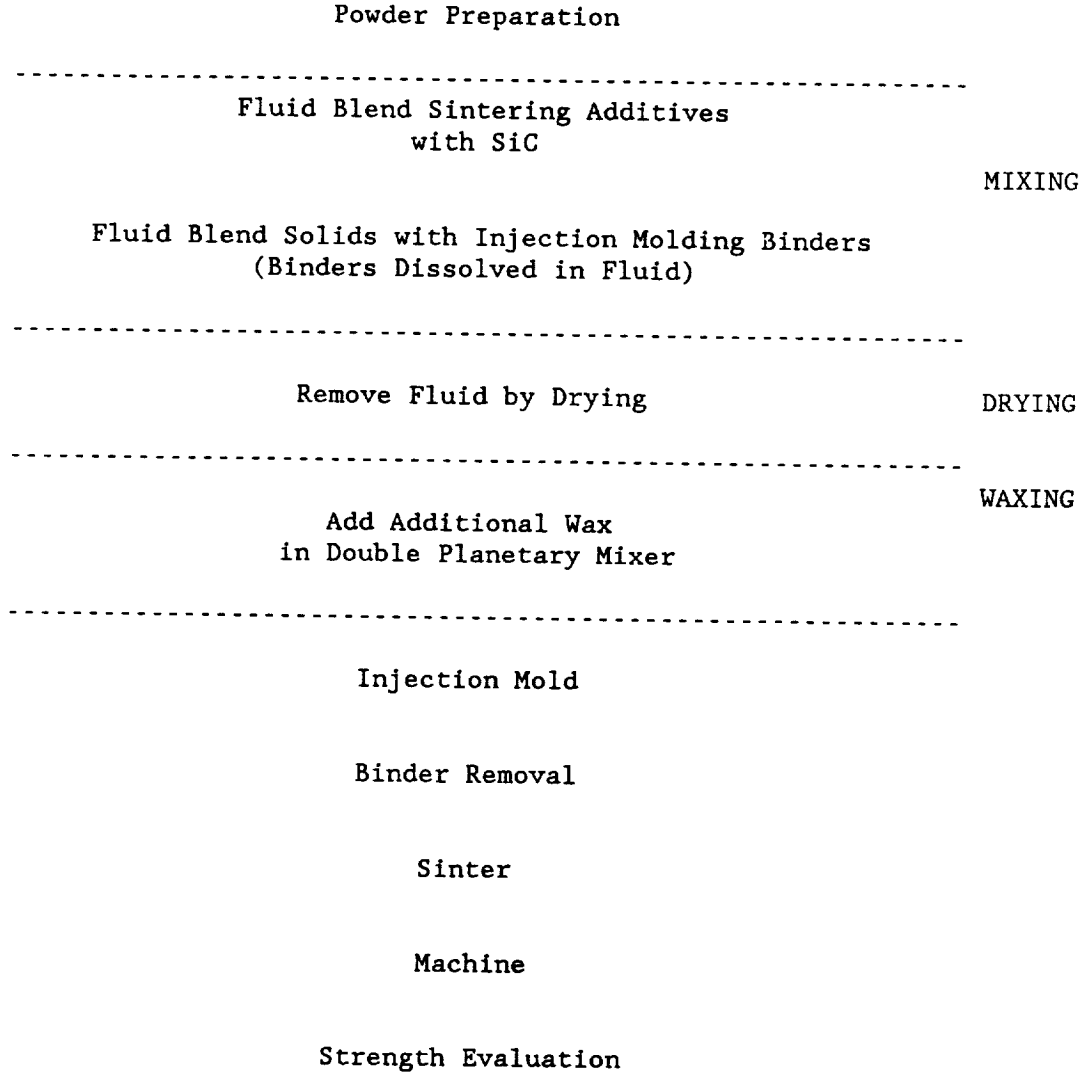

FIGURE 13

FLUID MIX PROCESS

PROCESS	TIME *(HOURS)	DATA COLLECTED
Begin Mixing of Solids with Toluol	0	Weight
	24	Dip Slide, Micrograph, Viscosity, Temp.
	48	Dip Slide, Micrograph, Viscosity, Temp.
Addition of Wax plus Toluol	48	
	54	Dip Slide, Micrograph, Viscosity, Temp.
	72	Dip Slide, Micrograph, Viscosity, Temp.
Begin Stir Drying	72	Temp., Weight
	79	Temp., Weight
	86	Temp., Weight
Begin Pan Drying constant temp.	86	Weight
	102	Weight
	150	Weight
	174	Weight, Micrograph
Small Addition of Wax	174	Micrograph
Molding		Spiral Flow, Orifice Flow, Molded Density, Molded Yield Micrograph.

* 0 Time is start of batching process

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TABLE XV

STIR DRY WEIGHT LOSS
(Grams)

	1ST DAY	2ND DAY	TOTAL
NASA4H	1,727	1,059	2,786
NASA4J	2,037	955	2,992
NASA4K	1,487	840	2,327
NASA4L	1,959	760	2,719
AVE	1,803	904	2,706
NASA4I	1,839	1,389	3,228

a smooth melt consistency was achieved. An additional 2 percent of binder was then added to reach the desired 60 percent loading. This waxing procedure was adopted during the initial development of this process in order to fluidize the melt. It was found during this reproducibility study that acceptable viscosity for molding could be achieved without the waxing step.

Material sample observations Typical in-process sample photographs are shown in Figure 14 for six discrete points in the process. Microscopic examination of dip slide samples taken during the ball milling process clearly showed the distribution of carbon agglomerates within the mix. With continued milling and stir drying the carbon dispersion improved. At the completion of the pan drying step, the largest carbon agglomerates were approximately 10 - 15 micrometers in diameter in all five batches. Other types of agglomerates were not observed in the dip slide samples.

Two types of inhomogeneities, grey spots and boron agglomerates, were detectable microscopically after pan drying, mixing and waxing. Statistical Process Control (SPC) data were generated for both types of inhomogeneities. The SPC charts for the grey spots are shown in Figure 15. It is noted that grey spots are not detectable after the pan drying step, although most of the wax binders are already in the mix. The SPC chart also shows no significant change in the grey spots as additional waxes are added to dilute the mix to 60 volume percent.

Boron agglomerate SPC charts are shown in Figure 16. The charts indicate that the boron agglomerates remain essentially unchanged during mixing and waxing. Both figures show that the fluid mixing process is under statistical process control for these two inhomogeneities.

Flow Behavior Flow behavior of these mixes was measured using spiral flow and orifice flow tests. The spiral flow test measures the moldability of the material under typical injection molding conditions. Test results for all five batches are shown in Figure 17 and illustrate the consistency of the batches. The orifice flow test provides a measure of the apparent viscosity as a function of shear rate and is a common parameter used to characterize materials for injection molding. Data for the last four batches is shown in Figure 18 illustrating the uniformity of viscosity/shear rate. The test equipment was not available for the first batch, but based on the spiral flow data, the viscosities would be similar to that obtained for the other mixes.

Summary The results of the Fluid Mixing Process Reproducibility Study demonstrated that:

...The fluid mixing process provides reproducible mixes and is under statistical process control.

...The size of inhomogeneities are consistent with those found in the first fluid mix batch (4E) which had a strength approaching 415 MPa (60 KSI).

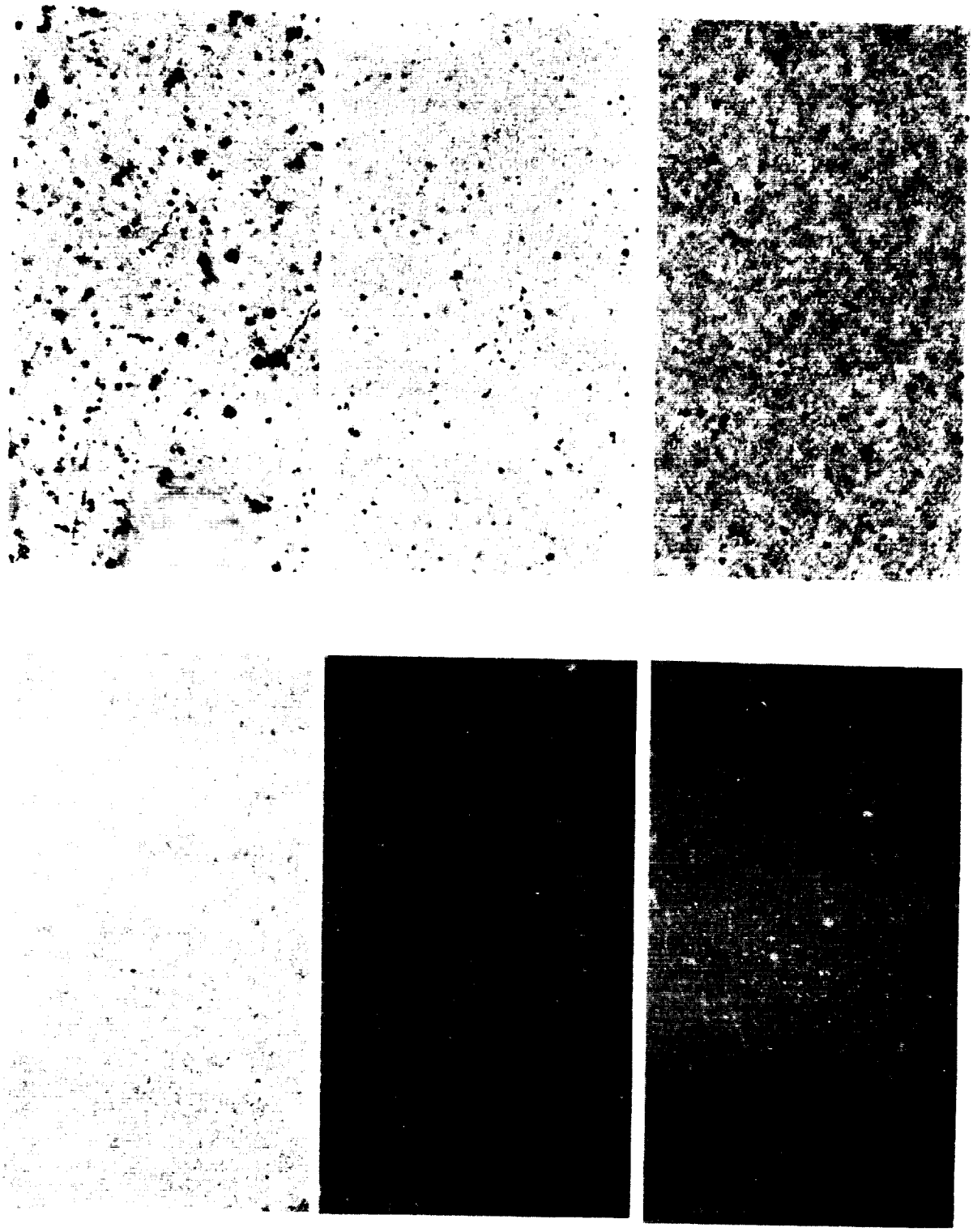

Figure 14

Dip Slide Micrographs (100 X) Fluid Mixing Process.
a) 24 hrs Wet Ball Mill (solids)
b) 48 hrs Wet Ball Mill (solids)
c) 72 hrs (24 hrs with Binders)
d) After Drying
e) After Mixing
f) After Waxing

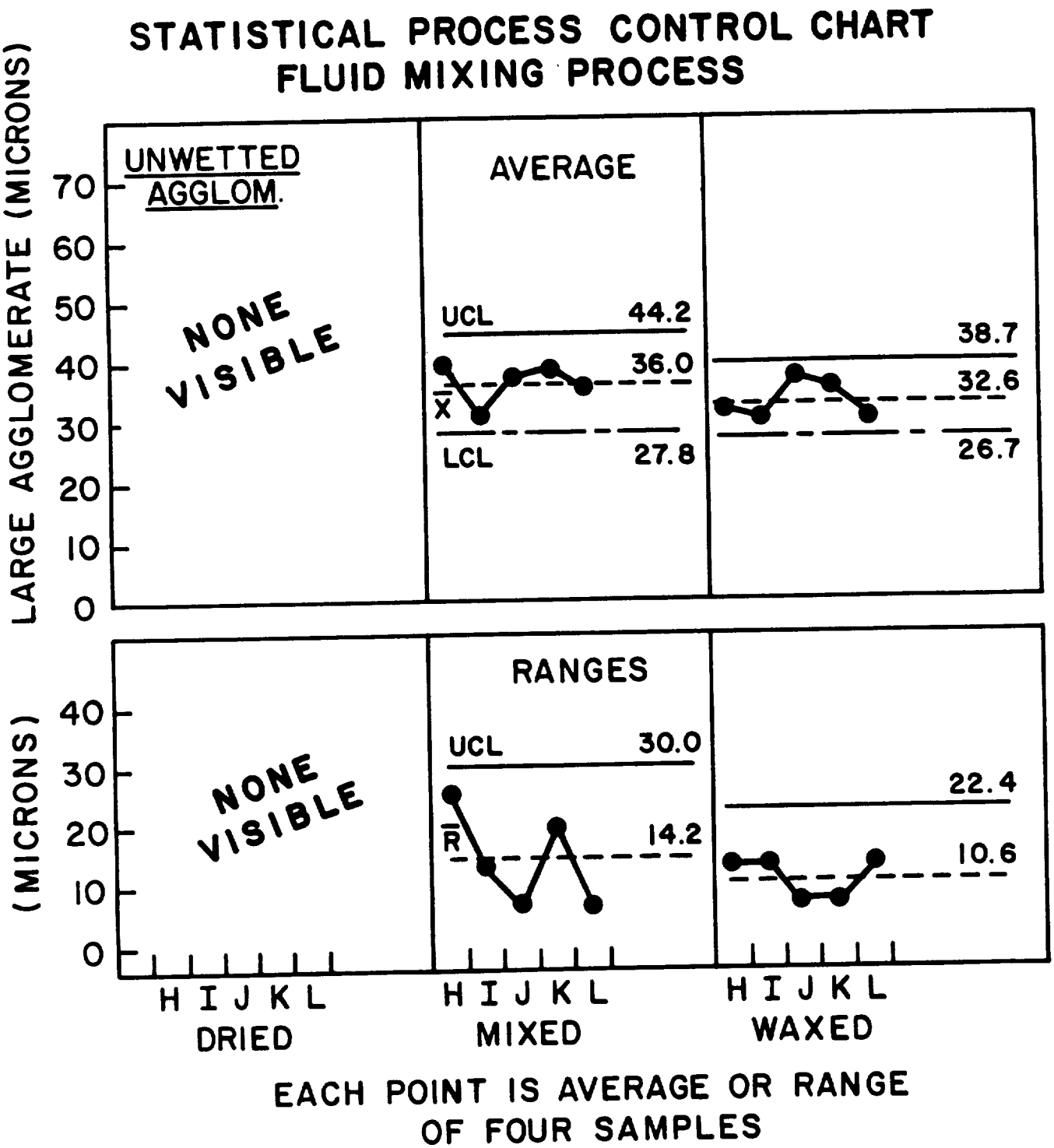

Figure 15: Statistical Process Control Chart
For Unwetted Agglomerates

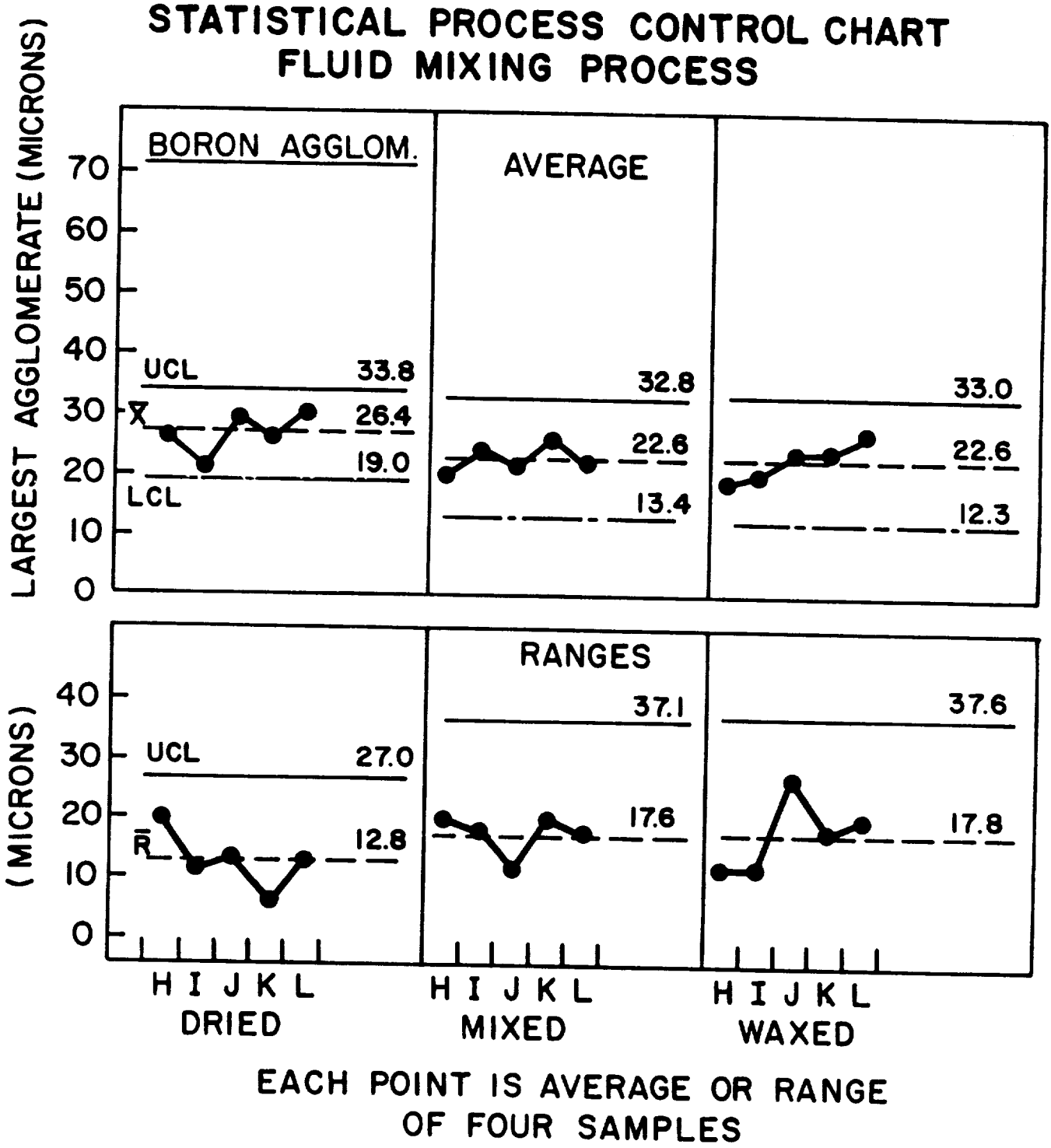

Figure 16: Statistical Process Control Chart
For Boron Agglomerates

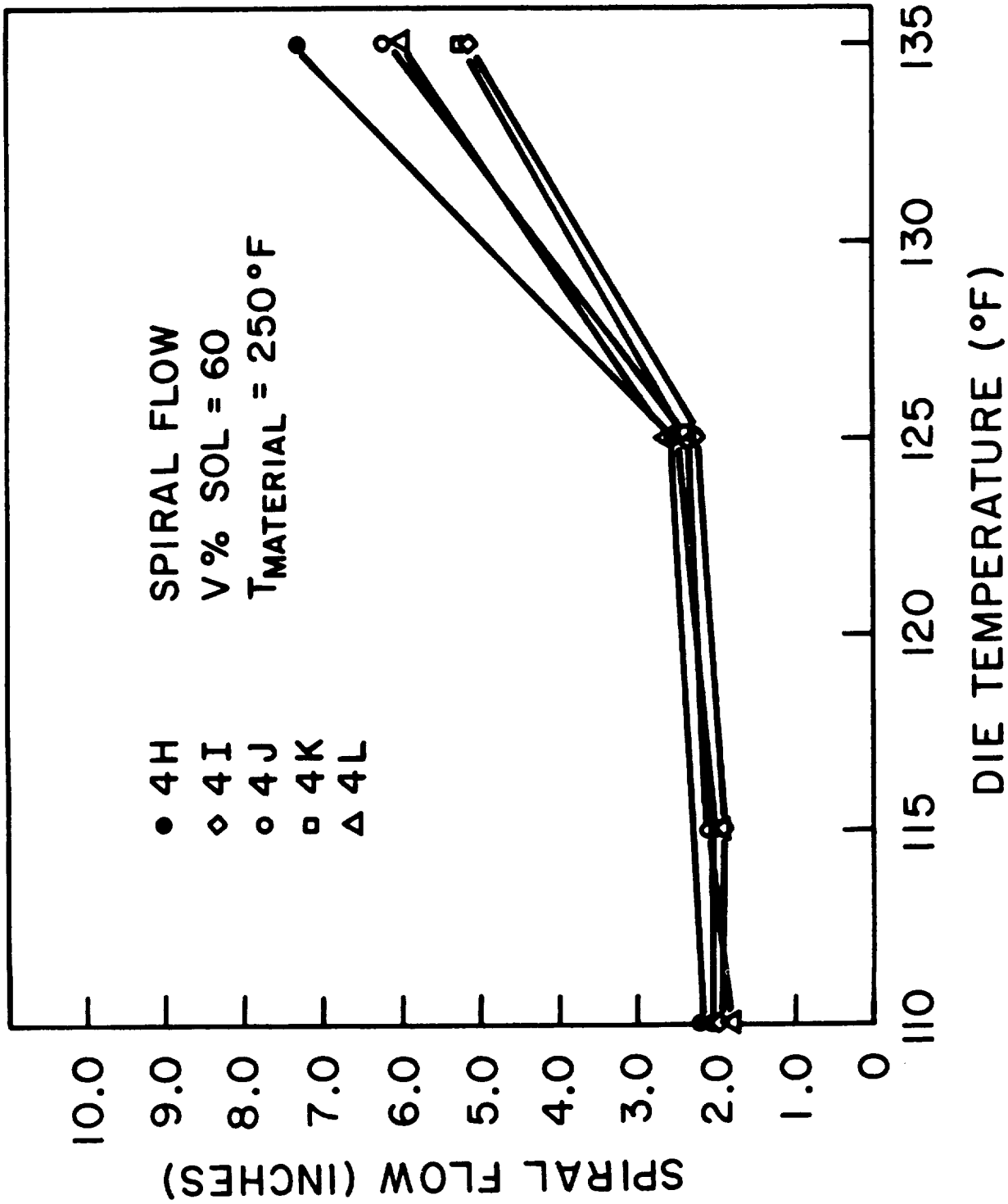

Figure 17: Spiral Flow Tests On Five Duplicate Batches

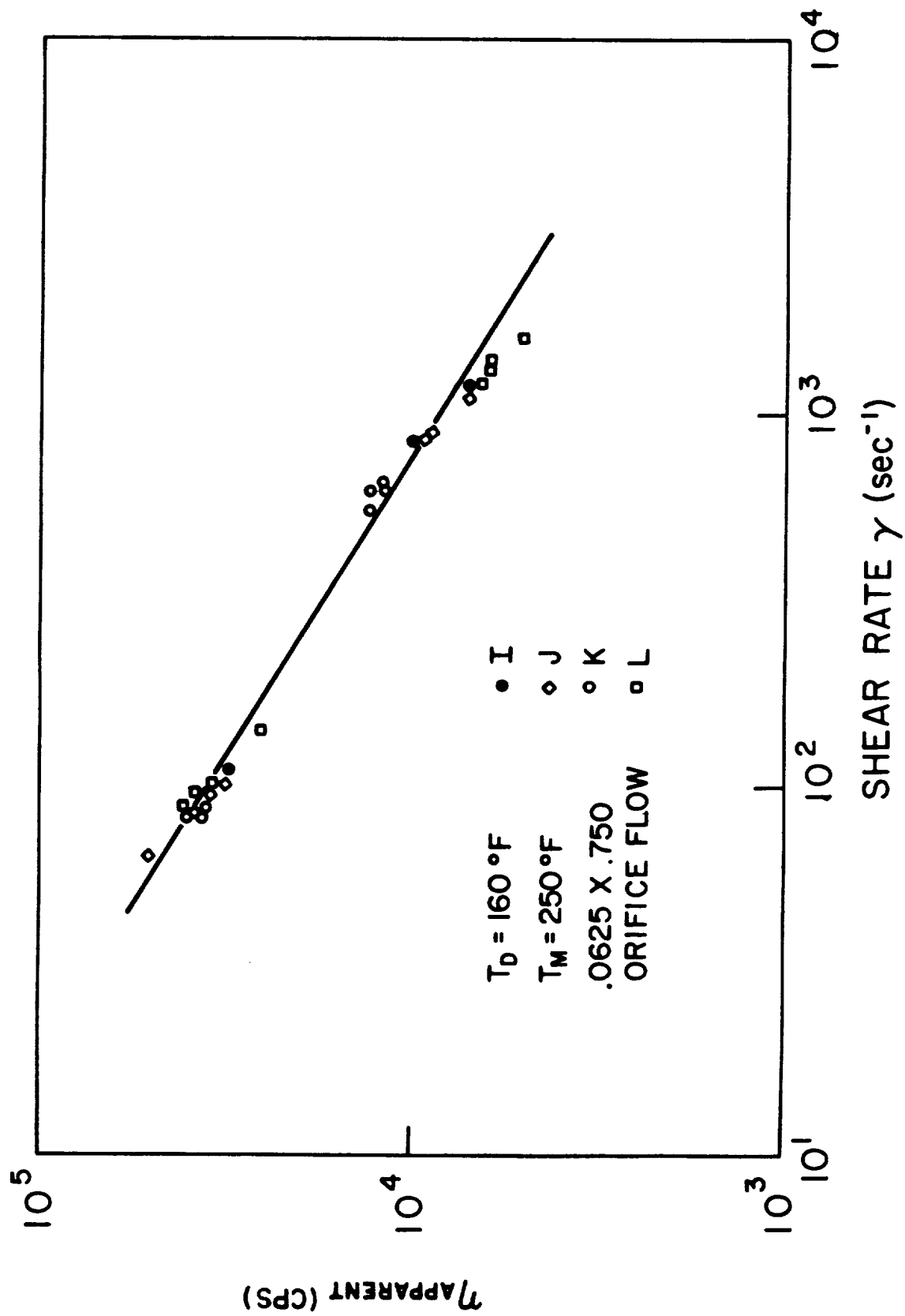

Figure 18: Orifice Flow Test Showing Uniformity of Duplicate Batches

...Opportunities exist to significantly reduce processing time for some process steps.

...Opportunities have been identified for further improving the mix quality through longer and more intense ball milling, and predispersion of the sintering aids.

VII.2.2 Fluid Mixing Process Improvement Study

Experimental Matrix This study was undertaken to further improve the molding mix inhomogeneities based on observations made during the reproducibility study. The experimental design was a half-fraction 2^4 factorial experiment comparing four variables at two levels each, Table XVI. The experiment evaluates the effects of carbon screening, boron screening, ball mill load and ball mill time on the size of agglomerates, distinguished as grey spots and red spots, in the mixed material. Grey spots are believed to be wax-rich inhomogeneities and the red spots are known to be boron agglomerates.

Procedure All mixes were formulated at the 60 V% loading level, that is, no "waxing" step at the end of the process. Carbon screening involved pretreatment of the carbon black by dispersing it in toluol using a sonic dismembrator. Boron screening consisted of washing the amorphous powder through a 325 mesh (45 micron) screen using toluol. The high and low milling times were 98/72 and 48/24 hours, with the first figure representing the milling time of the solids, and the second, the additional hours of milling after adding the wax binders. The stir-drying step was reduced to 4 hours by blowing air over the mixes while stirring.

Results A summary of the experimental matrix, presenting yields in terms of agglomerate size, is shown in Table XVII The plus and minus signs indicate the higher and lower levels, respectively, for each variable. The agglomerate data indicate that experiments 5 and 8 give the lowest values for both grey and red spots. The agglomerate size was determined by microscopically (100X) inspecting five samples from each batch, observing six discrete areas on each sample. Red spot density was determined and ranged from 0.05 to 0.7 spots per square millimeter. Grey spot density was not quantified, but appeared was much lower in experiments 5 through 8.

Statistical analysis An analysis of variance of the data is shown in Table XVIII in which the **Total** column is the sum of the experimental yields with the proper sign when the data are listed in standard order (Yates Algorithm). The **Effects** column is the Total value divided by four, and the **Sum of Squares** values are the square of the Total values divided by 8.

For grey spot size the most significant variables were the number of balls used in milling and the milling time. A large two-factor interaction was present as either AB or CD variable interaction. Since variables A and B

TABLE XVI

MATRIX 1: MIXING STUDY TO REDUCE AGGLOMERATE SIZE

Yield - Agglomerate Size Measurement

Design 2^{4-1}_{IV} - Main Effects and Some Two-Factor Interactions

Variables -
1. Carbon Screening (W & W/O)
2. Boron Screening (W & W/O)
3. Ball Mill Load (10 & 40 Ball)
4. Ball Mill Time (48 & 96 Hrs.)

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TABLE XVII

TASK VII

MIXING STUDY TO REDUCE AGGLOMERATE SIZE

	EXPERIMENT NO.							
	1	2	3	4	5	6	7	8
	BATCH NO.							
	J	T	V	U	W	R	S	M
VARIABLES								
C-Screen	-	+	-	+	-	+	-	+
B. Screen	-	-	+	+	-	-	+	+
No. of Balls	-	-	-	-	+	+	+	+
Mill Time	-	+	+	-	+	-	-	+
	GRAY SPOT - MAXIMUM SIZE (μm)							
Average 5 samples	36	29	26	38	18	21	21	21
Range 5 samples	22	6	3	10	0	7	10	7
	RED SPOT - MAXIMUM SIZE (μm)							
Average 5 samples	24	21	22	22	10	15	13	8
Range 5 samples	7	7	13	7	13	5	0	13

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TABLE XVIII

TASK VII

MIXING STUDY TO REDUCE AGGLOMERATE SIZE GRAY SPOTS

EFFECTS AND ANALYSIS OF VARIANCE

COMPARISON	TOTAL	EFFECT	DEG. OF F.	SUM OF SQUARES
A (C-Screen)	8	2.0	1	8.0
B (B-Screen)	2	0.5	1	0.5
C (No. of Balls)	-48	-12.0	1	288.0*
D (Mill Time)	-22	-5.4	1	60.5*
AB,CD	16	4.0	1	32.0
AC,BD	-2	0.5	1	0.5
AD,BC	4	1.0	1	2.0

VARIANCE = 14.4 *HIGHLY SIGNIFICANT

INTERACTION OF C (NO. OF BALLS) AND D (MILL TIME)

	C	
	-(10 Balls)	+(40 Balls)
- (48 Hrs.)	37	21
+ (96 Hrs.)	27.5	19.5

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are not significant as main effects, the CD interaction is assumed to be the controlling factor.

If the influence of variables C and D are considered separately, the average of the two measurements gives the relationship shown at the bottom of Table XIX. At the shorter milling times (48/24 hrs), an increase in the number of balls from 10 to 40 has a larger effect on agglomerate size than at long (96/72) milling times. Similarly, milling time has a greater effect at the lower ball-loading level. These trends indicate a levelling off of the effects at longer milling times and higher ball loads.

For red spots, Table XIX, the milling intensity variables (time and balls) were again the most significant. Two-factor interactions were not important.

Conclusions The results of this process improvement study support these conclusions relative to agglomerates in the fluid mixed molding mixture:

1. Boron and carbon screening had no significant effect.

2. Higher ball load (40) significantly decreases both grey and red spot maximum size.

3. Increasing milling time from 48/24 to 96/72 hours significantly decreases grey spot maximum size.

4. Interaction between the number of balls and milling time exists and suggests that the combination of 40 ball and the higher mixing times evaluated may be approaching a maximum effect for decreasing grey spot size.

5. Experiment number 8, batch M is the best choice for further evaluation in Task II.

The fluid mixing procedures and parameters used to prepare these improved batches were identified as Process B. A comparison of the two fluid mixing processes is presented in Table XX. One additional batch (Q) was prepared using this process, but formulated at the 55% loading level for use in Task II.

Matrix 6: Dewaxing Cycle Factors

A study to evaluate the factors of greatest importance in the dewaxing process was completed. The design of the experiment was a 2^{5-2} fractional factorial with 5 variables in 8 experimental runs as summarized in Table XXI. The five variables considered were the following:

- Gas type (nitrogen and argon)
- Gas pressure (150 and 15 psi)
- Temperature (399 and 260 ^{0} C)

TABLE XIX

TASK VII

MIXING STUDY TO REDUCE AGGLOMERATE SIZE RED SPOTS

EFFECTS AND ANALYSIS OF VARIANCE

COMPARISON	TOTAL	EFFECT	DEG. OF F.	SUM OF SQUARES
A (C-Screen)	-3	-0.75	1	1.1
B (B-Screen)	-5	-1.25	1	3.1
C (No. of Balls)	-43	-10.75	1	231.1*
D (Mill Time)	-13	-3.25	1	21.1
AB, CD	-7	-1.75	1	6.1
AC, BD	3	0.75	1	1.1
AD, BC	-3	-0.75	1	1.1

VARIANCE = 16

*HIGHLY SIGNIFICANT

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TABLE XX

FLUID MIXING PROCESSES

PROCESS STEP	HOURS	
	PROCESS A	PROCESS B
WET BALL MILL		
SOLIDS	48	96
SOLIDS + BINDERS	24	72
DRYING		
STIR DRY	14	4
PAN DRY	100	100
PREPARE FOR MOLDING		
MIX	4	4
ADD WAX	4	---

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TABLE XXI

TASK VII - MATRIX 6

Dewax Cycle Factors

Factor ID	Factor Name	Levels +	Levels -
A	Gas Type	N_2	Argon
B	Pressure (psi)	150	15
C	Temperature (°F)	750	500
D	Hold Time (hr.)	30	5
E	Heating Rate (°C/hr.)	5	2

2^{5-2} Fractional Factorial Design

Experiment ID	Factors A	B	C	D	E
de	-	-	-	+	+
a	+	-	-	-	-
be	-	+	-	-	+
abd	+	+	-	+	-
cd	-	-	+	+	-
ace	+	-	+	-	+
bc	-	+	+	-	-
abcde	+	+	+	+	+

Burnout Cycles

Run *	Gas Type	Pressure (psi)	Temp. (°F)	Hold (hr.)	Rate (°C/hr.)
1	Ar	15	500	30	5
2	N_2	15	500	5	2
3	Ar	150	500	5	5
4	N_2	150	500	30	2
5	Ar	15	750	30	2
6	N_2	15	750	5	5
7	Ar	150	750	5	2
8	N_2	150	750	30	5

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- Hold time at maximum temperature (30 and 5 hours)
- Heating rate (5 and 2 ^{0} C per hour)

Two groups of injection-molded MOR bars, NASA 4G baseline (2%C) and NASA 12A (3%C) were used in the experiment. The yield in each run was the average burn out percentage of either 6 or 10 duplicate bars.

The results of the study are highlighted in the analysis of variance table shown in Table XXII. The Yates algorithm gives the sum of squares for each of the main effects listed in the last column, and the significant effects are determined by the sum of squares divided by the variance. With an experiment of this 2^{5-2} design, there is considerable confounding of the variable effects. The Table lists only the main effects and only those that are marked with an asterisk are considered significant.

The conclusions drawn from this experiment are the following:

Temperature and pressure have a significant effect on the percentage of wax removed during burnout. High pressure and high temperature yield higher wax removals.

Gas type, hold time and heating rate do not significantly influence the amount of wax removed.

A significant temperature-pressure interaction is indicated by the results of this experiment.

These dewaxing process characteristics will be used in designing the processing for complex shaped parts.

Recently attempts have been made to improve the argon sintering process by improving the quality of the sintering atmosphere. Previous experience with the vacuum sintering process has shown the desirable effects of vacuum (see Annual Report, September, 1986, p. 30) on maintaining the low oxygen content of the atmosphere and the sintered material, leading to high density and strength in the sintered SiC. The benefit of argon sintering is related to the suppression of SiC dissociation which results in improved surface appearance and permits the use of higher sintering temperatures. Efforts to improve the argon sintering process have included the development of a vacuum-argon cycle and improvements in the vacuum capability of the argon furnace.

A preliminary vacuum-argon sintering experiment (run LA-10) was carried out with four MOR bars of 4M and 12A mixes. The sintering temperature was 2120^{0} C for 30 minutes. A vacuum ambient was used in the initial part of the sintering cycle, to 1500^{0} C, followed by argon. Acceptable densities of 95.6% and 94.4% and mean strengths of 447 MPa and 335 MPa (64.9 and 48.7 Ksi) were achieved for the 4M and 12A batches, respectively. The strength level of the 4M material is comparable to that for the best group of eight bars sintered in vacuum in Task II - Matrix 1A, 444 MPa (64.6

TABLE XXII

TASK VII - MATRIX 6

2^{5-2} DESIGN

DEWAX CYCLE FACTORS
ANALYSIS

NASA 4G (2% C)

RUN	YIELD	DEG. OF FREEDOM	SUM OF SQUARES	MAIN EFFECTS
1	96.4			AVE. = 98.48
2	95.2	1	0.005	A GAS TYPE
3	98.0	1	0.300*	B PRESSURE
4	99.4	1	0.009	D TIME
5	99.3	1	0.750	C TEMP
6	99.9	1	0.003	E RATE
7	100.3	1	0.228*	BC PRESSURE-TEMP
8	99.3	1	0.138*	ABC TYPE-PRESS-TEMP

σ^2 = VARIANCE = 0.02

NASA 12A (3% C)

1	94.4			AVE. = 97.05
2	93.4	1	0.025	A GAS TYPE
3	97.8	1	0.551*	B PRESSURE
4	97.9	1	0.003	D TIME
5	97.9	1	0.690*	C TEMP
6	98.3	1	0.000	E RATE
7	99.0	1	0.428*	BC PRESSURE-TEMP
8	97.7	1	0.061	ABC TYPE-PRESS-TEMP

σ^2 = VARIANCE = 0.18
*DENOTES SIGNIFICANT EFFECT

CONCLUSIONS

1. TEMPERATURE AND PRESSURE ARE SIGNIFICANT AND REAL EFFECTS ON % DEWAX.
2. GAS TYPE, HOLD TIME AND HEATING RATE DO NOT HAVE AN EFFECT ON THE % DEWAX.
3. TEMPERATURE - PRESSURE INTERACTION IS REAL EFFECT.

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Kpsi), Table VI. The low strength value for 12A was not surprising since the material contained large agglomerates. The Task VII-Matrix 7 experiment was designed to investigate four vacuum-argon sintering parameters and the sintered properties of injection molded SiC material from four different batches.

Matrix 7 Vacuum - Argon Sintering Cycle Factors

Design of the Experiment

The matrix was of the 2^{4-1} design in which 4 factors are examined in 8 experiments, Table XXIII. The confounding between the 3- and 2-factor interactions is illustrated in the table. The factors examined - backfill temperature, hold time before backfill, temperature ramp rate and batch composition - are also shown in the table. Since there were two sets of material factors, D_1 and D_2, the design can be considered as four separate matrices involving the materials combinations (12A - 13A), (4Q - 4M), (12A - 4M), and (4Q - 13A). Measured differences in density and strength were evaluated for each of these matrices.

As-Sintered vs. Machined Density

Immersion density measurements revealed small variations, both positive and negative, between the as-sintered and machined densities of the bars. Evaluation of the % change in theoretical density resulting from machining for each matrix, Figure 19, indicates that the variations are random and not related to any of the four factors being examined. The following analyses are based on the % theoretical density of machined bars.

% Theoretical Density

The effects derived from variations in % density for the matrices are given in Figure 20 on a normal probability scale. The estimated standard error in these densities is about 0.2%. As illustrated in Figure 20, the variables of material, backfill temperature, and hold time all have significant effects on density. Ramp rate had no measurable effect.

Material 13A had the highest density of the four batches evaluated as shown in the plots of the mean density of 8 samples in Figure 20. Material 13A was prepared by an early version of the fluid mixing process, Process A, at a low solids loading level of 52% with 3 weight percent carbon added as a soluble resin. Its superior densification may be the result of the more uniform distribution of carbon in the mix attained with a dissolved resin source rather than carbon black.

Raising the backfill temperature from 1470 to 1760^0 C also increased densification. Visual examination of the bars sintered in a cycle using the 1760^0 C backfill temperature disclosed a darker surface appearance which may indicate the onset of surface evaporation as seen in vacuum sintering. This would indicate that 1760^0 C is probably close to the upper temperature limit for backfill in the vacuum-argon sintering cycle.

TABLE XXIII

2^{4-1} Matrix Design (D=ABC)

Exp.#	A	B	C	D
1	-	-	-	-
2	+	-	-	+
3	-	+	-	+
4	+	+	-	-
5	-	-	+	+
6	+	-	+	-
7	-	+	+	-
8	+	+	+	+

Confounding Pattern for 2^{4-1}

A=BCD	AB=CD
B=ACD	AC=BD
C=ABD	AD=BC
D=ABD	

Matrix Factors

ID	Factors	-	+
A	Backfill Temperature	370mV (~1470°C)	495mV (~1750°C)
B	Hold Before Backfill	0 hrs. (no hold)	2 hr.
C	Ramp Rate	141 mV/hr.	70 mV/hr.
D	Material (D_1 / D_2)	12A / 4Q	13A / 4M

Data

Exp.#	Run#	Material	% Ther. Density As Sintered	% Ther. Density Machined	% Change in Density
1	14	12A	94.96	94.63	-.36
2	16	13A	98.01	98.09	+.08
3	17	13A	97.82	98.32	+.52
4	15	12A	96.52	96.38	-.14
5	13	13A	97.85	97.06	-.50
6	11	12A	95.86	95.36	-.53
7	18	12A	95.07	95.07	-.16
8	12	13A	98.98	97.90	-1.09
1	14	4Q	94.61	94.26	-.36
2	16	4M	96.37	95.82	-.57
3	17	4M	95.93	96.69	+.79
4	15	4Q	96.59	95.85	-.77
5	13	4M	95.99	95.58	-.74
6	11	4Q	95.70	95.21	-.50
7	18	4Q	94.92	95.06	+.12
8	12	4M	98.25	97.64	-.62

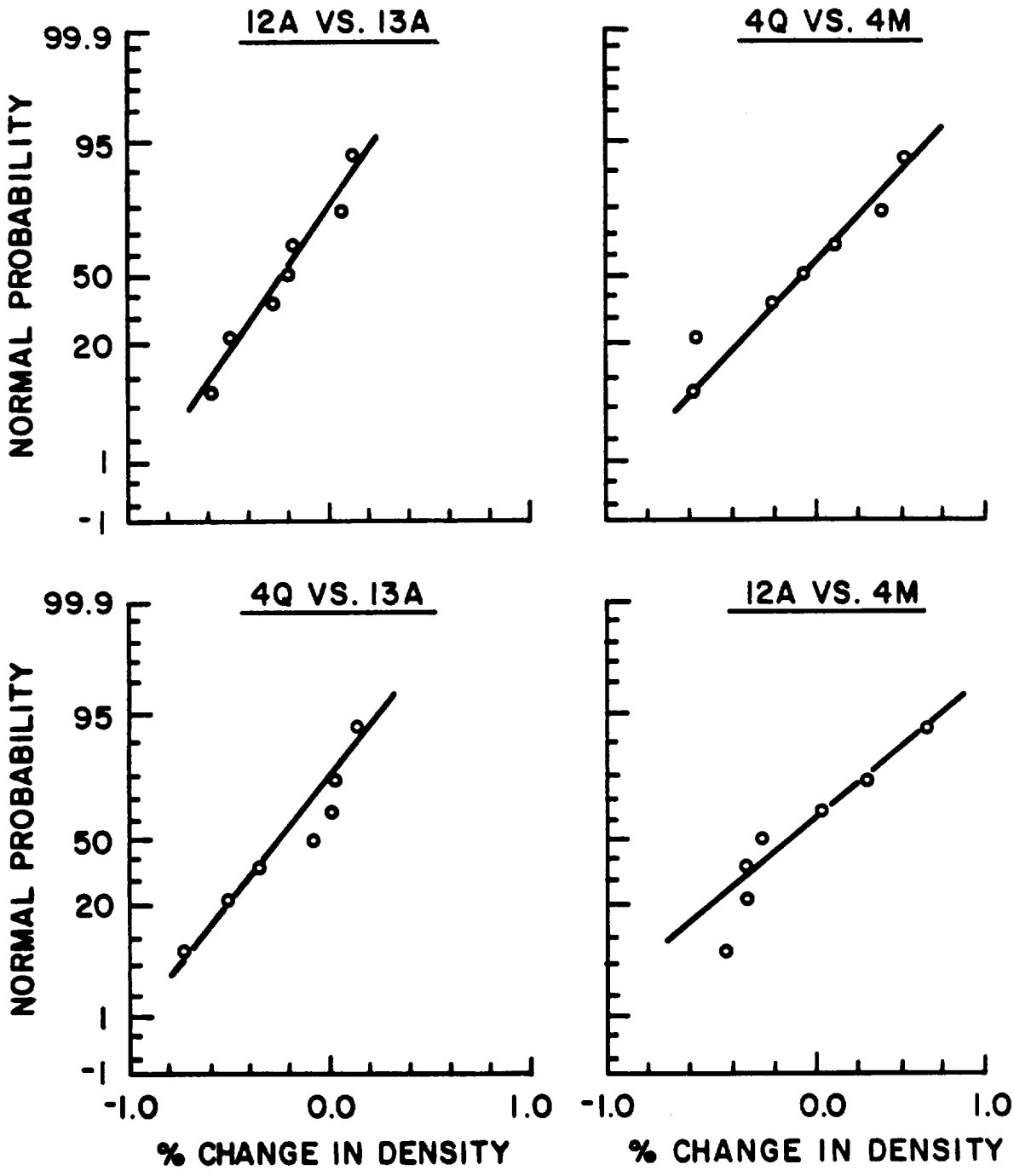

Figure 19: Normal Variations Shown In Density Changes

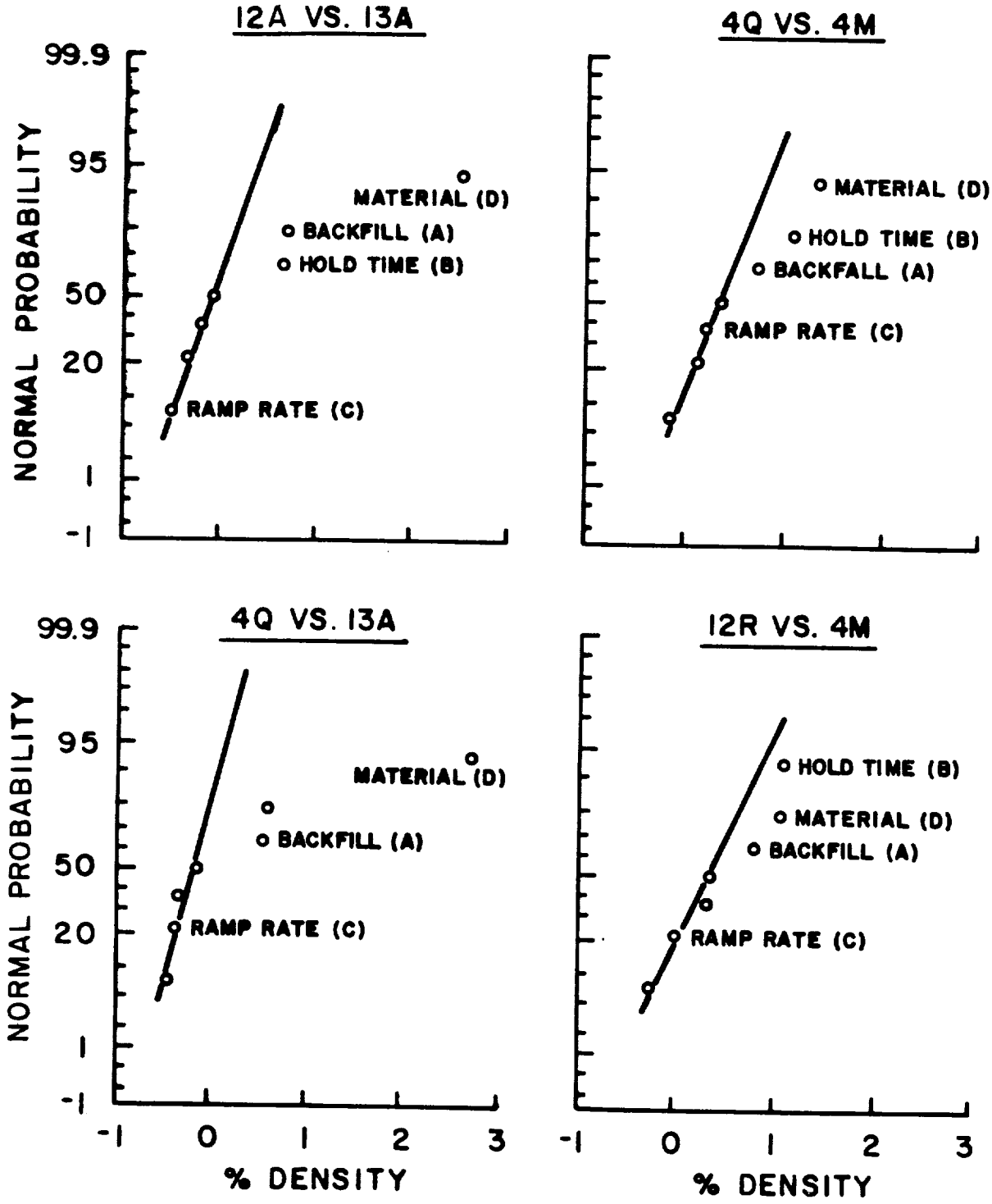

Figure 20: Significant Effects Shown
To Lie Off Of Normal Variation Line

The addition of a two-hour hold period before backfilling with argon improved the density. It is assumed that the hold time allows the vacuum pump additional time to remove outgassed products which are apparently detrimental to the densification process. Changing the ramp rate had no effect on densification for the ramp rates investigated in this experiment.

Strength of MOR Bars

The mean and Weibull characteristic strengths were evaluated for samples of 8 MOR bars from each of the 8 experiments and grouped according to the carbon content of the material, 2 or 3 %. Plots of the effects of each matrix are given in Figure 21. None of the variables are judged to be significant in altering the strengths in the matrices of (4Q - 4M) and (4Q - 13A); i.e., none of the effects are greater than two times the estimated standard error of the experiment. However, in the matrices (12A - 13A) and (12A - 4M), the material variable has a highly significant effect on the strength, and the hold time and the interaction between either backfill temperature/hold time or ramp rate/material may be significant.

Material 13A is the strongest of the materials tested in this matrix, followed by 4M, 4Q and 12A. When 13A is compared with 4M in the four experimental runs (#2, 3, 5, 8) in which both materials were sintered concurrently, material 13A has a mean strength of 417 MPa (60.5 Ksi) and 4M, a mean strength of 380 MPa (55.1 Ksi). Under these conditions 13A is shown to be significantly stronger at the 0.03 level of probability than 4M. As seen in Table I, however, 13A is not stronger than the best 4M group sintered in vacuum or in vacuum-argon in the Task II - Matrix 1 study.

In the past, the strength of these materials has been found to be controlled by the size of inclusions, pore volumes, porous agglomerates and surface imperfections acting as fracture origins. Studies were performed to identify fracture origins in the MOR bars and to attempt a correlation with processing flaws.

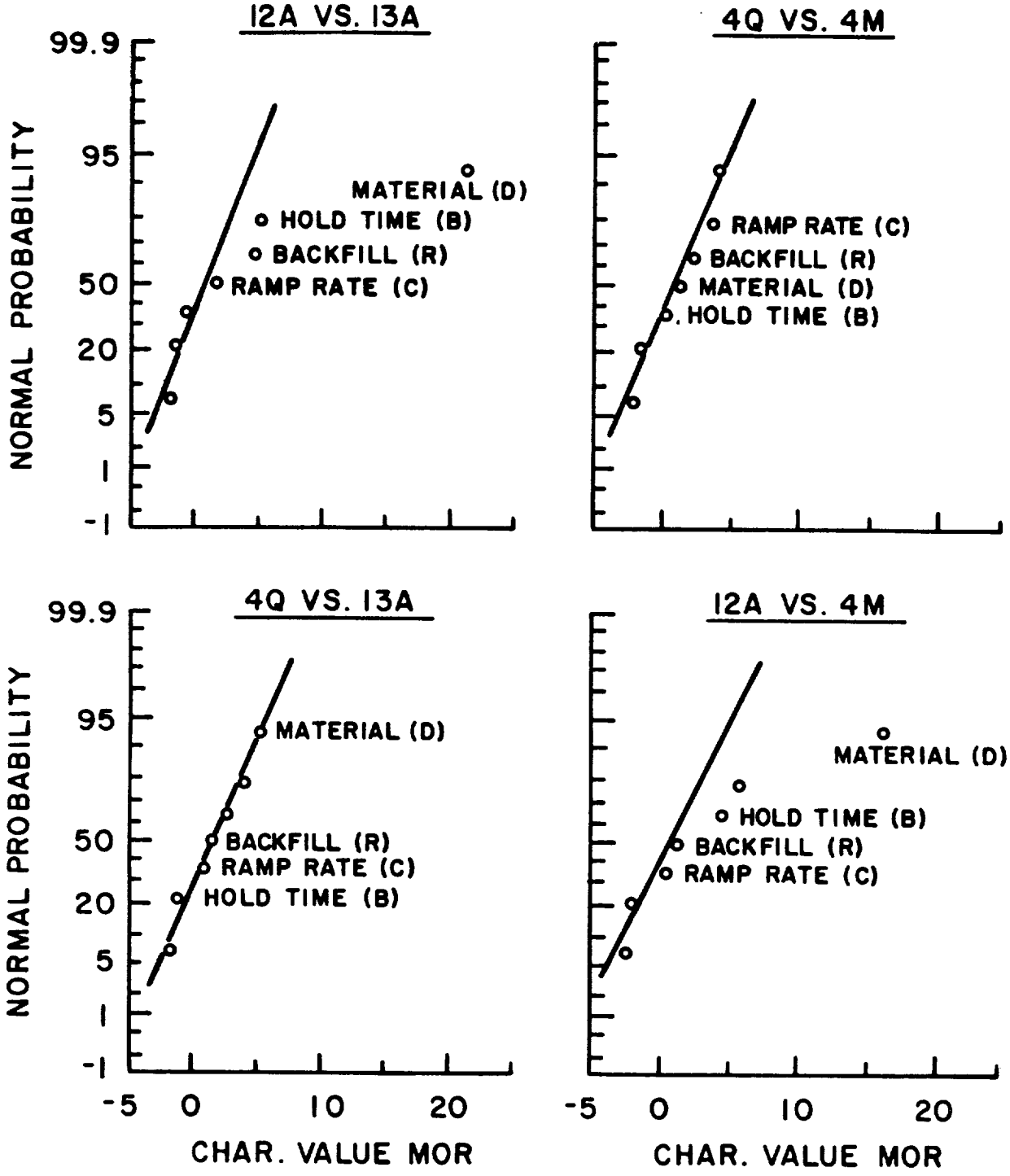

Figure 21: Significant Effects
Lie Off Of Normal Variation Line

TASK VIII TURBOCHARGER FABRICATION

VIII.1 Objective

This task has as an objective the evaluation of an improved, fluid-mixed, Process B molding material as a candidate for fabrication of a complex shape, such as a turbocharger rotor.

The effort under this task was performed at Ford expense in consideration of the Company's cost sharing requirement. This task is complete.

VIII.2 Matrix 1 Molding Study

The turbocharger rotor molding matrix evaluated the influence of injection pressure, die temperature, material temperature , flow rate and time-at-pressure on the density, volume and number of cracks in the molded components. This 2^{5-1} factorial designed experiment evaluated five factors in sixteen runs. In this design (Table XXIV) main effects are confounded with four-factor interactions, which provides adequate resolution for the main factors. The design and variables are also given in the table. The three yields studied were the density and volume of the rotor (measured by water immersion) and the number of cracks observed at 7X in an optical microscope. All rotors were inspected by X-ray for voids and no voids were observed by this technique. The yields in each run are the average of two rotors. A picture of a molded turbocharger rotor is shown in Figure 22.

The effects of the five variables on density are given in Table XXV. The material temperature, Variable C, is the only significant parameter to influence the molded density of the rotors, with the higher material temperature (250 ^{0}F) producing the higher molded density. One sees in the Table that the density range is narrow and the standard error of the experiment is only 0.0017 grams per cubic centimeter.

The effects of the five variables on the molded volume of the rotors are shown in Table XXVI. The variables of injection pressure (A) and material temperature (C) have a significant effect on the volume of the rotors and there is an indication of a strong two-factor (AC) interaction between the two variables. The largest volumes are observed when the injection pressure was at 70 psi and the material temperature was at 250 ^{0}F. Since the size of the tool is constant, the smaller volumes indicate incomplete filling of the tool.

The effects of the variables on the number of cracks observed are presented in Table XXVII. Die temperature (B) is the significant main effect with the fewer cracks produced by the condition of the higher die temperature (115^0 F). The influence of flow rate (D) appears marginal but may be important and further study is desirable. The lower flow rate,

TABLE XXIV

STATISTICAL MOLDING MATRIX FOR A COMPLEX SHAPE

MATRIX NO.	A	B	C	D	E	RUN SEQUENCE
1	-	-	-	-	+	3
2	+	-	-	-	-	2
3	-	-	-	-	-	7
4	+	+	-	-	+	4
5	-	-	+	-	-	11
6	+	-	+	-	+	10
7	-	+	+	-	+	15
8	+	+	+	-	-	12
9	-	-	-	+	-	8
10	+	-	-	+	+	1
11	-	+	-	+	+	5
12	+	+	-	+	-	6
13	-	-	+	+	+	16
14	+	-	+	+	-	9
15	-	+	+	+	-	13
16	+	+	+	+	+	14

VARIABLES	+	-	DESIGNATION
INJECTION PRESSURE (PSI)	70	35	A
DIE TEMPERATURE (F)	115	100	B
MATERIAL TEMPERATURE (F)	250	200	C
FLOW RATE	INSTANT	BUILD	D
TIME AT PRESSURE (MINS.)	6	3	E

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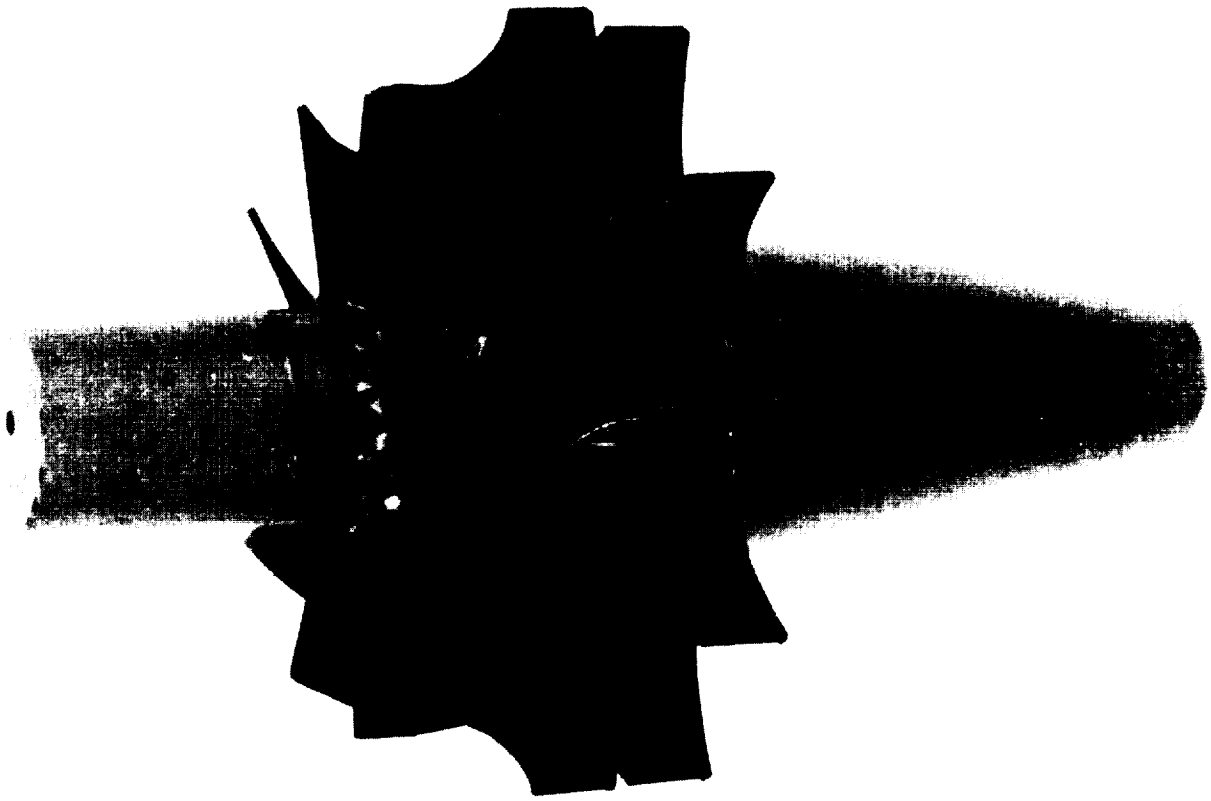

Figure 22

TABLE XXV

TASK VIII
MATRIX 1

TURBOCHARGER ROTOR MOLDING
EFFECTS AND YIELDS
DENSITY (g/cm^3)

DESIGNATION	EFFECTS	RUN NO.	YIELD (DENSITY)+
(AVE.)	(2.2137)1	1	2.211
A	0.0004 ± 0.0017*	2	2.212
B	0.0001	3	2.211
AB	-0.0024	4	2.206
C	0.0071	5	2.211
AC	0.0011	6	2.211
BC	0.0004	7	2.223
ABC,DE	0.0009	8	2.220
D	-0.0039	9	2.207
AD	0.0021	10	2.211
BD	0.0014	11	2.213
ABD,CE	-0.0001	12	2.210
CD	-0.0041	13	2.210
ACD,BE	0.0009	14	2.216
BCD,AE	-0.0014	15	2.212
E	0.0001	16	2.215

*Estimated Standard Error
+Average of Two Rotors

VARIABLE	-	+
A Injection Pressure (psi)	35	70
B Die Temp (°F)	100	115
C Material Temp (°F)	200	250
D Flow Rate	Build	Instant
E Time at Pressure (Min.)	3	6

CONCLUSIONS:

Material temperature is the only significant parameter to influence molded density, and higher material temperature yields higher molded density.

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TABLE XXVI

TASK VIII
MATRIX 1

TURBOCHARGER ROTOR MOLDING
EFFECTS AND YIELDS
VOLUME (cm^3)

DESIGNATION	EFFECTS	RUN NO.	YIELD (VOLUME)+
(AVE.)	(38.761)	1	35.64
A	1.716 ± 0.164*	2	39.47
B	0.204	3	37.07
AB	-0.166	4	39.70
C	1.604	5	39.16
AC	-1.471	6	39.68
BC	-0.209	7	39.40
ABC,DE	0.111	8	35.55
D	0.104	9	36.40
AD	-0.066	10	39.50
BD	-0.239	11	36.35
ABD,CE	0.226	12	39.54
CD	0.126	13	39.67
ACD,BE	-0.024	14	39.75
BCD,AE	0.178	15	39.53
E	-0.096	16	39.76

*Estimated Standard Error
+Average of Two Rotors

VARIABLE	-	+
A Injection Pressure (psi)	35	70
B Die Temp (°F)	100	115
C Material Temp (°F)	200	250
D Flow Rate	Build	Instant
E Time at Pressure (Min.)	3	6

CONCLUSIONS:

Injection pressure and material temperature strongly influence the volume (filling) of molded rotors. A strong interaction (AC) between these two variables is noted. High injection pressure and higher material temperature yield higher molded volumes (better die filling).

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TABLE XXVII

TASK VIII
MATRIX 1

TURBOCHARGER ROTOR MOLDING
EFFECTS AND YIELDS
CRACKS

DESIGNATION	EFFECTS	RUN NO.	YIELD (CRACKS)+
(AVE.)	(5.44)	1	0
A	-0.38 ± 0.40*	2	11.0
B	-3.88	3	9.0
AB	-4.88	4	1.5
C	0	5	11.5
AC	-2.25	6	10.5
BC	-3.50	7	5.0
ABC,DE	4.50	8	0.5
D	-1.38	9	0
AD	0.13	10	11.5
BD	0.38	11	9.0
ABD,CE	0.63	12	1.5
CD	-1.50	13	9.0
ACD,BE	0	14	5.5
BCD,AE	0.50	15	1.5
E	0.75	16	0

*Estimated Standard Error
+Average of Two Rotors

VARIABLE	-	+
A Injection Pressure (psi)	35	70
B Die Temp (°F)	100	115
C Material Temp (°F)	200	250
D Flow Rate	Build	Instant
E Time at Pressure (Min.)	3	6

CONCLUSIONS:

Die temperature (variable B) has a significant effect on number of cracks--the fewer number of cracks are observed with the higher die temperature of 115°F. Several strong two-factor interactions (AB, BC, AC and DE) are observed. Three conditions (runs 1, 9 and 16) yield crack-free rotors.

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designated as "build", resulted in more cracks than the faster flow rate, designated as "instant". Several strong two-factor interactions, AB, BC, AC, and DE, were observed. Three conditions (runs 1,9, and 16) produced crack-free rotors.

Dewaxing temperature cycles are now under investigation for these rotors. A much slower heating rate shown in Figure 23 will be required to provide crack-free dewaxed complex shapes, compared to simple MOR bars.

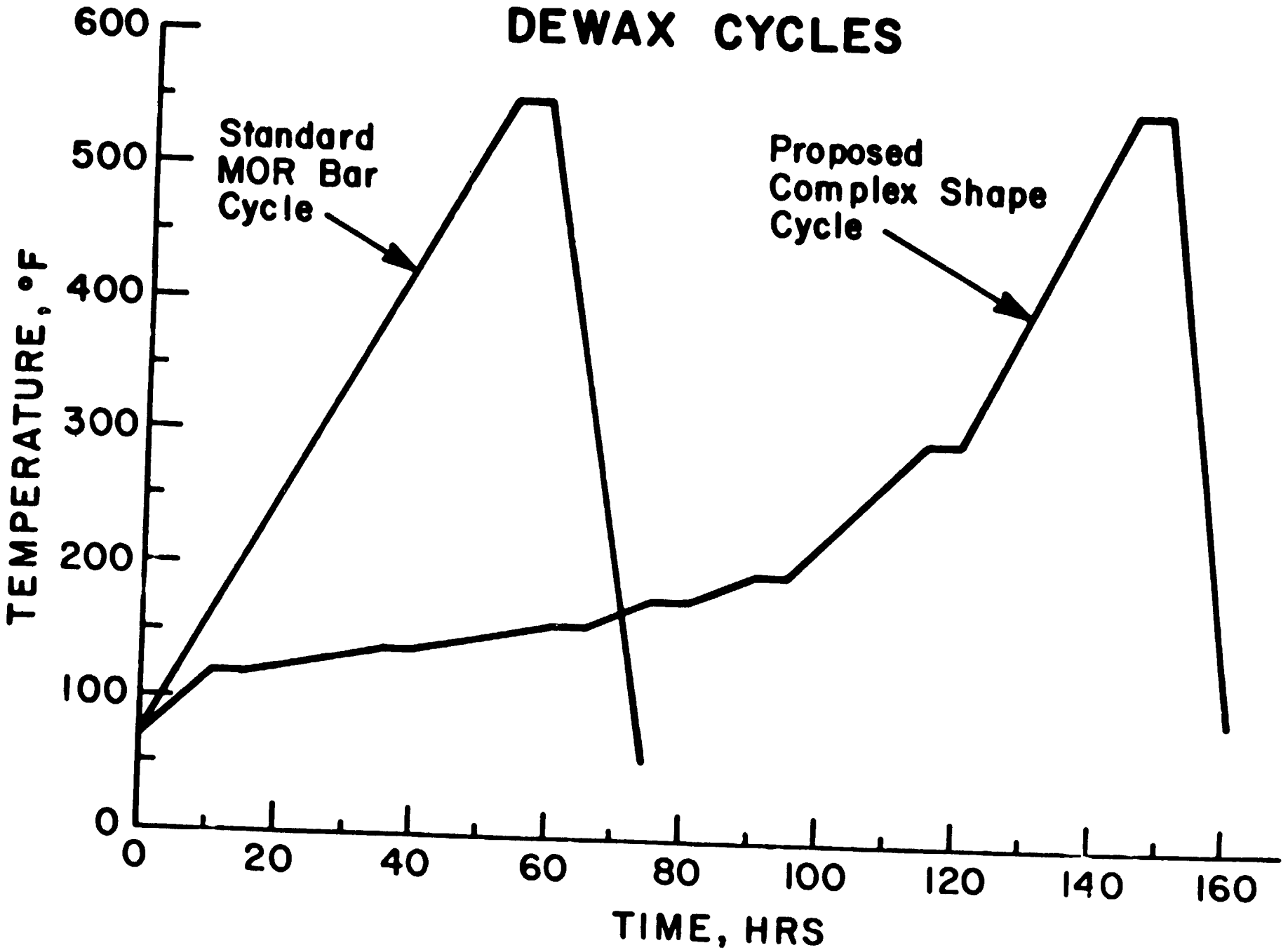

Figure 23: Dewax Cycles For MOR Bar and Complex Shapes

CONCLUSIONS

Strength improvements of 40% in Weibull characteristic strength and 31% in Weibull modulus over the baseline values for MOR bars have resulted from statistically designed experiments aimed at reducing flaw size and increasing density in injection molded and sintered SiC.

Significant effects were observed in factorial experiments which showed that the new fluid mixing process with improvements (Process B) was superior to earlier mixing processes, that the mixing parameters of intensity and time were important, and that the backfill temperature and hold time factors during sintering were significant.

Statistical process control was found useful in the mixing, molding and dewaxing processes.

Turbocharger rotors were molded according to a statistically-designed matrix which evaluated five factors at two levels each. The molded volumes were significantly influenced by injection pressure and material temperature, and the number of observed cracks was affected by die temperature and several two-factor interactions. Three molding conditions were found to yield crack-free rotors.

Significant progress has been realized by the use of statistically-designed experiments to improve processing and properties of SiC.

FUTURE PLANS

1. General Considerations

The emphasis of the program on material and process improvement, Task VII, has been changed toward strengthened SiC with whiskers and fibers and away from monolithic SiC. The best-effort goals for the program remain at a Weibull characteristic strength of 551 MPa (80 Ksi) and a Weibull modulus of 16. A Timing Chart for the remaining part of Phase I is shown in Figure 24.

2. Task II MOR Matrix

Matrix 2

Work on Matrix 2 will begin following completion of Matrices 7 through 10 in Task VII. As shown in the attached Timing Chart, work will commence about June 1, and be completed in early January. Matrix 2 is aimed at improving strength by decreasing flaw size and increasing density.

3. Task VII Material and Processing

Matrices 7 through 10

Matrices 7 through 10 (Figure 24) will be completed by July, 1987, the data analyzed, and the results will be used to plan Task II Matrix 2.

Matrix 11 - SiC-Whisker-Strengthened SiC

The initial experiment involves strengthening SiC with a second phase. Timing for this experiment is shown on the Timing Chart (Figure 24). If significant progress is shown, we will proceed to plan and carry out Matrix 12 to further improve the mechanical properties and reliability of a strengthened SiC.

Matrix 12 - Improved Strengthened SiC

A 2^{5-1} statistically-designed experiment with five variables at two levels each will be planned and executed (Timing Chart, Figure 24) to improve the mechanical properties and fracture toughness of strengthened SiC. The five variables will probably be the following:

1. Volume % Second Phase
2. Process Parameter A
3. Carbon Content
4. Mixing Time
5. Mixing Process

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15. Supplementary Notes

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16. Abstract

This is the second annual technical report for the program entitled "Improved Silicon Carbide for Advanced Heat Engines" and includes work performed during the period February 16, 1986 to February 15, 1987. The program is conducted for the National Aeronautics and Space Administration (NASA) under contract number NAS3-24384. The objective of the program is the development of high strength, high reliability silicon carbide parts with complex shapes suitable for use in advanced heat engines. The fabrication methods used are to be adaptable for mass production of such parts on an economically sound basis. Injection molding is the forming method selected for the program. This objective is to be accomplished in a two phase program: Phase I—achieve a 20 percent improvement in strength and a 100 percent increase in Weibull modulus of the baseline material; Phase II—produce a complex shaped part, a gas turbine rotor, for example, with the improved mechanical properties attained in Phase I. Eight tasks are included in Phase I covering the characterization of the properties of a baseline material, the improvement of those properties and the fabrication of complex shaped parts. Activities during the first contract year concentrated on two of these areas: fabrication and characterization of the baseline material (Task I) and improvement of material and processes (Task VII). Activities during the second contract year included an MOR bar matrix study to improve mechanical properties (Task II), materials and process improvements (Task VII), and a Ford-funded task to mold a turbocharger rotor with an improved material (Task VIII).

17. Key Words (Suggested by Author(s))

Silicon carbide
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