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Improved Silicon Carbide for Advanced Heat Engines: Third Annual Report

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FOREWORD

Experimental planning, the processes of mixing, forming, sintering of SiC powder batches, the testing of SiC MOR bars, 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 is Dr. Thomas J. Whalen. The project manager is Dr. N. Shaw of the NASA Lewis Research Center, Cleveland, Ohio. Significant contributions in the third year of the program were made by W. Trela, Dr, R. K. Govila, J. R. Baer, L. V. Reatherford and E. L. Cartwright.

NASA - FORD THIRD ANNUAL REPORT
FOR THE PERIOD FEBRUARY 16, 1987 TO FEBRUARY 15, 1988

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EXECUTIVE SUMMARY

This is the third annual technical report for the program entitled "Improved Silicon Carbide for Advanced Heat Engines" and includes the work performed during the period February 16, 1987 to February 15, 1988. The program is conducted for the National Aeronautics and Space Administration (NASA) under contract number NAS3-24384.

The objective of the original program was the development of high strength, high reliability silicon carbide parts with complex shapes suitable for use in advanced heat engines. Injection molding is the forming method selected for the program because it is capable of forming complex parts and is adaptable for mass production on an economically sound basis. The goals of the present program are to reach a Weibull characteristic strength of 550 MPa (80 Ksi) and a Weibull modulus of 16 for bars tested in 4-point loading.

Eight tasks were included in the original program, and two of them, Tasks I (Baseline MOR Data) and VIII (Turbocharger Fabrication) were completed and reported in the first and second annual reports. At NASA direction, the two tasks involving the fabrication of large complex shapes will not be done. Two tasks are discussed in this report; Task VII which is entitled Materials and Processing Improvements and Task II which is the MOR Matrix. Work is underway on the second matrix iteration in Task II and will be reported in greater detail in the final report.

Many statistically-designed experiments were performed under Task VII to improve the processing of injection molded SiC. Sintered density and machined bar MOR strength were the yields of these experiments.

Matrix 8 contained seven variables at two levels each in a 2^{7-4} experiment comparing two fluid mixing processes, two types of carbon as additives and five processing parameters. Mean densities between 92 and 97% of theoretical density and mean strengths between 365 and 455 MPa (53.2 and 66.0 Ksi) were observed. Results were that fluid mixing for 168 hours was superior to fluid mixing for 62 hours, either carbon source was equally acceptable, a 5 ^{o}C /min sintering temperature ramp rate was better than a 9 ^{o}C/min rate, 30 minute sinter time was better than 12 minutes, and that a 1760 ^{o}C backfill temperature was better than 1620 ^{o}C.

Matrix 9 compared two sources of SiC powder, Ibiden and Superior Graphite, at two levels of boron, 0.5% and 1.0%. Mean densities from 94.1 to 98.4% of theoretical density and mean strengths from 344 to 503 MPa (49.9 to 72.9 Ksi) were measured. Ibiden powder and 1% boron were better for density, but no significant strength effects were observed.

Matrix 10 dealt with the influence of annealing or heat treating on the strength of MOR bars. Initially a 2^2 experiment was performed in which annealing was done at two temperatures, 1200 and 1400 ^{o}C in two environments, air and argon. Strengths from 382 to 458 MPa (55.4 to 66.4 Ksi) were observed and it was concluded that annealing at 1200 ^{o}C in air for a period of 18 hours gave the best results within the scope of the

experiment. Further studies with and without annealing clearly shows the beneficial effects of annealing and is discussed below under Matrix 11.

Matrix 11 involved the evaluation of attritor processed material and the reproducibility of attritor process and the sintering cycle. The design of the experiment was 2^3 and the variables were two similar attritor processing cycles, two sintering runs and two (with and without) heat treatments, determined by Matrix 10 above. The two attritor cycles and the two sintering runs showed no significant differences, indicating good process reproducibility within the scope of the experiment. The heat treatment, however, showed a highly significant improvement in mean strength to a value of 570 MPa (82.8 Ksi). A Weibull characteristic value of 580 MPa (84.2 Ksi) was measured for a group of 9 samples, which is above the strength goal of the program. The Weibull modulus of 6.7 was below the value of 16, which is the reproducibility goal of the program. High temperature fast-fracture testing of these materials have been completed at 1200 and 1400 ^oC and there appears to be no reduction in strength up to these temperatures. The most optimistic results were obtained with a group of 9 annealed samples tested at 1400 ^oC that gave a Weibull characteristic strength of 564 MPa (81.8 Ksi) and a Weibull modulus of 16.8.

A summary of the mean MOR strengths determined for the baseline material and the process improvements during this program are shown in Figure 1.

Molding yields defined as the percentage of void-free or inclusion-free bars were determined and shown to improve significantly over the course of the program.

The distributions of the numbers of flaws observed visually and by x-radiography on selected samples of molded and sintered MOR bars were shown to be approximated by a Poisson distribution.

The second iteration of Task II, Matrix 2, has been planned as a 2^{5-1} experimental design with two face points. The five variables at two levels each are carbon-boron ratio, carbon-plus-boron concentration, carbon source, with and without annealing, and with and without hot isostatic pressing. Batches were prepared and MOR bars were molded.

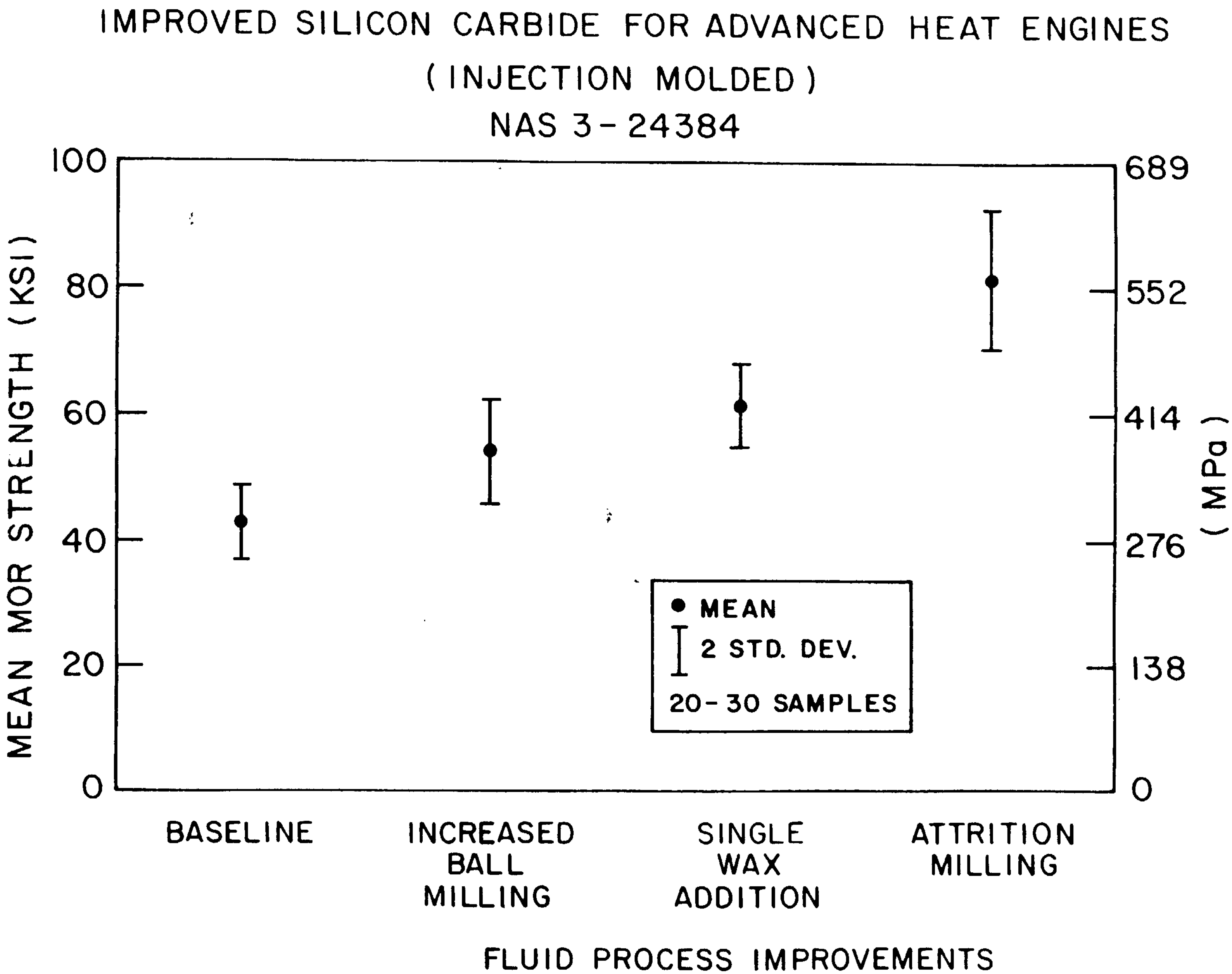

FIGURE 1. Summary of the Strength Increase From Process Improvements in the Program.

INTRODUCTION

This is the third annual technical report on the program entitled "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. This report covers the period from February 16, 1987 to February 15, 1988.

The objective of this program is to develop high strength, high reliability silicon carbide material, with the potential to form complex shapes suitable for advanced heat engines. The fabrication method is to be adaptable to mass production of complex parts on an economically sound basis.

The revised program schedule is shown in Figure 2. Tasks I and VIII were completed and reported in earlier annual reports (ref. 1,2). The program contains the fabrication, evaluation and improvement of test bars and is divided into five tasks:

Task I - Fabricate and characterize the baseline silicon carbide material. The results of this task were reported in the first annual report (ref. 1).

Task II - Improve silicon carbide MOR test bars with process and material improvements by iterative, statistically-designed experiments and show an increase in strength to above the 550 MPa (80 Ksi) level and an increase in the Weibull modulus to 16 or above level. This is an improvement of 75 % in strength and 100 % in Weibull modulus over the baseline values.

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 which were planned for large complex shapes, and which were later cancelled. Ford supported Task VIII as a cost-sharing effort. Results of this work were reported in the second annual report (ref. 2).

During the first year of the program more than twenty material and process variables were studied in statistically-designed experiments to determine their relative importance on the properties of the sintered material. Variables related to powder processing in the mixing through sintering steps were placed under statistical process control.

During the second year of the program the major efforts were given to Task II (MOR Matrix), Task VII (Material and Process Improvement) and Task VIII (Turbocharger Molding). Strength improvements of 40% in Weibull

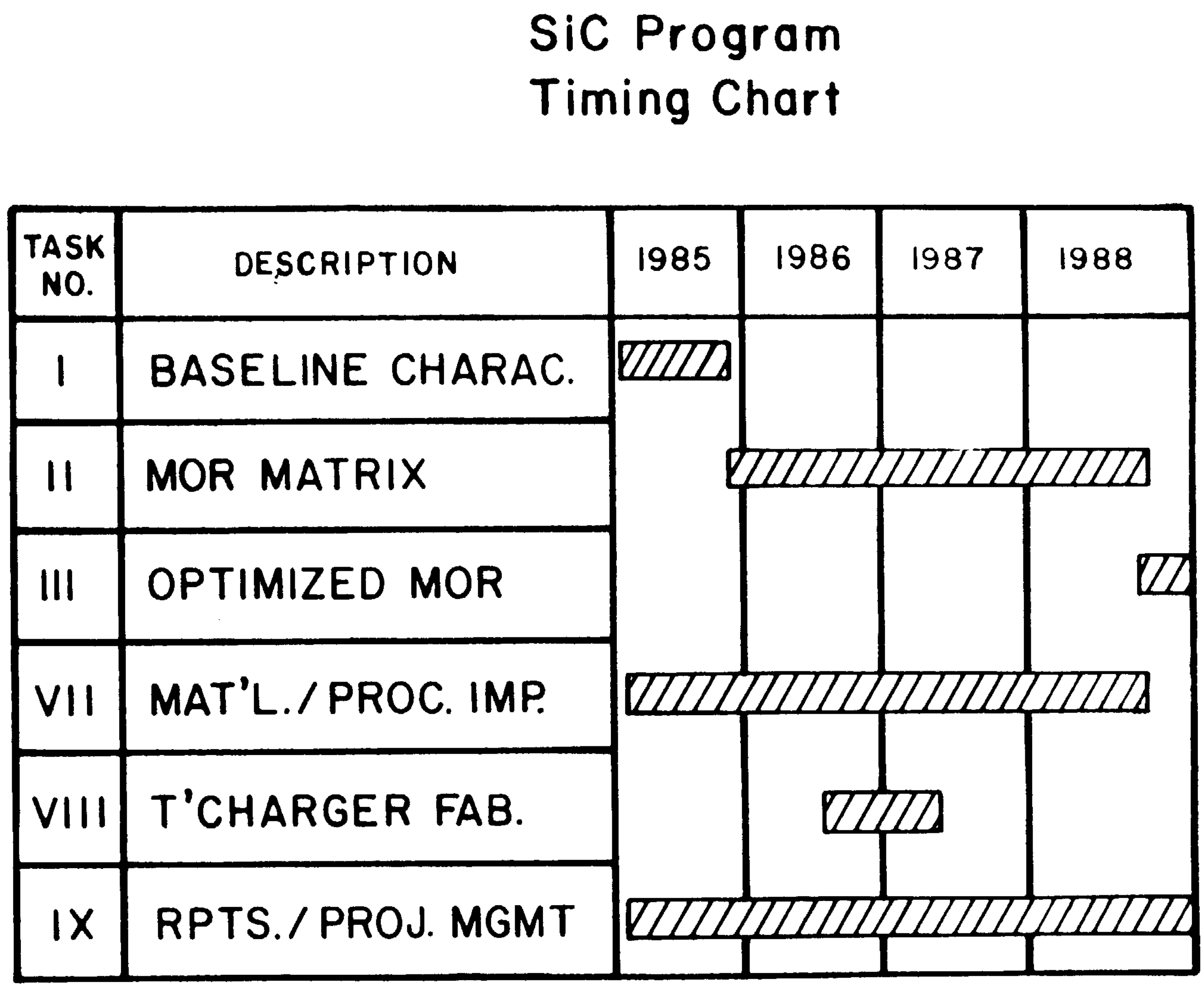

FIGURE 2. Revised Program Schedule.

characteristic strength and 31% in Weibull modulus over the baseline values for MOR bars were achieved by employing statistically-designed experiments aimed at reducing flaw size and increasing density in injection molded and sintered SiC. Turbocharger rotors were molded according to designed experiments which evaluated five processing variables at two levels each and three molding conditions were found to yield crack-free rotors.

During the third year of the program, which is discussed in this report, the major effort was centered on Task VII (Material and Process Improvement) and on planning and beginning the Task II (MOR Matrix) work on the second iteration of the matrix for improved MOR bars.

TECHNICAL PROGRESS

1. TASK VII - MATERIALS AND PROCESS IMPROVEMENTS

1.1 Matrix 8 Plan - Fluid Mix Process, Carbon Source and Sintering Parameters

Matrix 8 contained seven variables at two levels each comparing two fluid mixing processes, two types of carbon as additives and five processing parameters. Densities as high as 97% of theoretical density and strengths as high as 455 MPa (66 Ksi) were observed. Results were that fluid mixing for 168 hours was superior to 62 hours, either source of carbon was equally acceptable, a 5 ^{o}C /min sintering temperature ramp rate was better than 9 ^{o}C/min rate, 30 minute sintering time was better than 12 minutes, and that 1760^{o}C backfill temperature was better than 1620 ^{o}C.

Results of our earlier experimental study (Ref. 2) showed that the sintering cycle parameters of backfill temperature and ramp rate could improve the density of injection molded SiC. Since that time improvements in the fluid mixing process, the sintering equipment, and the sintering cycle were made and a new source of carbon (suspended in toluene from Degussa) was identified. Distribution of carbon has been recognized in the past as a potential problem leading to an undesirable formation of agglomerates during the mixing process. It was anticipated that the new carbon source would reduce the agglomeration problem by permitting a more uniform carbon distribution.

An experimental design was chosen to compare two levels of seven variables which were indicated from past work to influence the density and strength of sintered SiC. A 2^{7-4} matrix design was chosen, as outlined in Table I, and the defining relationship and confounding pattern, shown in Table II, was adequate. This design permits an evaluation of the seven main effects of the variables (one process variable, one material variable and five sinter-cycle variables) in eight experiments. The seven variables evaluated at two levels each (Table III) are the fluid mixing process, carbon source, argon ramp rate, sintering temperature and time, backfill temperature and vacuum holding time.

1.1.1 Sample Preparation

The 4M material was used as the control batch. The experimental matrix was designed to investigate process or compositional variations which have shown to have an effect on the molding behavior. In addition, these batches were processed with procedural changes during the final mixing step. This change has resulted in a significant reduction in the number of inclusions in the molded MOR bars.

Table I
2^{7-4} Matrix Design
(D=AB/E=AC/F=BC/G=ABC)

Exp.#	A	B	C	D	E	F	G	Material
1	-	-	-	+	+	+	-	4Z2
2	+	-	-	-	-	+	+	4AA
3	-	+	-	-	+	-	+	4Z
4	+	+	-	+	-	-	-	4M
5	-	-	+	+	-	-	+	4Z2
6	+	-	+	-	+	-	-	4AA
7	-	+	+	-	-	+	-	4Z
8	+	+	+	+	+	+	+	4M

Table II
Defining Relationship & 2-Factor Confounding Pattern

I=ABD=ACE=BCF=ABCG=BCDE=ACDF=CDG=ABEF=
BEG=AFG=DEF=ADEG=BDFG=CEFG=ABCDEFG

A=BD=CE=FG
B=AD=CF=EG
C=AE=BF=DG
D=AB=EF=CG
E=AC=DF=BG
F=BC=DE=AG
G=CD=BE=AF

Table III
Matrix Factors

ID	Factor	-	+
A	Fluid Mix Process	"C"	"B"
A	Carbon Source	DeGussa Carbon	Carbon Black
C	Argon Ramp Rate	9°C/Min.	5°C/Min.
D	Argon Temperature	2080°C	2120°C
E	Argon Hold Time	12 Min.	30 Min.
F	Backfill Temp.	1620°C	1760°C
G	Vacuum Hold Time	4 hr.	2 hr.

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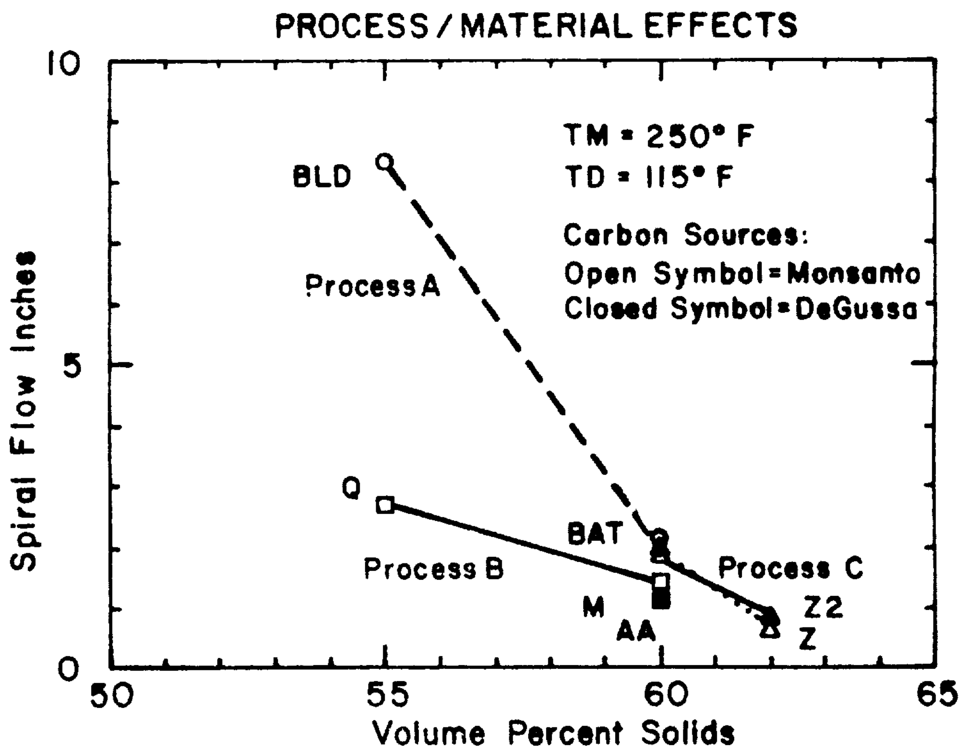


FIGURE 3. SPIRAL FLOW CHARACTERISTICS FOR SEVERAL MATERIALS AND PROCESSES

The mixes involved are:

Batch	Process	Carbon Source	Composition (%) SiC	C	B
4Z (60)	C	Monsanto	97.0	2.0	1.0
4Z2 (60)	C	DeGussa	97.0	2.0	1.0
4AA (60)	B	DeGussa	97.0	2.0	1.0
4M (60)	B	Monsanto	97.0	2.0	1.0

The spiral flow test results for these materials are shown in Figure 3, along with the results obtained earlier with the Task II materials. Process C data (batches 4Z and 4Z2) are shown for loading levels of 62 and 60%. Process B data (batches 4M and 4AA) are given only at the 60% loading level because that process involves preparing the mix directly to the desired loading, and the effect of loading is not being investigated in this matrix.

The Process C mixes have essentially the same spiral flow characteristics as seen earlier using Process A, and the spiral flow is unaffected by the carbon source. However, when the DeGussa carbon-black is used in conjunction with Process B, the spiral flow was slightly reduced (1.17 inches for mix 4AA vs 1.43 inches for mix 4M).

Viscosity data, generated using the orifice flow test, are presented in Figure 4. The figure shows viscosity data for all four mixes at the 60% loading level, plus the process C mixes (4Z and 4Z2) at the 62% level. The relative viscosities are in general agreement with the spiral flow results. One obvious discrepancy shows up in mixes 4M(60) and 4Z(62); both mixes having very nearly the same viscosities, but different spiral flow. The reason for the difference is related to material cooling rate during the spiral flow injection which is dependent on the amount of wax. In general, those mixes containing the DeGussa carbon-black show very little shear thinning (change in viscosity with shear rate) compared to all previous mixes.

1.1.2 Analysis of Data and Discussion of Results

Densities and strength evaluations were made on MOR bar samples prepared in the Matrix 8 experiment. X - radiography and visual and microscopic observations were used for non-destructive evaluation. Groups of 10 replicates were treated according to the matrix listed in Table I and the data of densities and strengths of machined MOR bars were statistically analyzed.

Table IV lists the mean densities and the main effects of the experiment. Main effects are defined as differences between the means of the observed quantity for levels of one factor, averaged over all levels of the other factors. Four main effects which are highlighted in the Table are noted to be highly significant. The very low values of the "t" test probabilities, as well as the value of the main effects compared to the estimated standard error of the experiment, suggest that the effects

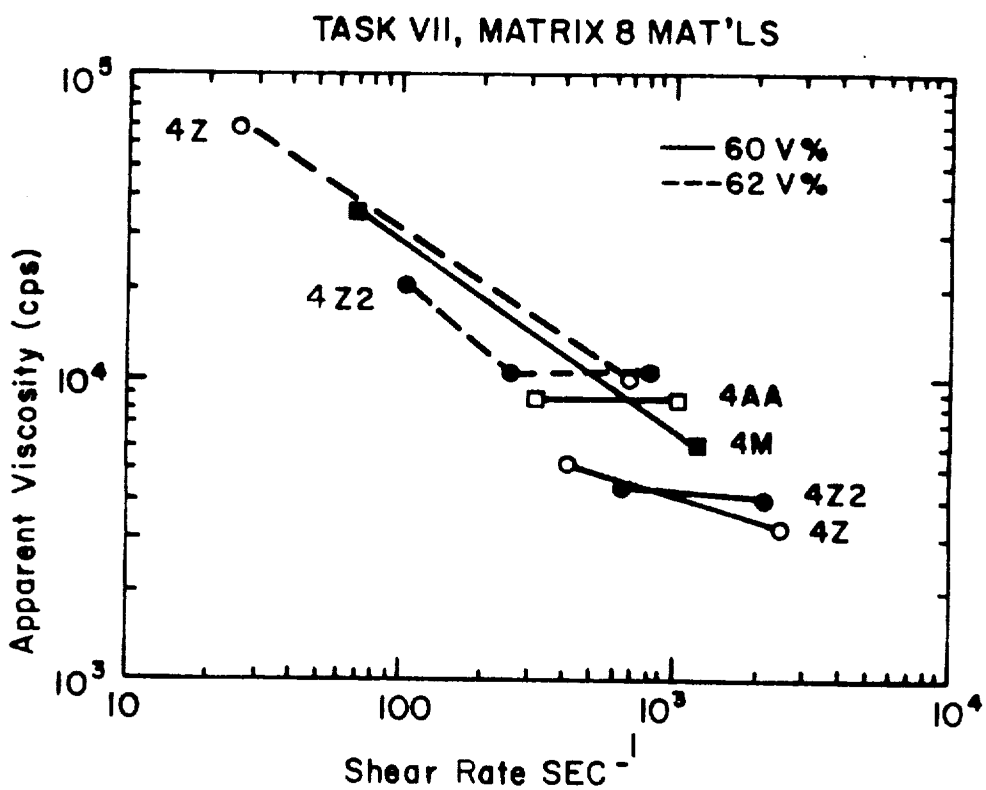


FIGURE 4. VISCOSITY DATA FOR MATRIX 8 MIXES

Table IV
Task VII
Matrix 8
Mean Densities of Machined MOR Bars
Effects (% T.D.)

Expt. No.	Variables	Mean Yields*	Main Effects
1	(Ave.)	96.3	
2	A	94.0	$\boxed{1.08}$ ± .15**
3	B	92.7	-0.23
4	C	94.3	0.38
5	D	93.4	$\boxed{1.53}$
6	E	94.8	$\boxed{1.43}$
7	F	93.5	$\boxed{1.43}$
8	G	97.1	-0.43

* 10 Samples
**Estimated Standard Error from Task II - Matrix 1 Experiments

Variables	-	+	"t" Test Probability
A Fluid Mix Process	"C"	"B"	0.001
B Carbon Source	DeGussa	Carbon Black	0.600
C Argon Ramp Rate	9°C/Min.	5°C/Min.	0.2[illegible]
D Argon Sinter Temp	2080°C	2120°C	0.00[illegible]
E Argon Sinter Time	12 Min.	30 Min.	0.000
F Backfill Temp.	1620°C	1760°C	0.000
G Vacuum Hold Time	4 Hr.	2 Hr.	0.200

are highly significant. The experimental data indicate that for machined MOR bar density, Process B (fluid mixing for 168 hours) is better than Process C (fluid mixing for 72 hours), that 2120 ^{o}C is a better sintering temperature than 2080 ^{o}C, that 30 minutes is a better sintering time than 12 minutes, and that a backfill temperature of 1760 ^{o}C is better than 1620 ^{o}C. The highest mean density of these groups, 97.1 % of theoretical density, was attained under the conditions of Experiment #8.

The data on MOR mean strengths are listed in Table V, which also shows the main effects calculated from the matrix data. The significant main effects are highlighted in the Table and the significance was determined by comparison with the estimated standard error as well as the individual "t" test probabilities. The process, sinter time and backfill temperature effects are the same as those found to be significant for high density in Table IV. However, the ramp rate was found to be significant for strength, but had no effect on density. The sintering temperature, which was important for high density, had no significant effect for higher strength. The highest mean strength measured, 455 MPa (66.0 Ksi), was obtained under the conditions of Experiment #8, which were also the conditions yielding the highest density (Table IV). The mean strengths in Experiments #6 (439 MPa - 63.7 Ksi) and #1 (420 MPa - 61.0 Ksi) are next in order of magnitude.

Extreme value statistics were used to gain further insight on the effects of the treatments on the maximum values of the MOR strength. Since we are attempting to reach new, high values of strength first, and reliability next, we must be aware of the effects of our variables on the highest values of strength. 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 (Ref. 3).

The results of the statistical analysis with the yield in the matrix equal to the highest value for strength in each group of 10 samples is shown in Table VI. The highlighted values of the main effects are considered highly significant on the basis of the comparison to the estimated standard error of the experiment derived from the large pool of similar data available from the Task II - Matrix 1 experiments (Ref. 2). Process B is again shown to be better than Process C, and the 1760 ^{o}C backfill temperature is again shown to be the better one. The 30-minute sinter time is also shown, even more strongly than in the mean strength data in Table V, to be better than the shorter, 12-minute sinter time. The highest value of 546 MPa (79.2 Ksi) is found in Experiment #8, and the values in Experiment #1 (531 MPa - 77.1 Ksi) and in Experiment #6 (524 MPa - 76.1 Ksi) are quite similar and next in order. Analysis of the extreme value statistics does not indicate that the temperature ramp rate is significant as does the mean strength analysis in Table V.

Optical microscopy indicated that the flaw size and distribution was similar to other similarly-processed materials and no further fractography was performed.

Table V
Task VII
Matrix 8
Mean Strengths of Machined MOR Bars
Effects (Ksi)

Expt. No.	Variables	Mean* Yields	Main Effects
1	(Ave.)	61.0	
2	A	59.1	$\boxed{3.34}$ ±0.88**
3	B	55.0	-1.01
4	C	53.2	$\boxed{3.27}$
5	D	53.5	-0.76
6	E	63.7	$\boxed{5.25}$
7	F	59.0	$\boxed{4.95}$
8	G	66.0	-0.84

* 10 Samples
**Estimated Standard Error

Variables		-	+	"t" Test Probability
A	Fluid Mix Process	"C"	"B"	0.08
B	Carbon Source	DeGussa	Carbon Black	0.65
C	Argon Ramp Rate	9°C/Min.	5°C/Min.	0.07
D	Argon Sinter Temp	2080°C	2120°C	0.74
E	Argon Sinter Time	12 Min.	30 Min.	0.01
F	Backfill Temp.	1620°C	1760°C	0.01
G	Vacuum Hold Time	4 Hr.	2 Hr.	0.71

Table VI
Task VII
Matrix 8
Extreme Value Statistics
MOR Strengths (Ksi)

Expt. No.	Variables	Highest Single Strength* (Ksi)	Main Effects (Ksi)
1	(Ave.)	77.0	
2	A	72.0	$\boxed{3.6}$ $\pm$0.7**
3	B	73.9	-0.3
4	C	64.9	-1.4
5	D	60.5	-1.7
6	E	76.1	$\boxed{10.6}$
7	F	66.3	$\boxed{4.8}$
8	G	79.2	0.3

* From Group of 10 Samples
**Estimated Standard Error from Task II - Matrix 1 Experiments

Variables		-	+
A	Fluid Mix Process	"C"	"B"
B	Carbon Source	DeGussa	Carbon Black
C	Argon Ramp Rate	9°C/Min.	5°C/Min.
D	Argon Sinter Temp	2080°C	2120°C
E	Argon Sinter Time	12 Min.	30 Min.
F	Backfill Temp.	1620°C	1760°C
G	Vacuum Hold Time	4 Hr.	2 Hr.

1.2 Matrix 9 Plan - SiC Powder Source and Boron Level

→ Matrix 9 compared two sources of SiC powder at two levels of boron, 0.5% and 1.0%. Densities as high as 98.4% of theoretical density and mean strengths up to 503 MPa (72.9 Ksi) were measured. Ibiden powder and 1% boron were better for density, but no significant strength effects were observed.

The effects of two sources of silicon carbide powder and two levels of boron concentration on density and strength of sintered silicon carbide were evaluated in a 2^2 designed factorial experiment.

Two sources of sinterable silicon carbide powder were available to the program; the Ibiden powder from Japan which we have used since the beginning of the program , and a powder purchased from the Superior Graphite Company, Chicago, Illinois, which became available recently. The Ibiden powder was prepared with a total of 2% free carbon, whereas the Superior Graphite was prepared with a total of 4% free carbon. Additions of 0.5% and 1.0% boron were made to each powder to make up the four batches listed in Figure 5.

1.2.1 Sample Preparation

The powders were mixed with boron, carbon and wax in fluid mix process B. Injection-molded bars were prepared, dewaxed in our standard vacuum dewaxing cycle and sintered in the improved sintering cycle (5^{0} C ramp rate, 1760 ^{o}C backfill temperature, and 30 minute sinter time at 2120 ^{o}C in argon). Two sintering runs (LA 31 and LA 33) were made with 10 MOR bars in each sintering run from each batch listed in Figure 5. Five bars were machined and tested from each sintering run, and 5 bars were machined, heat-treated (annealed) and tested. The mixes involved in this matrix are:

Batch	Boron	Powder Source
4M (60)	1.0%	Ibiden
14A (60)	0.5%	Ibiden
15A (60)	1.0%	Superior Graphite
16A (60)	0.5%	Superior Graphite

Spiral flow data for these mixes are given in Figure 6, along with that for the Task II materials. All mixes were prepared using Process B, therefore data were obtained only at the 60% loading level. The Superior Graphite mixes (15A and 16A) clearly show a reduced spiral flow to less than 1.0 inches. For either powder type, the lower boron level tends to yield slightly lower flow. Mix 15A was also checked at an elevated material temperature (300 F). This 50 F increase in material temperature raised the spiral flow to 1.37 inches, clearly showing that the moldability could be improved, if necessary, to fabricate complex parts.

Viscosity data for these materials are shown in Figure 7. Again, the viscosity and spiral flow data are in good agreement.

TASK VII - MATRIX 9

Design of Experiment

Exp.#	A	B	Batch
1	-	-	14A
2	+	-	16A
3	-	+	4MNO
4	+	+	15A

Experiment Factors

ID	Factor	-	+
A	SiC Source	Ibiden	Superior Graphite
B	Boron Content	.5%	1%

FIGURE 5: DESIGN OF EXPERIMENT FOR MATRIX 9

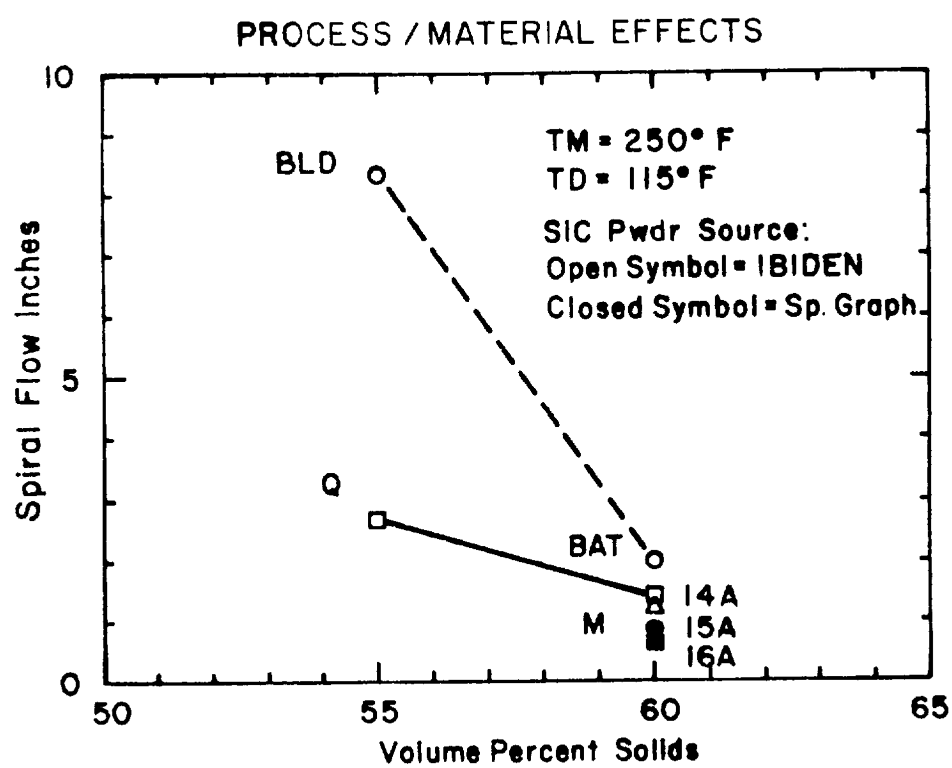


FIGURE 6. SPIRAL FLOW DATA FOR MATRIX 9 MIXES

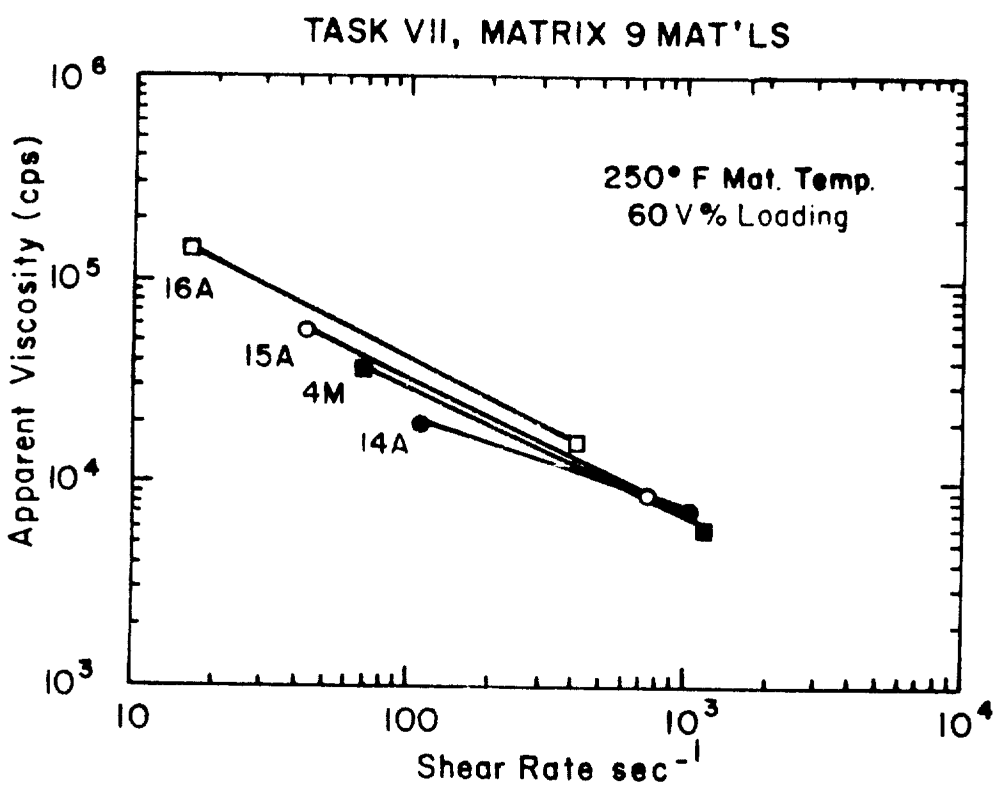


FIGURE 7. VISCOSITY DATA FOR MATRIX 9 MIXES

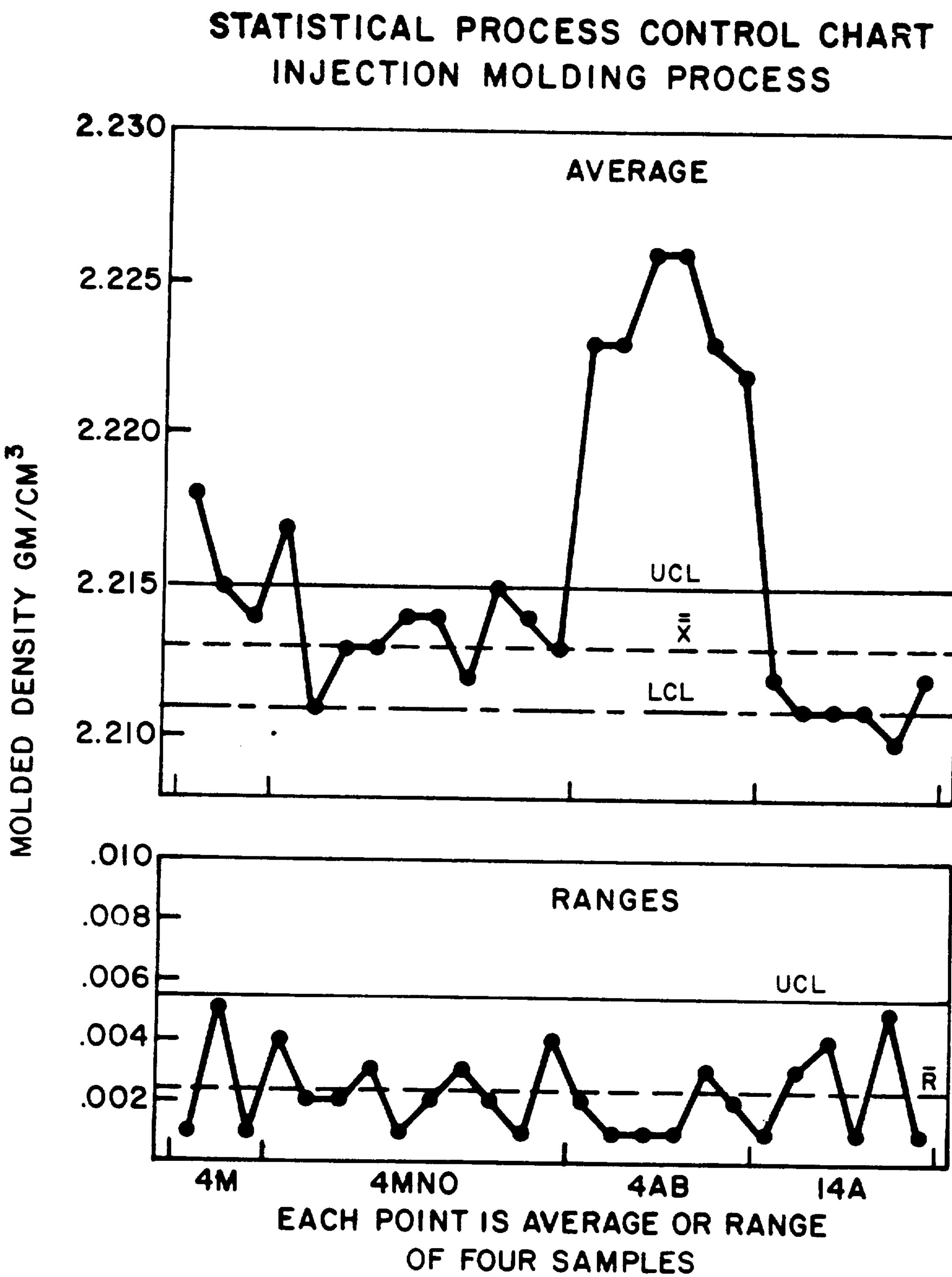


FIGURE 8. SPC Chart for Molded MOR Bars From Process B Mixes.

The statistical process control (SPC) chart for batches made with Process B is shown in Figure 8 with the density of the as-molded MOR bars as the control variable. All the batches were made to 60 V% solids, with formulations expected to yield the same as-molded densities. _The ranges for all the batches were within the control limits but one batch was significantly above the upper control limit for averages. Batch 4AB was discarded on the basis of the high molded density and further analysis of this batch was not pursued.

Some of the variables monitored during the molding process were Process A or B, ambient temperature, humidity, amount of water vapor in the environment, and graphite source (lamp black or DeGussa carbon). A linear regression model for the molding process was developed and the following equation described the process well (R^2 adjusted = 97.4%):

$$Y = 2.203 + 0.0197\ X1 + 0.00023\ X2 - 0.0108\ X3$$

where Y = mean molded density (grams/cm^3)
X1 = Process (B = 0, C = 1)
X2 = Humidity (%)
X3 = Source of Graphite (lamp black = 0, DeGussa = 1).

The C_p criterion (Ref. 4) was used to find the minimum number of predictor variables. The variables of ambient temperature and the amount of water vapor are not needed to adequately represent the data, and the effects of Process, humidity and carbon source are relatively small.

1.2.2 Analysis of Data and Discussion of Results

The mean densities and the effects of the two variables on density are listed in Table VII. Mean densities from 94.1 to 98.4 % of theoretical density were observed and significant effects of the variables were noted. The low estimated standard error in the density data from past experience permits conclusions from small differences in density. Materials containing Ibiden SiC powder sintered to higher density than the Superior Graphite powder and this effect is highly significant. Batches containing 1% boron sintered to slightly higher density than those of 0.5% boron, but this effect is only of marginal significance. A strong two-factor interaction between the powder source and the boron level is noted in the data.

The data on the mean and highest value strengths of sintered-machined MOR bars are listed in Table VIII. Neither the effect of powder source nor boron level is significant on the strength of these bars when one considers the size of the estimated standard error in the strength data. One should recognize that the levels of strength for the mean exceeds 482 MPa (70 Ksi) for one group and a highest value exceeds 551 MPa (80 Ksi) for a group of 8 to 10 samples. This is a new high for strength in this program.

TABLE VII

TASK VII - MATRIX 9

Mean Densities of Machined MOR Bars

Yields and Effects (% T.D.)

Batch	Expt. No.	Effects	Means** Yield	Means** Effects
14A	1	(Ave)	98.4	(96.4)
16A	2	A	94.1	-3.0 ± .1*
4N	3	B	97.4	0.3
15A	4	AB	95.7	1.3

*Estimated Standard Error From Task II - Matrix 1
**Means of 10 Samples

Variable	-	+
A (SiC Source)	Ibiden	Superior Graphite
B (Boron Level)	0.5%	1.0%

TABLE VIII

TASK VII - MATRIX 9

Mean and Highest Value Strengths
of Sintered Machined MOR Bars

Yields and Effects (Ksi)

Expt. No.	Effects	Means*		Highest Values*	
		Yields	Effects	Yields	Effects
1	(Ave)	66.6	(61.4)	80.6	(75.1)
2	A	49.9	0.0 ± 3.4**	67.9	-3.7 ± 2.9**
3	B	56.3	6.3	73.4	1.8
4	AB	72.9	16.7	78.7	9.0

*Mean and Highest Value of 8 to 10 Samples
**Estimated Standard Error

Variable	-	+
A (SiC Source)	Ibiden	Superior Graphite
B (Boron Level)	0.5%	1.0%

It is concluded from this experiment that both powder sources can be used to achieve adequate density for sintered SiC, that both powder sources achieved the same strength level under the conditions of the experiment, that boron level does not significantly improve the density or the strength of these materials within the bounds of this experiment. The role of carbon level was not addressed in this experiment and another, much larger matrix would be required to adequately determine the role (if there is one) of carbon level and boron level and their interaction on the strength of these materials. Fracture origins (flaw sizes and locations) are believed to be still controlling strength in these materials and further work on flaw sizes and origins is required. A typical fracture surface is shown in Figure 9. The failure site shown in the figure is believed to be a porous region at the surface.

1.3 Matrix 10 Plan - Annealing Study

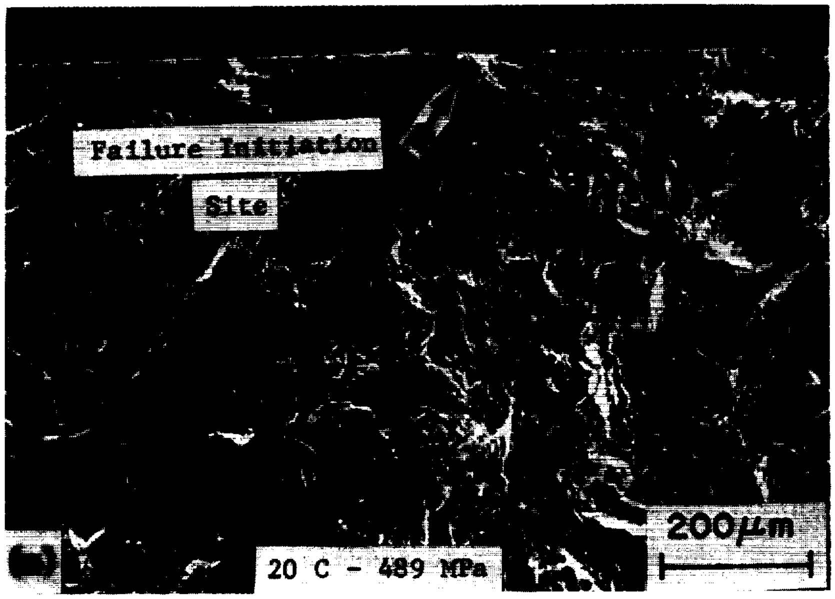
Matrix 10 investigated the effect on strength of annealing at 1200 and 1400 ^{o}C in two environments, air and argon. Strengths as high as 458 MPa (66.4 Ksi) were observed and it was concluded that annealing at 1200 ^{o}C in air for 18 hours gave the best results.

Previous work in this laboratory indicated that the room temperature strength of sintered SiC, purchased from a vendor, Kyocera, could be improved by an annealing treatment in air or in argon. It was felt worthwhile for the achievement of program goals to evaluate the influence of heat treatment on the mechanical properties of injection-molded SiC.

1.3.1 Sample Preparation

Injection-molded MOR bars of NASA-4M composition, processed by the fluid-mixing route, were sintered in the vacuum-argon cycle which is given as Experiment #8 in Task VII - Matrix 7 reported in the second annual report (ref. 2). The bars were machined following sintering (density of 97% of theoretical) and heat treated in two flowing atmospheres (argon and air) at two temperatures (1200 and 1400^{0} C) with a hold time at temperature of 18 hours.

The bars were inspected and weighed following heat treatment and a coating on all of the bars was observed. The bars heated in argon had a coating thickness gradient, observed by the change in color, with the thickest coating at the end of the bar nearer the gas inlet location of the tube furnace. This observation suggests that the argon atmosphere contained a small partial pressure of oxygen or water vapor which, over the long 18 hour period, was sufficient to form a visible coating. The samples heated in air had a uniform coating thickness along the length of the bar. The mean and standard deviations of the weight gains and calculated mean coating thickness are given in Table IX. The coating thickness was estimated by assuming that the composition of the coating was SiO_2 with a density of 2.2 grams per cubic centimeter. As expected, the coating thickness was greater for the bars heated in air than those heated in argon.



3707. LA 31-Batch 15A/Unannealed

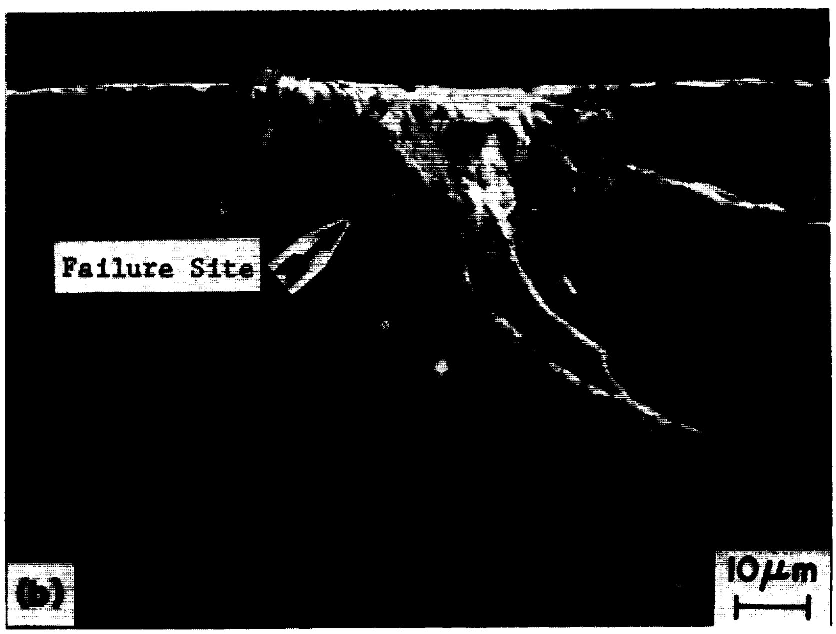


FIGURE 9. Typical Fracture Surface AS Seen In The Scanning Electron Microscope.

Table IX

WEIGHT GAINS ON SINTERED SIC MOR BARS
AFTER HEAT TREATMENT FOR 18 HOURS

Atmosphere	Temp °C	n	Weight Gain (GMS X10^4) BAR $\bar{x}$	σ	Calculated Thickness (μm)
Argon	1200	7	0.6	3.9	0.2
Argon	1400	7	0.4	3.3	0.1
Air	1200	8	3.3	2.1	1.0
Air	1400	8	4.5	2.1	1.4

n = Number of samples

Table X

STRENGTH OF HEAT TREATED MOR BARS

Atmosphere	Temp °C	Strength n	$\bar{x}$ (ksi)	σ (ksi)	Probability "t" Test	$\bar{x}$ % Change*
Argon	1200	7	63.8	6.7	.04	15.6
Argon	1400	8	55.4	11.5		0.4
Air	1200	8	66.4	9.4	.03	20.3
Air	1400	7	57.1	4.1		3.4

*Baseline - 28 MOR Bars - 4M - Task VII - Matrix 7, $\bar{x}$=55.2 ksi, σ=9.3 ksi

n = Number of Bars

Table XI

STRENGTH OF MOR BARS
FOR TWO HEAT TREATING TEMPERATURES

Temp °C	n	Strength $\bar{x}$ (ksi)	σ (ksi)	Probability "t" Test	$\bar{x}$ % Change*
1200	15	65.2	8.1	.007	18.2
1400	15	56.2	8.6		1.8

*Baseline - 28 MOR Bars - 4M - Task VII - Matrix 7, $\bar{x}$=55.2 ksi, σ=9.3 ksi

n = Number of Bars

1.3.2 Analysis of Data and Discussion of Results

The MOR strength results of the four heat treatment runs are shown in Table X. The data are listed for n (number of samples tested), X (mean value of MOR strength), and sigma (standard deviation of the sample distribution). Statistical analysis of the data, assuming the sample population as part of a normal population, was performed by generating an analysis of variance table, student's t tests, and F tests. The data given in Table X show that the atmosphere effect is insignificant but that the temperature effect is significant. The strengths of MOR bars heated at 1200 °C in air or argon are significantly greater than the strength of either the baseline samples or the samples heated in air or argon at 1400 °C. This is highlighted in Table XI where it is seen that the temperature effect is highly significant (the t test probability is .007, indicating we would expect this result to occur by chance only 7 times in 1000). The conclusion from this study is that the strength of these materials at this level of development can be improved by 15 to 20 percent by a heat treatment at 1200 °C.

Samples of bars from Matrix 9 above were also annealed and tested. The strength data on the sintered-machined-annealed MOR bars are shown in Table XII for mean and highest values. The effects of powder source and boron level are small compared to the estimated standard error of the experiment and no significant effects are concluded. A comparison between strengths of sintered-machined and sintered-machined-annealed MOR bars is given in Table XIII with the overall samples showing a significant improvement for the annealed bars in two of the four experiments. A decrease in strength with annealing in the fourth experiment is not understood. Again, however, we are measuring strengths of greater than 482 MPa (70 Ksi) for some means and a strength greater than 551 MPa (80 Ksi) for the highest value of one group, which are new ranges of strength for this program.

1.4 Matrix 11 Plan - Attritor Process and Annealing

→ Matrix 11 evaluated the attritor processed material and the reproducibility of the attritor process and the sintering cycle. The three variables at two levels each were attritor processing cycles, sintering runs, and with and without annealing. Results were that the attritor cycles and sintering runs showed no significant differences, indicating good processing reproducibility. The annealing process resulted in highly significant improvement in mean strength to 570 MPa (82.8 Ksi). High temperature fast fracture testing of these materials at 1200 and 1400° C gave no indication of reduction in strength up to these temperatures. The best results were obtained with a group of 9 annealed samples tested at 1400° C which had a Weibull characteristic strength of 564 MPa (81.8 Ksi) and a Weibull modulus of 16.8.

A new fluid mixing process (Process D) was developed to improve the homogeneity of the SiC molding batches and to reduce the ball milling time which is a significant portion of overall processing time in our standard cycle (Process B). The time reduction for ball milling is from 168 hours,

TABLE XII

TASK VII - MATRIX 9

Mean and Highest Value Strengths
of Annealed Machined MOR Bars

Yields and Effects (Ksi)

Expt. No.	Effects	Means* Yields	Means* Effects	Highest Values* Yields	Highest Values* Effects
1	(Ave)	70.1	(67.4)	88.1	(78.0)
2	A	69.0	-1.4 ± 2.2**	75.4	-7.3 ± 3.0**
3	B	66.4	-4.3	75.2	-7.5
4	AB	64.2	-0.4	73.4	5.5

*Mean and Highest Value of 8 to 10 Samples
**Estimated Standard Error

Variable	-	+
A (SiC Source)	Ibiden	Superior Graphite
B (Boron Level)	0.5%	1.0%

TABLE XIII

TASK VII - MATRIX 9

Comparison of MOR Strengths of
Sintered-Machined and Sintered-Machined-Annealed Bars

Expt. No.	Strength (Ksi) Sintered			Annealed			Probability "t" Test
	n	$\bar{X}$	σ	n	$\bar{X}$	σ	
1	10	66.6	10.3	10	70.2	11.0	.526
2	10	49.9	12.3	8	69.0	6.8	.002*
3	10	56.3	12.9	16	66.4	9.1	.028*
4	9	72.9	5.4	10	64.2	5.4	.003*
All Samples:							
	39	61.1	13.7	44	67.2	8.6	.015*

*Means Strengths are considered significantly different

TABLE XIV

FLUID MIXING
PROCESS AND TIME VARIATIONS

	PROCESS / (HOURS)			
	A	B	C	D
WET BALL MILL:				
SOLIDS	48	96	96	--
SOLIDS + WAX	24	72	--	2-1/2
DRYING:				
STIR DRY	14	4	2-1/2	--
PAN DRY	100	100	24	100
PREPARE FOR MOLDING:				
"V" BLEND	--	--	4	--
MIX	6	4	--	4-1/2
ADD WAX/MIX	4	--	4	--

TABLE XV

TASK VII - MATRIX 11

Design of Experiment

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

Experiment Factors

ID	Factor	-	+
A	Attritor Batch	1	2
B	Sintering Run	LA-31	LA-33
C	Heat Treatment	None	Anneal 1200°C

used in Process B, to 2.5 hours employed in Process D.. A comparison of the mixing times of the four mixing processes evaluated in this program is shown in Table XIV.

The design of the matrix (Table XV) is a 2^3 factorial experiment with the three variables (attritor batch, sintering run and heat treatment) at two levels each. The yields of the matrix experiment were mean density, mean strength and highest value of strength from groups of 5 machined MOR bars.

1.4.1 Sample Preparation

The mixing is done in a plastic bottle with a few alumina balls in the A, B, and C processes, whereas it is performed in an attritor mill with SiC media in Process D. Process control is obtained through the monitoring of the appearance of the fluid mix on dip slides under 100 X magnification as a function of time. MOR bars were injection molded, dewaxed in our standard cycle and sintered in the standard sintering cycle as referenced in section 1.8 above. Annealing of one-half of the bars was performed in the standard cycle (1200 ^{o}C - 18 hrs. - air).

1.4.2 Analysis of Data and Discussion of Results

The results are given in Tables XVI (mean density), XVII (mean strength) and XVIII (highest strength value). The values for the effects which are statistically significant are highlighted. The data given in the tables are treated as normally distributed since they are means from groups of observations and form normal distributions as proven by the central limit theorem.

Two variables have significant effects on the mean densities; attritor batch and heat treatment. The absolute size of these effects on density is small, but the experimental error is also small and permits determination of these small differences. The differences in batch 1 and batch 2 are in the solids loading levels during attritor milling, which were 60% for batch 1 and 58% for batch 2. Minor differences in the two batches were also present during the final mixing step in that batch 1 was diluted to 58% before molding. Normal probability plots for the effects are given in Figure 10 and one sees that only the anneal (heat treatment) and the batch effects lie off the normal line for the density and highest strength, and for annealing only for the mean strength effect. This is a further confirmation of the significance of these effects. Plots for the residuals, which are determined by removing the influence of the significant effects, are shown in Figure 11 and one sees that the data lie close to a straight line, indicating that only the two effects are significant (Ref. 5).

The mean strengths and effects are shown in Table XVII. The highlight of this matrix is that it provided strength data in excess of 551 MPa (80 Ksi) for the first time in this program which is one of the goals.

TABLE XVI

TASK VII - MATRIX 11

Attritor Process Study

Mean Densities and Effects of Machined MOR Bars
(% T.D.)

Expt. No.	Mean Density	Variable ID	Effects
1	97.17	(AVE)	(96.34)
2	96.28	A	$\boxed{-0.82}$ ± 0.12**
3	96.98	B	0.00
4	95.98	AB	0.02
5	96.38	C	$\boxed{-0.52}$
6	95.54	AC	0.10
7	96.52	BC	0.24
8	95.83	ABC	0.08

* 5 Samples   **Estimated Standard Error

Variables	-	+
A Attritor Batch	1	2
B Sinter Run	LA-31	LA-33
C Heat Treatment	None	1200°C - 18 Hrs.

TABLE XVII

TASK VII - MATRIX 11

Attritor Process Study

Mean Strengths and Effects of Machined MOR Bars
(Ksi)

Expt. No.	Mean Strength*	Variable ID	Effects
1	69.5	(AVE)	(72.5)
2	61.4	A	0.2 ± 2.5**
3	66.7	B	-1.9
4	72.4	AB	2.9
5	80.0	C	$\boxed{10.0}$
6	82.8	AC	1.6
7	73.4	BC	-6.0
8	73.7	ABC	-4.1

* 5 Samples **Estimated Standard Error

Variables	-	+	"t" Test Probability
A Attritor Batch	1	2	0.71
B Sinter Run	LA-31	LA-33	0.60
C Heat Treatment	None	1200°C - 18 Hrs.	0.01

TABLE XVIII

TASK VII - MATRIX 11

Attritor Process Study

Extreme Value Statistics
MOR Strengths (Ksi)

Expt. No.	Highest Single Strength*	Variable	Effects
1	76.4	(AVE)	(85.5)
2	79.0	A	$\boxed{7.8}$ ± 2.2**
3	75.9	B	-2.6
4	85.6	AB	3.0
5	92.2	C	$\boxed{12.5}$
6	99.3	AC	1.7
7	81.6	BC	-5.6
8	93.6	ABC	-0.5

* From Group of 5 Samples **Estimated Standard Error

Variables	-	+
A Attritor Batch	1	2
B Sinter Run	LA-31	LA-33
C Heat Treatment	None	1200°C - 18 Hrs.

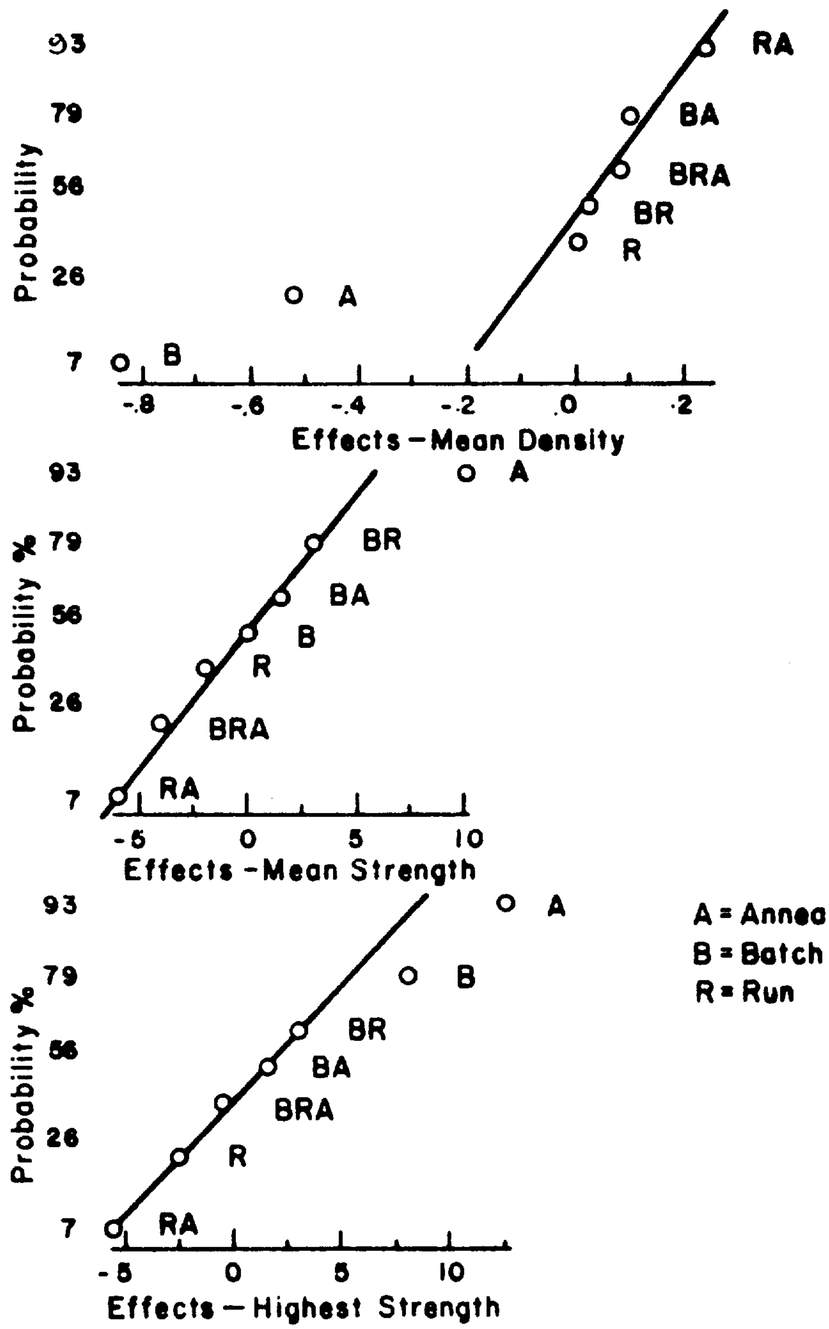


FIGURE 10. PROBABILITY PLOTS FOR MAIN EFFECTS ON DENSITY, MEAN STRENGTH AND HIGHEST STRENGTH

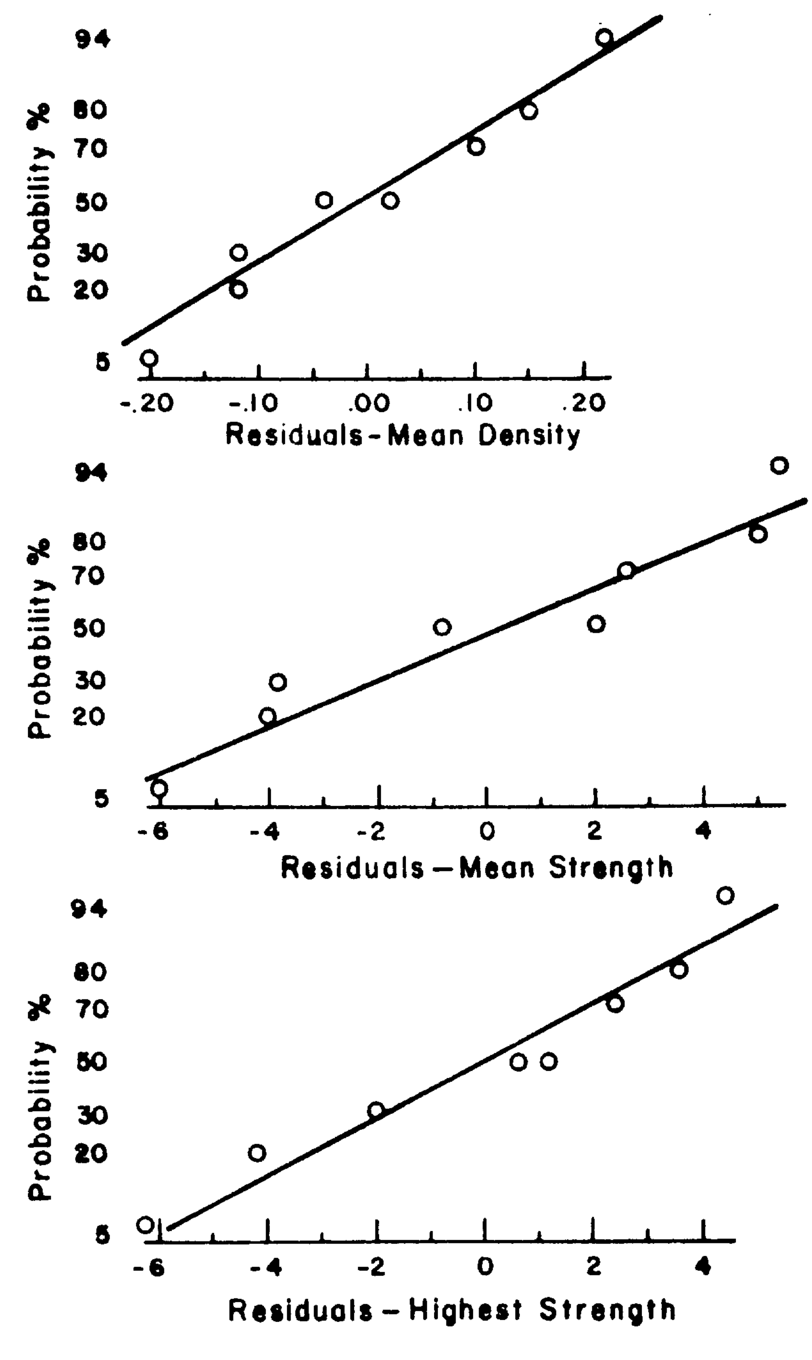


FIGURE 11. PROBABILITY PLOTS FOR RESIDUALS FOR EFFECTS ON DENSITY, MEAN STRENGTH AND HIGHEST STRENGTH

As in past work on heat treatment discussed in detail in Matrix 10, the heat treatment variable shown in Table XVII is statistically significant in increasing the strength of SiC bars. Also noted is an apparent interaction effect between sinter run and heat treatment. If one plots the probability against the effects for the mean strengths, as in Figure 10, one sees that the data lie on a line except for the data point for the anneal (heat treatment) effect. The interaction effect appears to lie within normal probability range and is not considered significant at this time. The residuals plot for mean strength in Figure 11 appear to be adequately represented by a single line when only the annealing effect is removed.

Extreme value statistics are shown in Table XVIII and they indicate in general that the same significant variable is seen in the highest value strength data as in the mean strength data in Table XVII. One exception is noted which is that the variable of attritor batch is significant for the highest value data and not significant for the mean strength data. The heat treat variable is highly significant for both the mean strength and the highest value strength. Also an interaction is noted between the sinter run variable and the heat treatment variable. However, when the probability is plotted against the effects, Figure 10, the anneal and the batch effects lie off the line, but the interaction effect is represented adequately by the line. The plot of residuals in Figure 11 can be adequately represented by a single line when the effects of the two variables, attritor batch and heat treatment, are removed from the data. It should be noted that values in excess of 620 MPa (90 Ksi) have been observed in these experiments, which is a new level of strength achieved in this program.

Data from the two sintering runs were combined, since no significant differences were observed between them, and Weibull statistics were investigated on groups of 9 or 10 samples from this matrix. The Figures 12 and 13 show the Weibull plots of attritor batches 1 and 2 in the annealed condition. Weibull characteristic values of 558 and 578 MPa (81 and 84 Ksi) were measured for heat treated samples from the two attritor batches. Weibull moduli of only 7 to 9 were observed, which is well below our goal of 16.

The annealing investigation was extended to determine if the increase from the annealing process was retained during elevated temperature testing. MOR bars of ATT1 and ATT2 batches were sintered, machined, annealed and tested in the fast fracture mode at room temperature, 1200 ^{o}C and 1400 ^{o}C. Stress rupture testing for long periods at 40 Ksi at 1200 ^{o}C and 1400 ^{o}C is in progress.

A summary of the MOR fast fracture data is given in Table XIX. A detailed statistical analysis of the data was made with the following results:

1) The strength data generated at room temperature, 1200 ^{o}C and 1400 ^{o}C are normally distributed as confirmed by the Shapiro-Wilk test (Ref. 6).

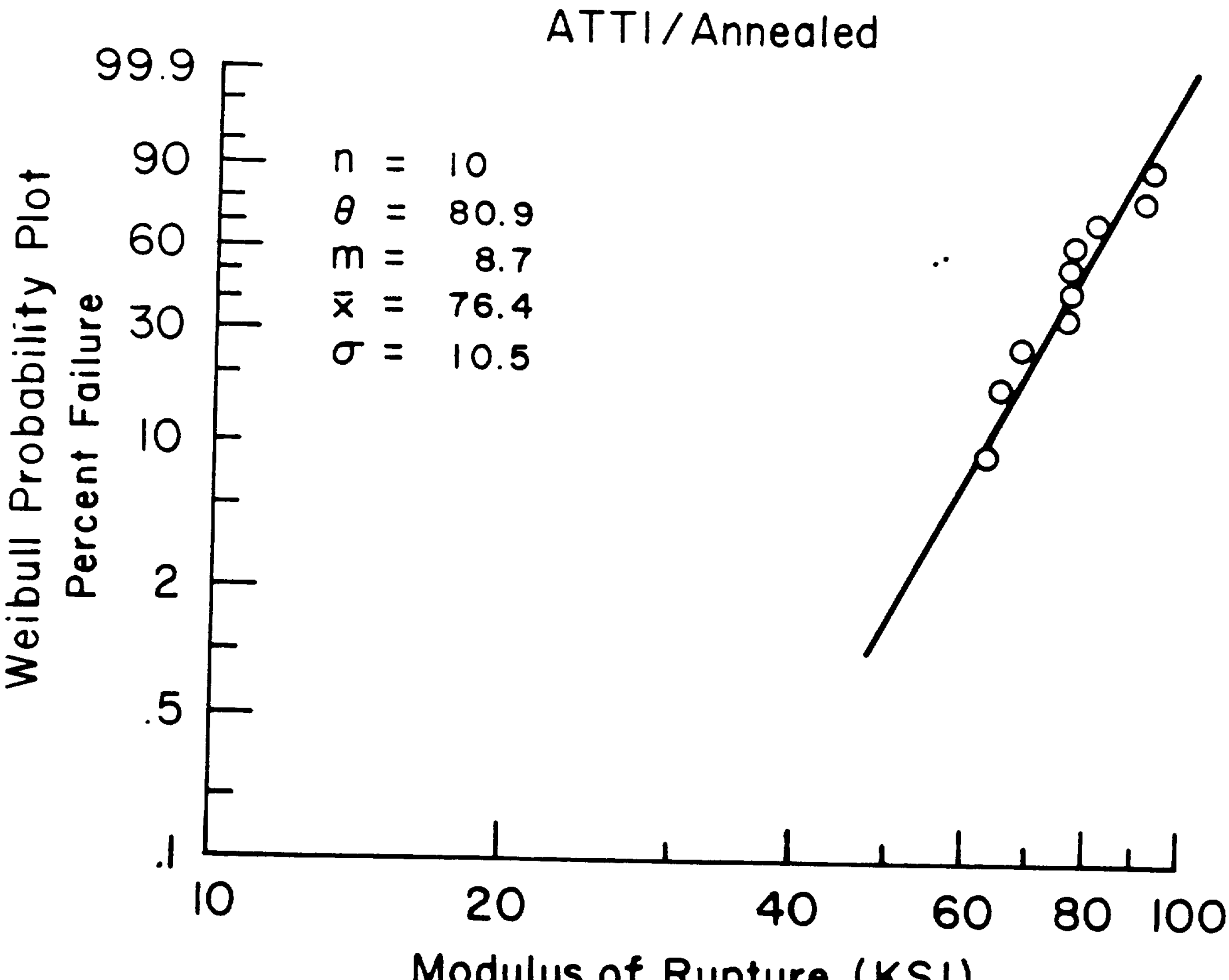


FIGURE 12. Weibull Probability Plots of Annealed MOR Bars From Attritor 1 Mix.

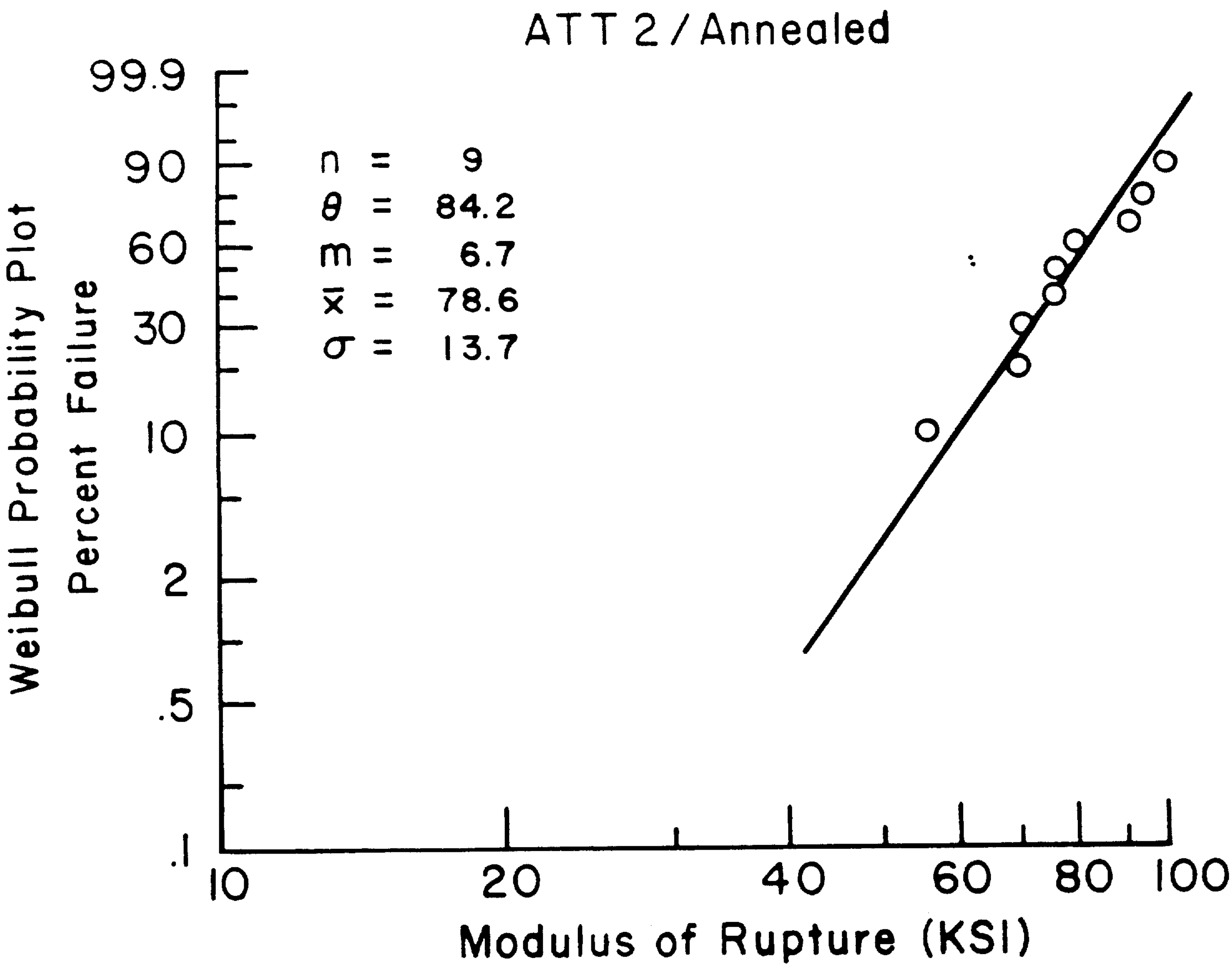


Figure 13. Weibull Probability Plots of Annealed MOR Bars From Attritor 2 Mix.

TABLE XIX

Statistical Description of Densities of MOR Bars
Used for Fast Fracture Tests at 20°C, 1200°C and 1400°C

MATERIAL	TEMP°C	n	MEAN	MEDIAN	STD DEV	MIN	MAX
ATT1	20	12	96.75*	96.75	0.33	96.13	97.48
ATT2	20	17	96.01*	96.10	0.31	95.46	96.45
ATT1	1200	6	96.98*	96.96	0.21	96.72	97.25
ATT2	1200	9	96.12*	96.21	0.31	95.53	96.59
ATT1	1400	9	96.94*	97.08	0.30	96.55	97.26
ATT2	1400	6	95.67*	95.60	0.25	95.40	95.97

*Highly significant differences in means by "t" test between ATT1 and ATT bars.

2) Boxplot exploratory data analysis (Ref. 7) showed no unusual features.

3) Correlations of strength with sintering run, molding order and molding humidity were not found.

4) Significant differences between mean strengths of ATT1 and ATT2 MOR bars at room temperature and 1200 °C were not found by "t" test analysis and analysis of variance evaluations.

5) Significant differences between ATT1 and ATT2 strengths tested at 1400 °C were found. ATT1 was stronger with a mean strength of 79.5 ksi, an extreme value of 86.0 Ksi, and a standard deviation of 5.6 Ksi, and ATT2 was weaker with a mean strength of 62.2 Ksi, an extreme value of 67.0 Ksi, and a standard deviation of only 3.7 Ksi. The detailed statistical descriptions for all the MOR data are given in Table XX and Weibull distribution plots for the 1400 °C data are shown in Figures 14 and 15. For the ATT1 material the Weibull characteristic strength is 81.8 Ksi with a modulus of 16.8 for a sample size of 9.

6) Significant differences in mean densities of ATT1 and ATT2 materials were found and the statistical parameters are listed in Table XIX. An acceptable linear regression model for all the MOR data with predictors of density and the attritor 1 and 2 materials was not found. A linear regression model for the 1400 °C MOR data was found (with a R^2 adjusted of 90.3%) to be:

$$Y = 101 - 17.2\,X1 - 7.16\,X2$$

where Y = MOR strength in Ksi
X1 = Attitor number (1 or 2)
X2 = $(\text{Density} - \text{Mean Density})^2$ in % of theoretical density

Three highlights of these results are:

1) These injection molded SiC materials maintain high strength to at least 1400 °C.

2) An ATT1 material was tested at 1400 °C which yielded a Weibull strength of 81.8 Ksi and a Weibull modulus of 16.8, which is above the goals of the program. A greater number of samples of this material will be evaluated to improve the confidence of this result.

3) ATT1 bars are consistently and significantly denser than ATT2 bars by about 1% of theoretical density.

TABLE XX

Statistical Description of MOR Data
for Fast Fracture at 20°C, 1200°C and 1400°C

MATERIAL	TEMP°C	n	MEAN	MEDIAN	STD DEV	MIN	MAX
ATT1	20	12	76.7	76.7	9.4	63.0	92.2
ATT2	20	17	77.2	77.3	11.4	55.7	99.3
ATT1	1200	6	66.5	67.8	9.4	55.7	80.4
ATT2	1200	9	70.4	74.2	12.2	49.2	88.2
ATT1	1400	9	79.5*	79.7	5.6	68.4	86.0
ATT2	1400	6	62.2*	62.1	3.7	57.5	67.0

*Highly significant differences between means of ATT1 and ATT2 1400°C MOR data by "t" test.

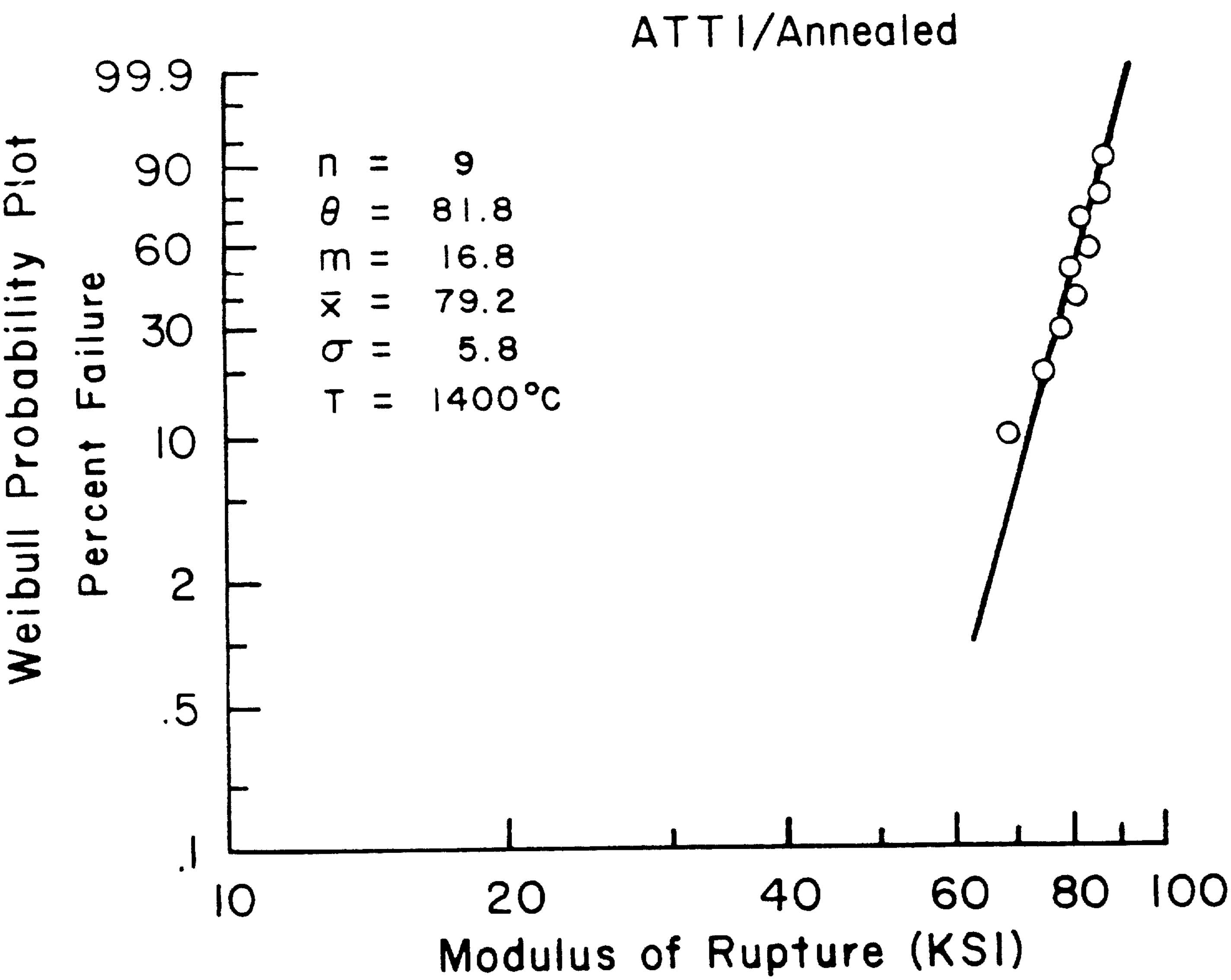


FIGURE 14. Weibull Probability Plots of Annealed MOR Bars Tested at 1400°C From Attritor 1 Mix.

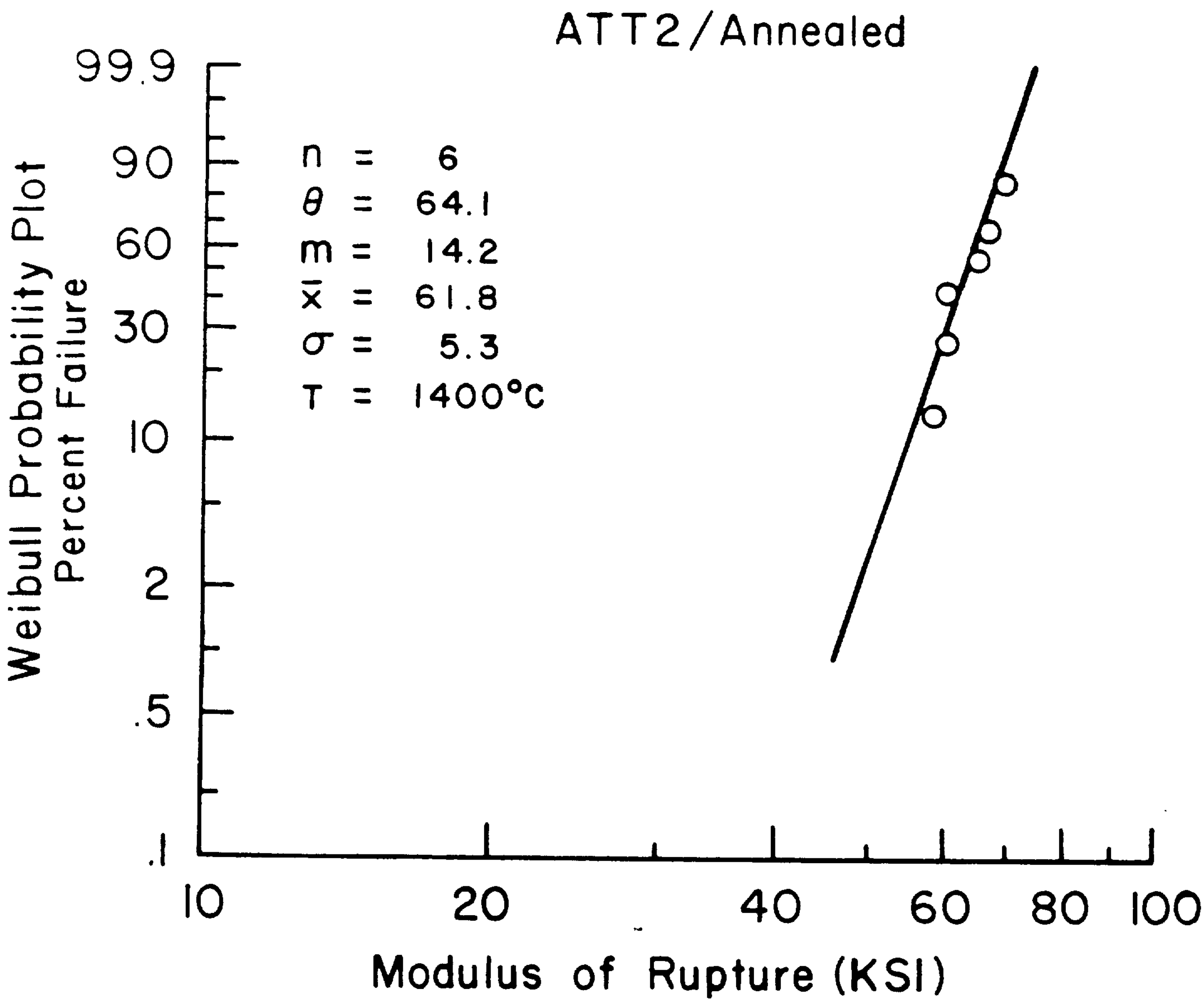


FIGURE 15. Weibull Probability Plots of Annealed MOR Bars Tested at 1400°C From Attr_tor 2 Mix.

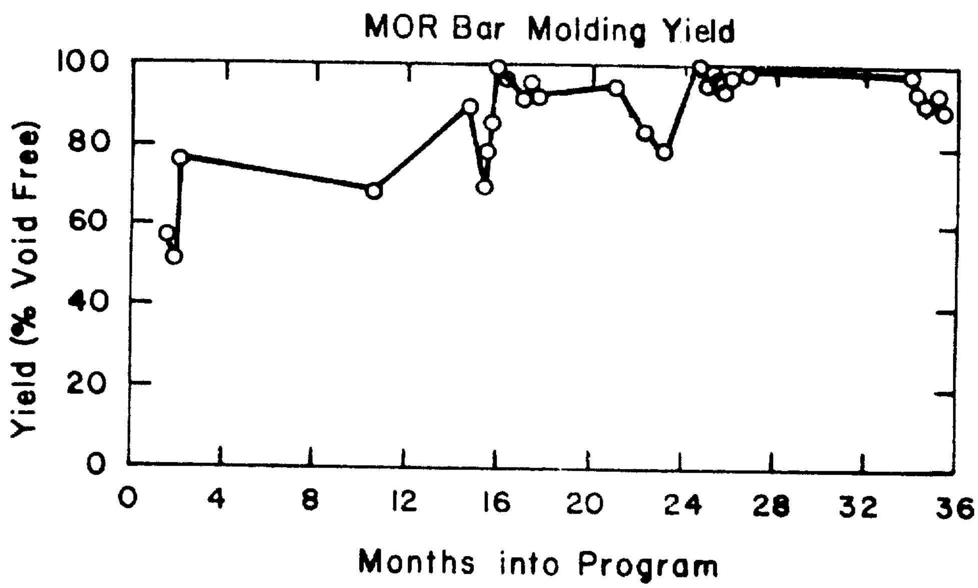


FIGURE 16. YIELDS OF VOID-FREE MOR BARS MOLDED DURING THE PROGRAM

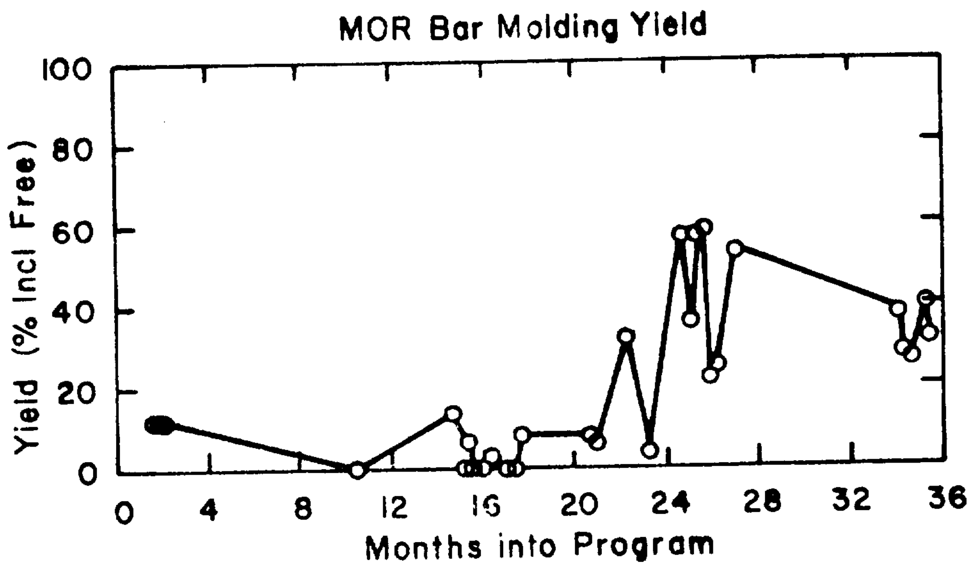


FIGURE 17. YIELDS OF INCLUSION-FREE MOR BARS MOLDED DURING THE PROGRAM

1.5 Molding Yields

→ Molding yields defined as the percentage of void-free or inclusion-free MOR bars were determined and shown to improve over the course of the program.

Molding characteristics for batches molded during the three years of the program have been analyzed. The data presented in Figures 16 and 17 show the yields as the percent of bars which were void-free or inclusion-free for the entire length of the MOR bar. Other data for both the void and inclusion yields relative to the gage length are available and those yields are generally 10-20 % higher. The gage length is defined as the center 0.88 inches of the molded bar, which covers the center span of the sintered bar in the MOR test. However, for purposes of making large parts, it is the entire part (bar) which is important.

Several features noted in the yield data, Figures 16 and 17,illustrate the effect of changes in the molding process made during the program. The void free yield data in Figure 16 shows that the first year yields averaged approximately 66 percent. For the second year the average is approximately 92 percent, when nominal molding conditions are held constant. The notable exceptions are for mixes 4I and 4J, at 15 months, when a substitute machine operator was used, and mix 4AA, at 22 months when bars were being molded with a smaller than normal amount of material. The increase in yield at 16 months coincides with an improvement in the molding machine when a vacuum leak found in the transfer tube was repaired.

Metallic inclusions have been identified by x-ray in all batches throughout the program. The inclusions were encountered in the first year of the program during mixing in equipment containing metal blades. Inclusions were reduced when the fluid-mixing processes were developed and the batches spent less time in equipment with exposed metal parts. Figure 17 shows that a significant improvement has been achieved with recent process changes. Beginning with batch 4AA, at 22 months, several technique improvements were incorporated in the last step of the mix preparation process. The effect observed to date has been an increase in the yield of inclusion-free bars from approximately 10 percent to 46 percent. Other factors appear to be influencing the inclusion contamination, and the problem continues under investigation.

1.6 Flaw Distributions in Molded and Sintered MOR Bars

→ The distributions of the numbers of flaws per bar observed visually and by x-radiography on selected samples of molded and sintered MOR bars were found to be approximated by a Poisson distribution. Sintering reduced the mean and the variance of the distribution compared to the same molded bars.

An analysis of flaws observed in MOR bars in the as-molded state and in the same groups of bars in the sintered-machined states was performed. The flaws observed are of two types; metallic inclusions which are

TABLE XXI

FLAWS OBSERVED IN MOLDED MOR BARS
AND PREDICTIONS BY A POISSON PROCESS
(X-RAY DATA)

POPULATION	NO. OF FLAWS PER BAR	OBSERVED NO. OF BARS	PREDICTED NO. OF BARS
TASK I	1 - 12	0	0
4 G Baseline	13	2	2
30 Bars	14	3	2
	15	5	2
	16	1	3
	17	1	3
	18	4	3
	19	5	3
	20	2	3
	21	4	2
	22	1	2
	23	1	1
	24	1	1
	25	0	0
TASK VII			
Matrix 7			
4 M	0	0	0
28 Bars	1	1	2
	2	3	4
	3	8	6
	4	10	5
	5	2	4
	6	2	3
	7	1	1
	8	1	1
4 Q	0	1	4
28 Bars	1	12	8
	2	8	8
	3	2	5
	4	4	2
	5	1	1
	6	0	0
13 A	0	1	2
28 Bars	1	5	5
	2	6	7
	3	6	6
	4	5	4
	5	5	3
	6	0	1

TABLE XXII

FLAWS OBSERVED IN MOR BARS AND PREDICTIONS BY A POISSON PROCESS

SINTERED - MACHINED SAMPLES

POPULATION	NO. OF FLAWS PER BAR	X-RAY FLAWS (3X MAG.) OBSERVED NO. OF BARS	X-RAY FLAWS (3X MAG.) PREDICTED NO. OF BARS	UPPER SURFACE VOIDS (7X MAG.) OBSERVED NO. OF BARS	UPPER SURFACE VOIDS (7X MAG.) PREDICTED NO. OF BARS	LOWER SURFACE VOIDS (7X MAG.) OBSERVED NO. OF BARS	LOWER SURFACE VOIDS (7X MAG.) PREDICTED NO. OF BARS
TASK I 4 G Baseline 30 Bars	0	2	1	14	8	17	14
	1	3	3	4	11	6	11
	2	6	6	6	7	4	4
	3	7	7	2	3	2	1
	4	4	6	3	1	1	0
	5	3	4	1	0	0	0
	6	1	2	0	0		
	7	2	1				
	8	1	1				
	9	0	0				
	10	1	0				
	11	0	0				
TASK VII Matrix 7 4 M 28 Bars	0	14	11	21	19	25	25
	1	7	10	5	7	3	3
	2	2	5	1	1	0	0
	3	4	2	0	0		
	4	1	0	1	0		
	5	0	0	0	0		
4Q 28 Bars	0	14	13	22	23	26	23
	1	8	10	6	5	0	5
	2	4	4	0	0	1	0
	3	2	1	0	0	0	0
	4	0	0			1	0
13A 28 Bars	0	15	12	20	15	17	15
	1	6	10	4	9	8	9
	2	3	4	1	3	1	3
	3	3	1	2	1	1	1
	4	1	0	0	0	0	0
	5	0	0	1	0	1	0
	6			0	0	0	0

observed as bright spots on X-ray film, and cracks and voids observed microscopically on the surface of machined bars. (Large voids, greater than 100 micrometers in diameter could be observed by X-ray and these led to rejection of the bar.) Flaws were observed in the as-molded state by inspection of X-ray negatives at a magnification of 3X, and these data are listed in Table XXI. Flaws were determined in the sintered-machined MOR bars by both radiographic analysis and by observing the upper and lower surfaces at 7 X magnification, and these data are shown in Table XXII. The bars designated 4G Baseline were the origin of the baseline results (n = 30, Weibull characteristic strength = 45.8 Ksi, m = 8) reported in the First Annual Report for this program (Ref. 1). The Task VII Matrix 7 bars were reported in detail in the Second Annual Report (Ref. 2). The mean strengths of 28 MOR bars of 4M, 4Q and 13A were 55.1 Ksi, 54.4 Ksi and 60.5 Ksi, respectively. Attempts to correlate the mechanical properties of the individual bars with the number of flaws per bar were not successful. As indicated in the Annual Reports, the flaw origins for fracture, determined by fractography, were usually found to be voids, the size of which were too small to detect by our radiography process.

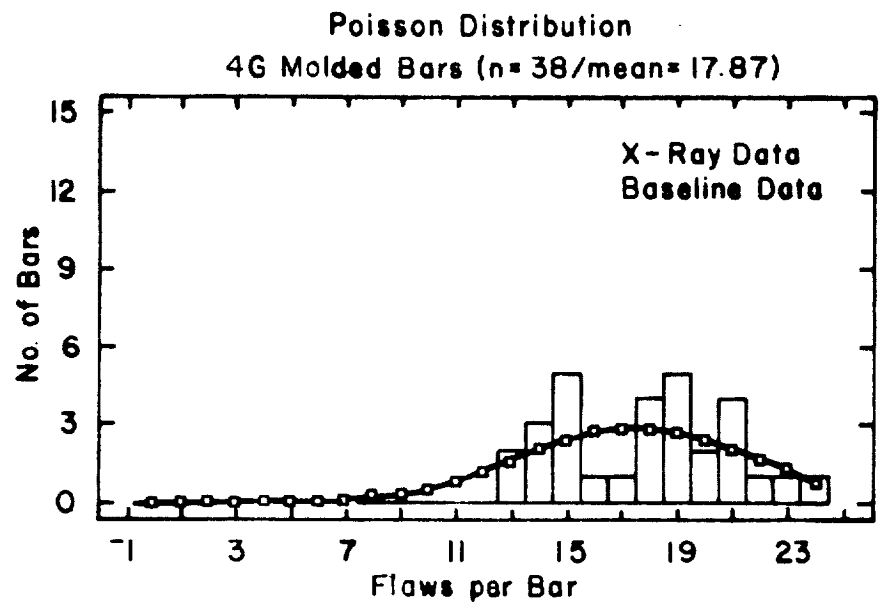
Attempts to model the flaw distributions given in Tables XXI and XXII were made and shown to be clearly represented by the Poisson distribution given by the equation:

$$f_x\ (x,L) = e^{-L}\ L^x/x!$$

where $fx\ (x,L)$ is the probability density of x, x is an integer random variable and the parameter L is greater than 0. The Poisson is an interesting distribution in that it is discrete, has only one parameter, L, and the mean and the variance of the distribution are equal to the parameter L. (Both normal and Weibull distributions, frequently used in this program, are continuous and each has two parameters.) It is frequently found in the literature that the Poisson distribution provides a realistic model for many random phenomena such as traffic accidents per week, number of radioactive particle emissions per unit time, and the number of defects per unit of some material (Ref. 8).

The Poisson distribution was used to predict the number of bars containing a given number of flaws from the mean value of flaws in the sample, and these are shown in several columns in Tables XXI and XXII. One can see that the predicted values are in reasonably good agreement with the observed values.

A comparison is made between the metallic inclusion flaws observed by X-ray in bars in the molded condition and bars in the sintered-machined condition. These comparisons are shown in Figures 18 through 21, which are plots of the predicted Poisson distribution (points and line) and the experimental data (histogram). One sees that for all four compositions the sintering process has drastically reduced the number of metallic inclusions observed by X-ray. In the case of the baseline data, the molded bars had many inclusions and these were greatly reduced in number by sintering in vacuum at 2100 ^{o}C for 10 minutes. For the Task VII-Matrix 7 materials, sintering has eliminated observable metallic



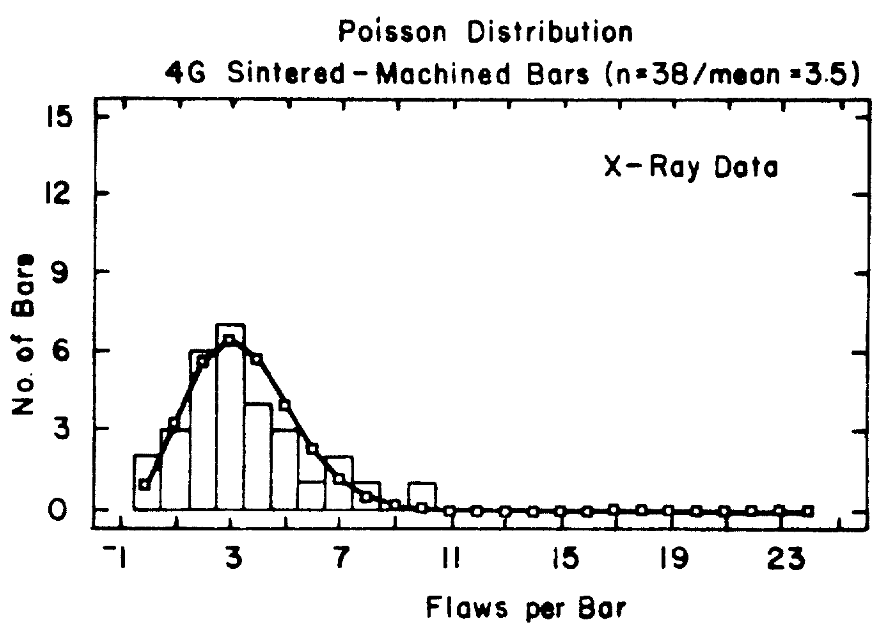


FIGURE 18. EXPERIMENTAL DISTRIBUTION OF FLAWS OBSERVED BY X-RADIOGRAPHY IN 4G MOLDED MOR BARS AND SINTERED BARS AND THE EXPECTED POISSON DISTRIBUTION

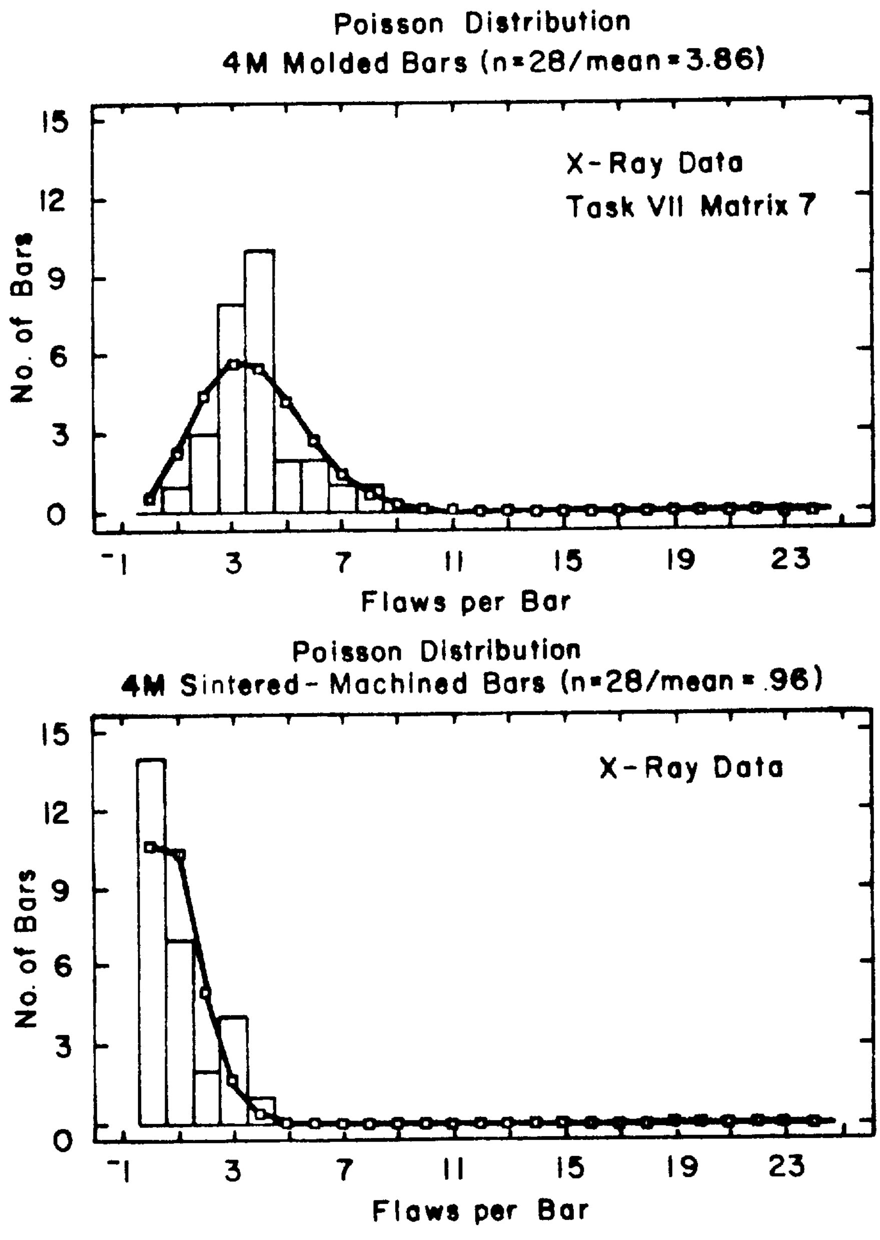


FIGURE 19. EXPERIMENTAL DISTRIBUTION OF FLAWS OBSERVED BY X-RADIOGRAPHY IN 4M MOLDED MOR BARS AND SINTERED BARS AND THE EXPECTED POISSON DISTRIBUTION

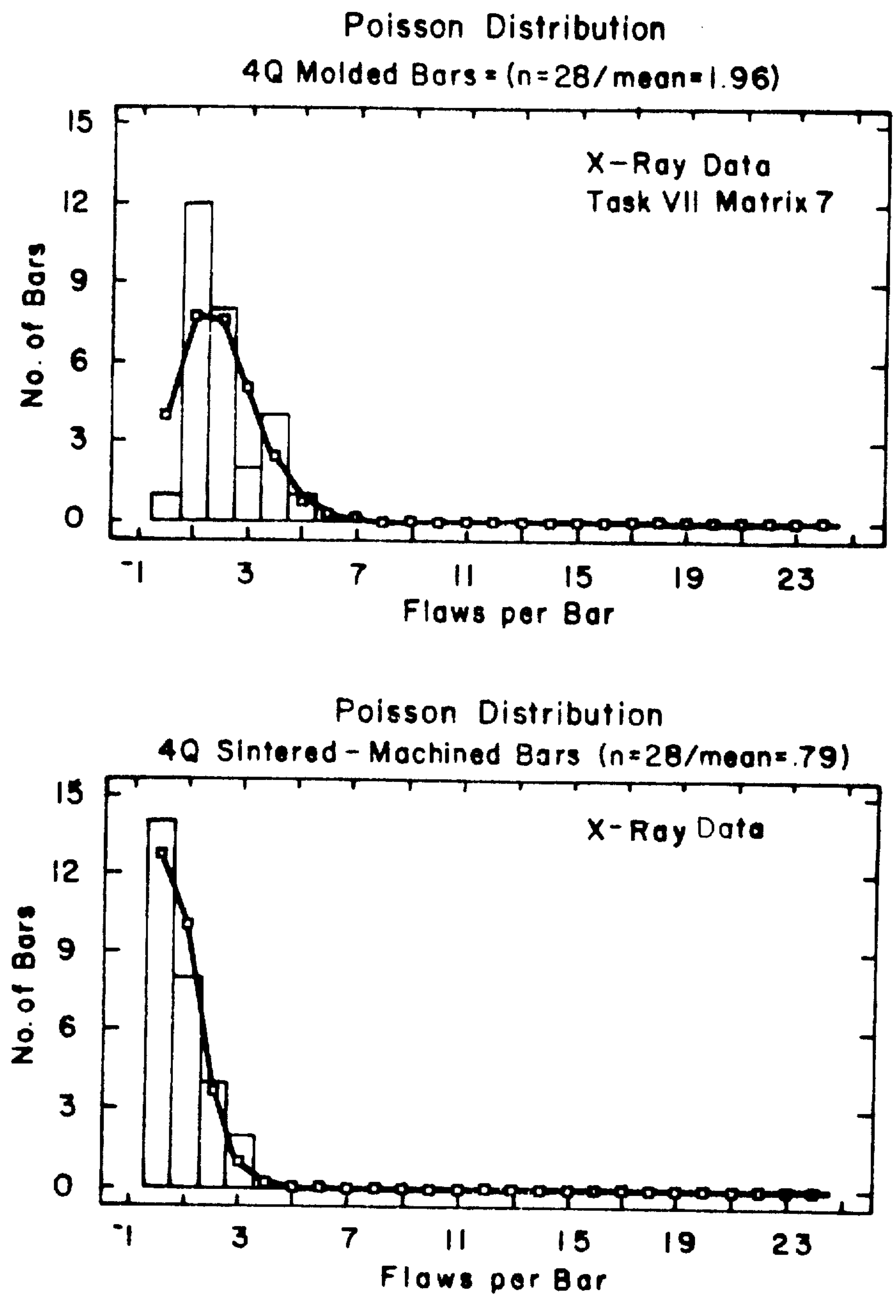


FIGURE 20. EXPERIMENTAL DISTRIBUTION OF FLAWS OBSERVED BY X-RADIOGRAPHY IN 4Q MOLDED MOR BARS AND SINTERED BARS AND THE EXPECTED POISSON DISTRIBUTION

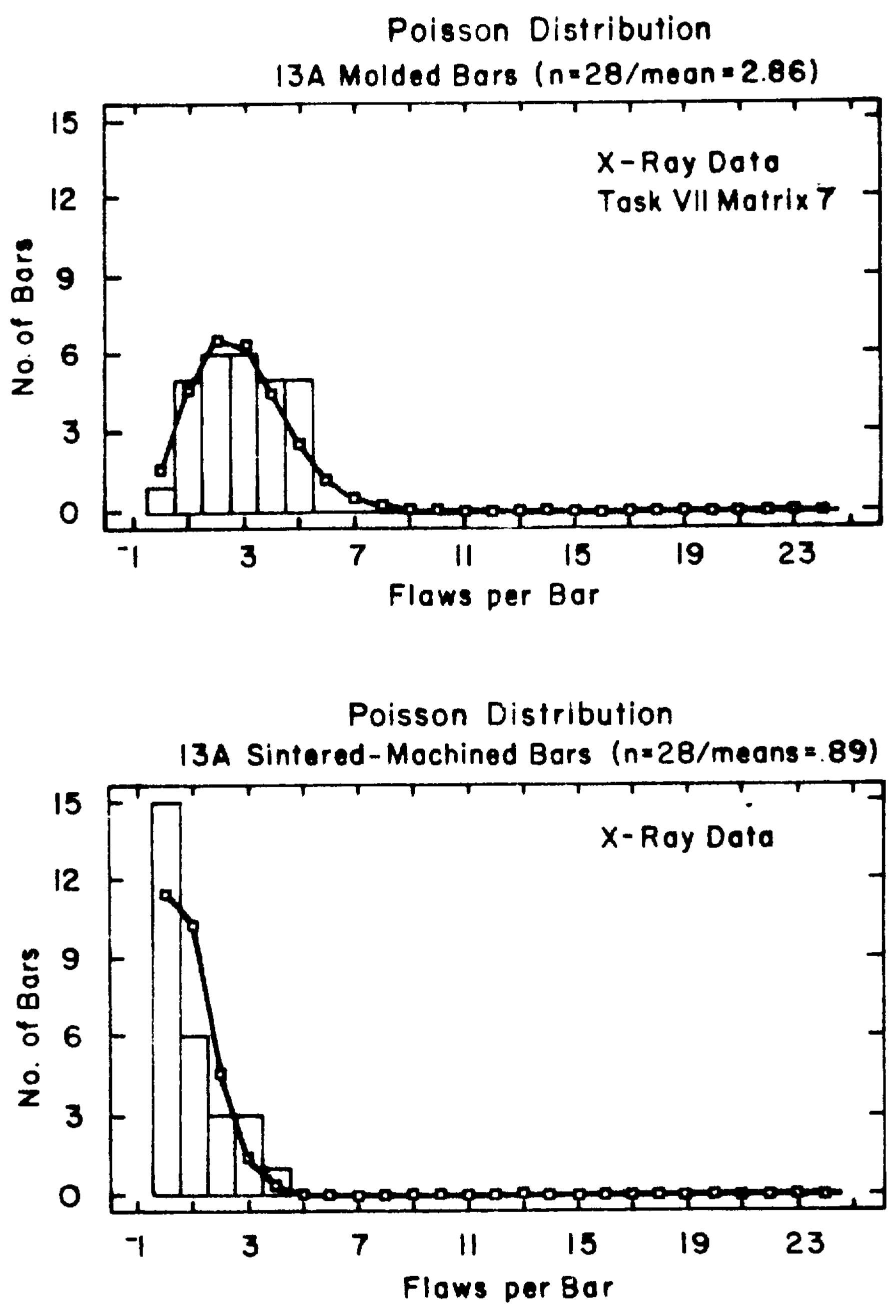


FIGURE 21. EXPERIMENTAL DISTRIBUTION OF FLAWS OBSERVED BY X-RADIOGRAPHY IN 13A MOLDED MOR BARS AND SINTERED BARS AND THE EXPECTED POISSON DISTRIBUTION

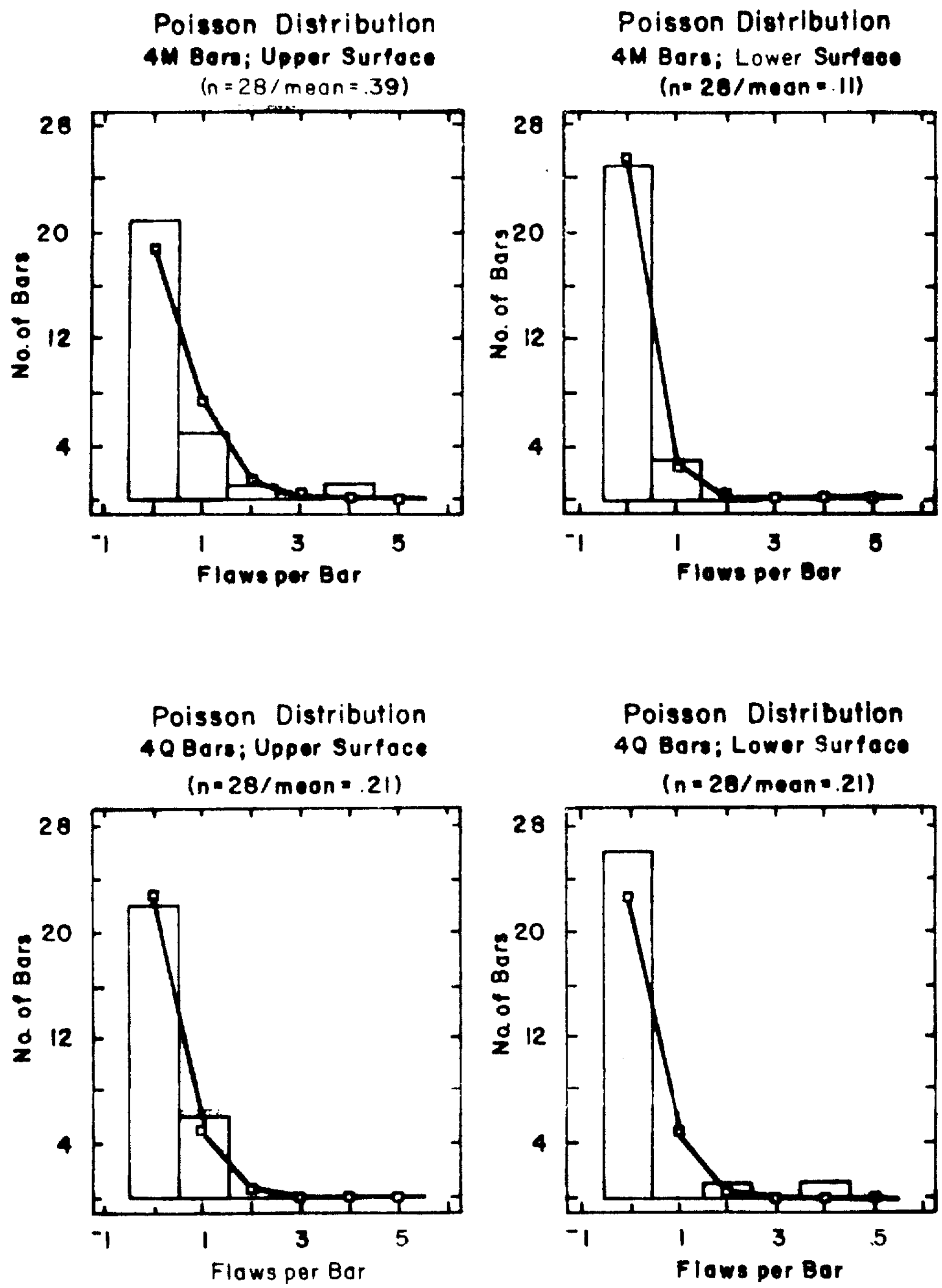


FIGURE 22. EXPERIMENTAL DISTRIBUTION OF FLAWS OBSERVED VISUALLY ON SINTERED AND OF MACHINED MOR BARS AND THE EXPECTED POISSON DISTRIBUTION

inclusions from about half of the MOR bars, and greatly reduced them in the rest of the bars. This result is certainly to be expected when one considers that the sintering cycle includes heating in vacuum to 1450 ^{o}C for half of the bars and to 1760 ^{o}C for the other half of the bars in this Matrix 7 study. All of these bars were sintered at 2120 ^{o}C in argon.

The Poisson distributions for the observed flaws on the upper and lower surfaces on the sintered-machined MOR bars from Task VII - Matrix 7 for two compositions are shown in Figure 22.

In summary, the flaw distributions are found to be adequately modeled by the Poisson distribution. The results of the reduced metallic inclusions by heating in vacuum and the elimination of metallic inclusions by vacuum treating at 1760 ^{o}C lend further support to the correctness of the present sintering cycle.

2 TASK II - MOR MATRIX

2.1 Matrix 2 Plan

The second iteration of Task II - Matrix 2 has been planned as a half fraction of a 2^5 factorial experiment with two face points. The five variables at two levels each at carbon-boron ratio, carbon-plus-boron concentration, carbon source, with and without annealing, and with and without a hot isostatic pressing post treatment. Batches were prepared and MOR bars were molded.

Plans for the second iteration of Task II (Matrix 2) have been completed and are shown in Tables XXIII, XXIV and XXV. The matrix is one of a half fraction of 2^5 factorial with each of five variables evaluated at two levels. The carbon-to-boron ratio and the total carbon and boron concentrations are evaluated in the first two variables. In recent studies we have observed some possible relationships between these two additives and this is an attempt to clarify those effects on strength and reliability. Past experience has also indicated that carbon added in the form of resin may be better than our standard lamp black additive since resin can be dissolved in a solvent and added more uniformly in our fluid mixing process. Preliminary experiments have indicated that we now have an improved method of introducing the resin material and the mix can be molded successfully. Early experiments with resin, about two years ago, produced batches which were difficult to mold. Since then, the fluid mixing processes and the attritor equipment have been utilized to improve the distribution of additives in the batches which have led to improved moldability.

Heat treatment has been shown to be beneficial for strength in several of our previous studies, and we now wish to see if heat treatment along with another post sintering treatment, hot isostatic pressing, can also lead to significant strengthening.

The half fraction of 2^5 matrix requires sixteen experiments, as seen in Table XXIV, and we have added two auxiliary points to provide continuity

TABLE XXIII

Task II/Matrix 2
Experimental Factors

ID	Factor	-	0	+
A	Ratio C:B	2:1	4:1	6:1
B	Total C+B	2%	2.5%	3%
C	C Source	Carbon Black	-	Resin
D	Annealed	No	-	Yes
E	Machined	No	-	Yes

Task II/Matrix 2
Material Composition

Ratio C:B	Total% C+B	Carbon %	Boron %	Equivalent Materials
2:1	2	1.3	.7	
2:1	3	2.0	1.0	4M/4MNO/ATT
6:1	2	1.7	.3	
6:1	3	2.6	.4	
4:1	2.5	2.0	.5	14A

TABLE XXIV

Task II/Matrix 2

Design of Experiment

(2^{5-1}; plus 2 facepoints)

Exp. #	A	B	C	D	E
1	−	−	−	−	+
2	+	−	−	−	−
3	−	+	−	−	−
4	+	+	−	−	+
5	−	−	+	−	−
6	+	−	+	−	+
7	−	+	+	−	+
8	+	+	+	−	−
9	−	−	−	+	−
10	+	−	−	+	+
11	−	+	−	+	+
12	+	+	−	+	−
13	−	−	+	+	+
14	+	−	+	+	−
15	−	+	+	+	−
16	+	+	+	+	+
17	0	0	−	+	+
18	0	0	+	+	+

(Columns A–E under the heading "Factors".)

Task II/Matrix 2

2-Factor Confounding Pattern

AB=CDE	BD=ACE
AC=BDE	BE=ACD
AD=BCE	CD=ABE
AE=BCD	CE=ABD
BC=ADE	DE=ABC

TABLE XXV

Task II/Matrix 2

Table of Experiments

Exp. #	Ratio (C:B)	Total% (C+B)	Carbon Source	Annealed (Y/N)	Hiped (Y/N)
1	2	2	C. Black	No	Yes
2	6	2	C. Black	No	No
3	2	3	C. Black	No	No
4	6	3	C. Black	No	Yes
5	2	2	Resin	No	No
6	6	2	Resin	No	Yes
7	2	3	Resin	No	Yes
8	6	3	Resin	No	No
9	2	2	C. Black	Yes	No
10	6	2	C. Black	Yes	Yes
11	2	3	C. Black	Yes	Yes
12	6	3	C. Black	Yes	No
13	2	2	Resin	Yes	Yes
14	6	2	Resin	Yes	No
15	2	3	Resin	Yes	No
16	6	3	Resin	Yes	Yes
17	4	2.5	C. Black	Yes	Yes
18	4	2.5	Resin	Yes	Yes

with previous work. The detailed list of the eighteen experiments is shown in Table XXV.

2.1.1 Preparation of Molding Mixes and Injection Molding of MOR Bars

Preparation of mixes for this matrix was initiated using Process D (attritor process). The five carbon black mixes were prepared first and showed good mixing as determined by microscopic examination (100X) of in-process dip slides. Resin batches were then processed using the same procedure, and appeared acceptable through the attritor mixing step. However, after pan drying, resin was observed to have precipitated on the surface of the dried material. The process was modified to add approximately one hour of stir drying time to increase the mix viscosity before pan drying. The process modification resolved the precipitation problem and five additional resin batches were prepared and used for the matrix.

Prior to MOR bar molding each batch is checked for spiral flow characteristics. For typical test bar molding conditions of 250 ^{o}F material and 115 ^{o}F die temperatures, the carbon black batches averaged 2.4 inches and the resin batches about 3.0 inches in the spiral flow test. Both systems were well above the 1.0 inches shown previously to be acceptable for complex shape (turbocharger) molding.

More than 1520 MOR bars were molded for this matrix; 152 bars from each of the 10 materials. Molding yields in terms of percent void-free or inclusion-free bars were determined from x-radiographs in the as-molded state. The data were shown previously in Figures 16 & 17 as the points clustered near the 35th month into the program. The void-free yield averaged about 92 % which is about normal during the third year of the program. The inclusion-free yield averaged about 35 %, slightly lower than the average of other batches prepared during the third program year. The attritor mixed materials may show a lower inclusion yield due to wear of the silicon carbide milling media. Attritor 1 & 2 batches (shown as the two data points at 26 months in Figure 17) also showed a reduced yield from ball milled batches.

CONCLUSIONS

Strength improvements in Weibull characteristic strength to above 550 MPa (80 Ksi) and an individual observation of a Weibull modulus above 16 have resulted from statistically-designed experiments focused on reducing the flaw size and determining the effects of process and composition variables on strength and reliability. Sintered densities have also increased in the injection molded and sintered SiC.

Flaw sizes were reduced from about 50 micrometers to about 15 micrometers with the introduction of the attritor processing of fluid-mixed batches and these attritor mixes have produced the highest strengths in the program.

Sintering cycle parameters were improved by the employment of two level factorial experiments.

Annealing of machined MOR bars significantly increased the strength.

Strength levels measured at 1200 and 1400 ^{o}C are the same as room temperature strength for attritor-processed bars.

Numbers of flaws per bar observed visually and by x-ray in molded and sintered bars were noted to follow a Poisson distribution. The number of flaws observed by x-ray in molded bars is drastically reduced by sintering.

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

From these results and from prior experience it appears that future improvements in the strength of silicon carbide will be found in the continual reduction in porosity, flaw size and surface damage which can be influenced by powder purity, additive and molding wax concentration and distribution, dewaxing proficiency and overall processing and handling skill and care. Careful design-of-experiment plans will lead the way in selecting the best values for the many variables involved. Improved reliability will be found with the aid of clean-room conditions with great care and skill for all processing steps which must be under statistical process control. Protection from surface damage in practical, highly-stressed applications will need to be addressed.

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15. Supplementary Notes

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16. Abstract

This is the third annual technical report for the program entitled 'Improved Silicon Carbide for Advanced Heat Engines' for the period February 16, 1987 to February 15, 1988. The objective of the original program was the development of high strength, high reliability silicon carbide parts with complex shapes suitable for use in advanced heat engines. Injection molding is the forming method selected for the program because it is capable of forming complex parts adaptable for mass production on an economically sound basis. The goals of the revised program are to reach a Weibull characteristic strength of 550 MPa (80 ksi) and a Weibull modulus of 16 for bars tested in 4-point loading. Two tasks are discussed in this report; Task VII which involves materials and process improvements, and Task II which is a MOR bar matrix to improve strength and reliability. Many statistically-designed experiments were completed under Task VII which improved the composition of the batches, the mixing of the powders, the sintering cycle and annealing. The best results were obtained by an attritor mixing process which yielded strengths in excess of 550 MPa (80 ksi) and an individual Weibull modulus of 16.8 for a 9-sample group. Strengths measured at 1200 and 1400 °C were equal to the room temperature strength. Annealing of machined test bars significantly improved the strength. Molding yields were measured and flaw distributions were observed to follow a Poisson process. The second iteration of the Task II matrix experiment is described.

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

Silicon carbide; Nonoxide ceramics; Injection molding; Sintering; Statistically-designed experiments; Factorial experiments; Flaw distribution; Poisson process; Weibull statistics

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