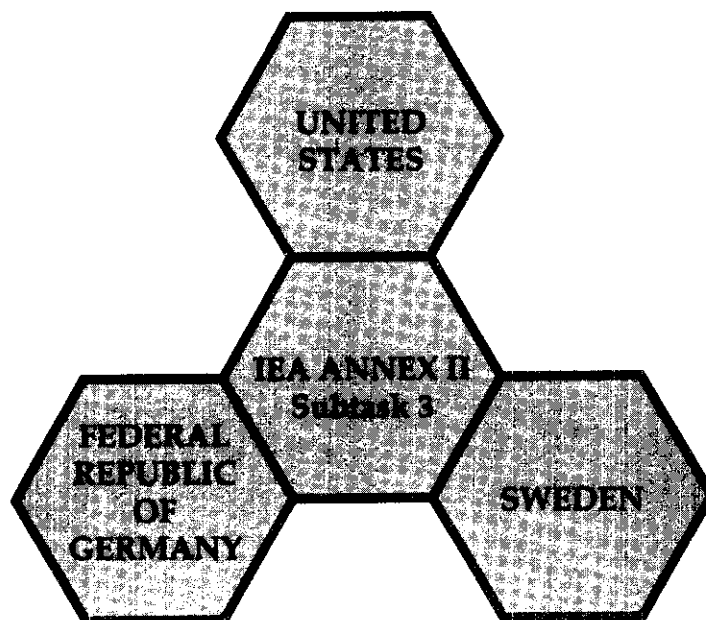


CHARACTERIZATION OF SINTERED SILICON NITRIDE AND SILICON CARBIDE STRUCTURAL CERAMICS



INTERNATIONAL ENERGY AGENCY

*CO-OPERATIVE PROGRAMME ON CERAMICS
FOR ADVANCED HEAT ENGINES
AND OTHER CONSERVATION APPLICATIONS*

PREPARED BY

KEMANORD INDUSTRIKEMI

FOR THE STYRELSEN FÖR TEKNISK UTVECKLING (STU), SWEDEN

October 1989

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BACKGROUND

The three major tasks addressed by the industrial and governmental laboratories participating in the IEA Annex II programme dealt with:

- Physical and chemical characterization of ceramic powders (Sub-task 2).
- Physical and chemical characterization of densified ceramic materials (Sub-task 3).
- Fracture strength in four-point flexure at room temperature and fractography of ceramic bar specimens (Sub-task 4).

Sub-task 1 was concerned with general information exchange in the field.

This report presents the results of work reported for Sub-task 3 by the 17 participating laboratories in the USA, Federal Republic of Germany and Sweden.

The three materials studied were provided by one company from each of the participating countries as follows:

- Hot-isostatically pressed Silicon Carbide by Elektroschmelzwerk Kempten, FRG.
- Hot-isostatically Pressed Silicon Nitride by ASEA Cerama (now ABB Cerama), Sweden.
- Sintered ("Pressureless") Silicon Nitride by GTE Wesgo, USA.

The Oak Ridge National Laboratory was responsible for sample randomization and distribution.

INTRODUCTION

A total of seventeen company and national laboratories from the United States of America, the Federal Republic of Germany and Sweden, participated in the IEA Annex II, Subtask 3 work concerned with physical and chemical characterization of densified structural ceramic materials. The work was administered by the Annex II Executive Committee and the national coordinators in each country. The detailed technical planning and organization of the Subtask was carried out by a Working Group consisting of representatives of the majority of the participating laboratories.

The overall objective of this work was to review the general status of methodology, reliability and accuracy of characterization techniques in use at the present time for densified, advanced or structural ceramic materials. In this technological survey, all methods were considered of equal interest, i.e. no restrictions were put on methodology or equipment utilized. The results are therefore to be considered as a valuable contribution to a subsequent, and vitally necessary, standardization process.

Three densified materials were chosen for study:

- A) a hot-isostatically pressed Silicon Carbide provided by Elektroschmelzwerk Kempten, FRG.
- B) a hot-isostatically pressed Silicon Nitride provided by ASEA Cerama (now ABB Cerama), Sweden.
- C) a "pressureless" sintered Silicon Nitride provided by GTE Wesgo, USA.

Great care has been taken by the material suppliers to provide homogeneous material. Oak Ridge National Laboratory, TN, USA has diligently administered the randomization and distribution of the material sample bars. These test bar materials are the same as those used in the "Subtask 4" study of fracture strength in 4-point flexure at room temperature and fractography of ceramic bar specimens. A comparative study and analysis of the results presented in the two Subtask reports could, therefore, be fruitful.

The set tasks for characterization were the determination of:

- 1) density
- 2) porosity
- 3) chemical composition
- 4) phase composition
- 5) microstructure

From the outset, it was agreed within the Working Group that the individual laboratories were recommended to take part only in the analytical tasks for which the laboratory had developed a routine and proven methodology.

The present report consists essentially of a condensed summary of the individual laboratory reports, and very little effort has been spent on critically evaluating the results. In at least one case, i.e. determination of density, sufficient data has been reported to warrant a deepened statistical treatment. In most other cases, where only a few laboratories have participated and widely differing experimental methods have been used, the results may serve only as guidelines; i.e. as a basis for further discussion and as pointers to the need for future work.

A problem encountered in the majority of reports was the brevity or absence of information on sample form ("as-received" surface, fracture surface, ground sample, etc.), sample preparation techniques for each specific analysis and indeed even the method of analysis. The same applies to definition of equipment used, instrumental conditions and calibration procedures. On request, complementary information on these points was submitted from many laboratories after the filing of the initial reports, and this present document has been amended with respect to that information. Likewise, notice of errors in the draft report were gratefully received from many sources via the coordinators in each participating country. These errors have been rectified. Nevertheless, it is felt that even more detailed information on sample treatment and method of analysis, presumably not proprietary, would have enhanced the value of the subtask report even more.

In accordance with ruling by the IEA Executive Committee for this Annex, participating company and government laboratories and their data are reported anonymously in this final report. Distribution is at the discretion of the Annex II Executive Committee.

GENERAL COMMENTS AND CONCLUSIONS

The formal objective of Subtask 3 has been to survey presently-applied methods for characterization of densified, advanced ceramic materials. The basic approach has been to allow use of all methods made available by the participating laboratories, and to study a rather broad range of characterization parameters in a "round-robin" study. In a critical review of the results, in hindsight, it is easy to identify weaknesses and faults. Considering the scope of work, the geographical distances and the large number of organizations involved, it is not surprising that difficulties in holding time schedules and generally coordinating the work have been experienced. By the same accounts, it is very difficult to come to any other conclusion than that this work has been very successful and is of great value.

The following general comments are put forward (by the editor of this report) relative to the various characterization parameters studied:

Density:

Reasonably good agreement was obtained between all participating laboratories. A number of laboratories demonstrated clearly that careful work should result in fully acceptable accuracy and reproducibility. Results and condensed statistics are given in graphic form in figs. 8 to 19.

Porosity:

It is apparent from the reported results, that the concept of "porosity" and the applicable methods for its determination should have been discussed and defined more clearly at the outset. Results refer to "total", "open" and "surface" porosity, and both volume-% and area-% values were reported. Utilization of density measurement (measured : theoretical) obviously requires that an accurate value for the "theoretical" density is available. Difficulties are encountered, particularly in the case of multi-phase ceramics and when high concentrations of sintering additives are used. The most comprehensive data, from Lab.# 2, are presented graphically in fig. 20.

Chemical analysis:

Detailed analysis of the data is difficult, since in most cases only a small number of laboratories have participated and the reported results are few from a statistical viewpoint. Considerable differences in sample preparation, method of analysis and equipment must also be taken into consideration. For example, the use of emission spectroscopy as a qualitative or semi-quantitative analytical technique may not be considered of value in standardization or even pre-standardization work. In many laboratories, however, it is a quick and available (and therefore "inexpensive") technique which may well serve its purpose in the "screening" of powders and densified materials. Therefore, it should be of significant interest in this present report and in future characterization work to be able to compare the accuracy, repeatability and amount of information obtained by use of various techniques in relation to the cost of work and equipment involved. The results and experience gained in the analytical chemistry work carried out within subtask 3 should be considered together with the vast amount of information gathered in subtask 2; powder characterization. Much of the experience gained and many of the problems encountered are relevant and common to both studies, and both will profit from a detailed comparison of the data, background information on methodology, etc.

Phase analysis:

No particular problems were encountered in connection with identification of the major phases, and good agreement was also reached for some of the minor phases, e.g. $\text{Si}_2\text{O}_3\text{N}_2$ in the HIP-silicon nitride. Differences in detection and identification of minor phases can probably be ascribed to variations in equipment and measuring conditions which affect resolution. Analysis of "as-received" sample surfaces and milled samples may give differing spectra, although there is no strong evidence that this is the general case. Variation in material composition from test-bar to test-bar may not be negligible, and some laboratory results would seem to indicate that such differences can exist. A standardized reporting of d-values and relative intensities would have been useful for data comparison. Far from all laboratories have submitted original spectra in their reports.

Microstructure:

Of the parameters included in this study, the task of quantifying the "microstructure" of a particular material is clearly the most difficult. The wealth of information contained in a micrograph is fairly easily, but subjectively, assimilated by the trained eye.

To describe what is to be seen is difficult, particularly in numerical terms. The different optical methods available and the choice of magnification lend themselves to the disclosure of different types of information and show different aspects of the microstructure, cf. low-power visible microscopy, SEM and high resolution TEM. Examples of excellent work utilizing these different techniques are to be found in some of the original laboratory reports. This material is well worth further study and discussion by qualified microscopists, and could presumably result in valuable recommendations concerning sample preparation and microscopy techniques.

Excellent work utilizing image analysis was contributed by Lab.# 12. The author of the laboratory report has also commented extensively on the theory and other aspects of the work, which would be of significant value in future activities in the field. An obvious drawback to date with image analysis techniques is that they are far from widespread and are expensive.

Reference should also be made to special studies reported such as the high-resolution TEM work by Lab.#6, the extensive ultrasonic testing of a very large number of test bars by Lab.#9 and residual stress measurements forwarded through Lab.#16. All these contributions are worthy of further study and analysis.

Finally, it is fervently hoped that the foundation put down by the participants in this "Sub-task 3" project be utilized and built upon. Conclusions to be drawn from the present study and recommendations for future work should be done by expertise and be a sound base for the planning of the standardization work to come.

ACKNOWLEDGEMENTS

The time, effort and funding provided by the individual laboratories and their staff participating in the planning, carrying out and reporting of this work cannot be overestimated and must be very gratefully acknowledged.

The participating laboratories, in alphabetical order and irrespective of nationality, were;

AC Spark Plug; Alcoa; Cremer FI; Feldmühle; GTE; Hoechst Ceramtec; Hutschenreuther; ISD; KemaNord Engineering Ceramics; KFA Jülich; Lonza; Mat.Tech.Lab, US Army; NASA; NBS (now NIST); Oak Ridge NL; Sigri; Sohio; Swedish Ceramic Institute (and the University of Technology Linköping).

The contracting parties of the Annex II Agreement, i.e. the U.S Department of Energy (DOE), the Kernforschungsanlage Jülich GmbH, authorized by the Bundesministeriums für Forschung und Technologie (BMFT) and the Swedish National Board for Technical Development (STU) are thanked for the provision of overall funding and organizational support.

The operating agent for the Agreement has been the DOE, with program management provided by the Heat Engine Propulsion Division of the Office of Transportation Systems (OTS). The DOE Oak Ridge National Laboratory has borne the overall management responsibility for coordinating the activity in the U.S. The responsible organization in the Federal Republic of Germany has been the Kernforschungsanlage Jülich GmbH, and within Sweden the Swedish National Board for Technical Development (STU) and the Swedish Ceramic Institute (SCI).

Appropriate thanks are given to the large number of individuals who have contributed in various ways to the completion of this present report. The valuable assistance of Dr. Victor J. Tennery, Oak Ridge and Dr. Richard Neumann of KFA Jülich, and their colleagues is to be particularly stressed in this context.

Ljungaverk, Sweden

August 1989

M.E.Hatcher

International Energy Agency : Annex II.
Co-operative Programme on Ceramics for Advanced
Engines and Other Applications.

SUBTASK 3 : CERAMIC CHARACTERIZATION

RESULTS
FOR
MATERIAL "A"
HOT-ISOSTATICALLY PRESSED SILICON CARBIDE

Test material provided by Elektroschmelzwerk Kempten (ESK), FRG.

- | | |
|-----|-------------------|
| A.1 | Density |
| A.2 | Porosity |
| A.3 | Chemical Analysis |
| A.4 | Phase Analysis |
| A.5 | Microstructure |

RESULTS

A. HIP-SiC (ESK) MATERIAL

A. 1 DENSITY.

Average density and standard of deviation are tabulated in table A1. All reported values for the geometric and immersion densities (in water and toluene) are presented in tables A2, A3, A4 and A5.

In table A1 below, these results are presented in condensed form as average values and standard deviations for each method and participating laboratory. For the sake of clarity, all averages have been rounded off to three decimals. (A "5" in the fourth decimal is rounded upwards, a "4" down). Standard deviations are given with two significant figures. (In case a third significant figure > 0 was reported, the second significant figure has been rounded upwards).

The column "n" gives the number of determinations. This is generally, but not always, equal to the number of specimens examined by that laboratory.

HIP-SiC BULK DENSITY (g/cm³) **TABLE A1.**

Lab#	Geometric	Immersion		n
		Water	Toluene	
1	3.197 ± 0.015	3.199 ± 0.016	3.198 ± 0.017	10
2	3.198 ± 0.013	3.193 ± 0.018	3.188 ± 0.020	10
3	3.160 ± 0.019	3.201 ± 0.019	3.205 ± 0.019	5
4	3.264 ± 0.020	3.208 ± 0.025		10
6	3.186 ± 0.025			10
7		3.200	3.204	2
8		3.214 ± 0.007	3.205 ± 0.005	10
9		3.230		6
10	3.190 ± 0.021	3.220 ± 0.013	3.197 ± 0.017	5
11		3.220		?
12			3.192 ± 0.001	60
16		3.178 ± 0.023		10
<hr/>				
Average	3.206 ± 0.038	3.200 ± 0.021	3.195 ± 0.015	
n	45	60	98	

General conclusions which may be drawn are:

- a) that there is no significant difference between reported density values determined by the two alternative immersion methods.

b) that standard deviations reported for all methods and by the majority of laboratories are comparable, ranging between 0.013 and 0.025 (in g/cm^3 units) or 0.4 - 0.8 %. Standard deviations reported by Lab# 8, and especially Lab# 12, are notably lower.

c) that geometric densities compare well with immersion densities, indicative of the "negligible" open porosity and low total porosity.

d) that of the measurement value populations of geometric densities reported, the average value reported by Lab# 4 is notably high.

Note: Lab# 11 has not reported individual values or the number of determinations/specimens. In calculating the average for the whole population, the reported value has been weighted as a single value for this laboratory.

HIP SILICON CARBIDE

TABLE A2.

BULK DENSITY (g/cm³)

Lab. #	Sample #	Geometric	Immersion			
			Water *	Water	Toluene	
1	152	3.211	3.2143	3.2071	3.2102	
	193	3.207	3.2135	3.2063	3.2070	
	153	3.206	3.2125	3.2053	3.2040	
	149	3.203	3.2127	3.2055	3.2047	
	138A	3.194	3.2030	3.1959	3.1900	
	118	3.200	3.2129	3.2057	3.2066	
	92	3.192	3.2145	3.2073	3.2054	
	171	3.162	3.1634	3.1563	3.1552	
	198	3.213	3.2120	3.2048	3.2022	
	43	3.183	3.2001	3.1930	3.1903	
		Average	3.197	3.2059	3.1987	3.1976
		Std. Dev.	.015	.0157	.0157	.0164
	2	427	3.1671		3.1496	3.1383
460		3.2014		3.1941	3.1971	
168		3.2119		3.2075	3.1935	
347		3.2043		3.1856	3.1799	
322		3.2046		3.1980	3.1855	
464		3.1926		3.1861	3.1816	
700		3.1937		3.2026	3.2018	
363		3.2086		3.2081	3.1908	
320		3.1985		3.2077	3.2069	
332		3.2008		3.1938	3.2024	
		Average	3.1984		3.1933	3.1878
	Std. Dev.	.0125		.0175	.0196	
3	534	3.185		3.183	3.209	
	403A	3.154		3.210	3.222	
	403B	3.133		3.178	3.173	
	438A	3.162		3.214	3.214	
	438B	3.167		3.219	3.207	
		Average	3.160		3.201	3.205
	Std. Dev.	.019		.019	.019	

* According to ASTM C-373 temperature, density of water, air not compensated.

HIP SILICON CARBIDE TABLE A3.
 BULK DENSITY (g/cm³)

Lab.#	Sample #	Geometric	Immersion	
			Water	Toluene
4	341	3.279	3.137	
	387	3.282	3.219	
	376	3.298	3.218	
	199	3.244	3.220	
	325	3.262	3.211	
	301	3.248	3.217	
	140	3.247	3.218	
	349	3.238	3.214	
	174	3.279	3.217	
	101	3.259	3.206	
	Average	3.264	3.208	
	Std. Dev.	.020	.025	
	6	418	3.1943	
614		3.1914		
202		3.2049		
231		3.1887		
159		3.1994		
233		3.2016		
221		3.1389		
463		3.1996		
575		3.1420		
615B		3.2027		
Average		3.1863		
Std. Dev.		.0247		
7		186		3.2017
	345		3.1981	3.2066
	Average		3.1999	3.2044
8	654		3.220	3.209
	278		3.225	3.205
	276		3.213	3.205
	699		3.218	3.206
	562		3.219	3.207
	636		3.218	3.207
	583		3.207	3.205
	690		3.205	3.206
	680		3.202	3.190
	671		3.212	3.205
	Average		3.214	3.205
	Std. Dev.		.007	.005

HIP SILICON CARBIDE TABLE A4.

BULK DENSITY (g/cm³)

Lab.#	Sample #	Geometric	Immersion	
			Water	Toluene
9	Average (n = 6)		3.230	
10	Reported (n = ?)		3.220	3.197
11	Reported (n = ?)		3.220	
12	(See Table A5)			
16	705		3.1985	
	741		3.1508	
	822		3.1783	
	828		3.2036	
	919		3.1577	
	Average		3.1778	
	Std. Dev.		.0236	
	705		3.2051	
	741		3.1491	
	822		3.1757	
	828		3.2019	
	919		3.1595	
	Average		3.1783	
	Std. Dev.		.0249	

HIP SILICON CARBIDE

TABLE A5.

BULK DENSITY (g/cm³)

Lab. #	Sample #	Immersion (Xylene)	Sample #	Immersion (Xylene)
12	786	3.193	851	3.197
	802	3.191	854	3.199
	814	3.200	883	3.189
	858	3.208	885	3.163
	862	3.199	902	3.198
	867	3.199	914	3.195
	875	3.198	925	3.206
	876	3.176	931	3.194
	890	3.179	955	3.183
	892	3.149	958	3.199
	904	3.197	962	3.209
	930	3.194	967	3.194
	942	3.200	970	3.198
	945	3.199	975	3.195
	948	3.206	993	3.193
	953	3.195	1001	3.198
	978	3.205	1003	3.142
	1011	3.176	1004	3.204
	1019	3.196	1074	3.198
	1033	3.197	1076	3.188
	1043	3.172	1102	3.182
	1081	3.196	1107	3.205
	1094	3.190	1113	3.168
	1096	3.196	1119	3.192
	1101	3.194	1122	3.204
	1111	3.208	1170	3.186
	1114	3.196	1184	3.206
	1123	3.207	1188	3.206
	1172	3.160		
	1175	3.199	Average	3.192
	1198	3.183		
	816	3.195	Std. Dev.	.014

RESULTS

A. HIP-SiC (ESK) MATERIAL

A.2 POROSITY.

TABLE A6.

Lab#	Spec.#	Porosity (vol%)	Note
2	427	0.064	Max. value = 0.627%
	460	0.627	
	168	0.026	Min. value = 0.013%
	347	0.102	
	322	0.064	
	464	0.026	
	700	0.026	
	363	0.013	
	320	0.051	
	332	0.013	
	Average	0.045	
	Std. Dev.	0.029	
4	341	2.63	ASTM Standard E 562-83 (Area% porosity by using several SEM micrographs)
	199	0.62	
	301	0.47	
	Average	1.24	
6	418	0.707	Based on theoretical density = 3.217 g/cc.
	614	0.794	
	202	0.375	Min. value = 0.375 Max. value = 2.43
	231	0.880	
	159	0.547	
	233	0.479	
	221	2.426	
	463	0.540	
	575	2.332	
	615B	0.445	
	Average	0.953	
	Std. Dev.	0.729	

A.2 POROSITY.

TABLE A6.

(Contd).

Lab#	Spec.#	Porosity (vol%)		Note
		Mean	Std.Dev.	
8	654	0.01		Max. value = 0.06%
	278	0		Min. value = 0
	276	0.03		
	699	0		
	562	0.01		
	636	0		
	583	0.01		
	690	0.01		
	680	0.01		
	6/1	0.06		
Lab#	Spec.#	Porosity (area%)		Note
		Mean	Std.Dev.	
12	876	1.80	0.09	Area% (Image analyzer IBAS 2 / Kontron)
	930	1.60	0.13	
	1114	2.47	0.10	
	Average	1.96	0.40	(5 measurements for each specimen)
16	-	0.020		Open porosity - surface water film.

Addendum.**Lab# 12.**

Quoting the original laboratory report;

"Measurement Data for HIP-SiC (ESK)".

- Mean value D/ standard deviation s

$$D = 3.192 \text{ g/cm}^3 / s = 0.001$$

- Mean total porosity Pt:

Taking $D_{th} = 3.217 \text{ g/cm}^3$ as the value of the theoretical density of α -SiC, the mean total porosity P_t is calculated as

$$P_t = 0.78 \%$$

RESULTS

A. HIP-SiC (ESK) MATERIAL

A.3 CHEMICAL ANALYSIS

HIP SILICON CARBIDE

TABLE A6.

BULK CHEMICAL ANALYSIS (MAJOR / MINOR)

All concentrations in wt%.

Lab.#	Sample#	Major		Minor			
		Si	C (tot.)	Si (free)	C (free)	N	O
2	363	69.40	29.60		.16		
	320	69.20	29.60		.15		
3	243		29.08				
	246		29.77				
	305		29.55				
	393		29.56				
	446		29.14				
	453		29.77				
	492		29.74				
	Avg.		29.52				
	Std. Dev.		.29				
5	172					.010	.064
	441					.010	.030
7	9	68.08	28.90				.12
	62	65.76	29.30				.12
	119	66.83	29.50				.23
	Avg.	66.89	29.23				.16
9			29.59	0.22	0.47	0.17	0.37
10	(*)		29.74		0.3	.063	.14
11	-		30.02	.24	.40		
	-		30.02	.22	.37		
	-		29.97		.37		
	-		30.03		.41		
	Avg.		30.01		.39		
12	-	69.81	29.92	.18	.15		
13	-			.03	.22/.15		.55

(*) Dry milled and mixed sample of IEA # 1112, 1126, 1131, 1143, 1186 and 1196.

HIP SILICON CARBIDE

TABLE A7.

BULK CHEMICAL ANALYSIS (TRACE)

All concentrations in wt%.

Lab.#	Sample#	Al	B	Ca	Co	Cr	Fe
2	332	.02	.04		.3		
	700	.01	.03		.2		
	320	.02	.03		.19		
	363	.02	.04		.15		
	Average	.02	.04		.21		
3	243	.04	.01	<.01			<.001
	246	.05	.01	<.01			<.001
	305	.05	.01	<.01			<.001
	393	.05	.01	<.01			<.001
	446	.05	.01	<.01			<.001
	453	.05	.01	<.01			<.001
	492	.06	.01	<.01			<.001
Average	.05	.01	<.01			<.001	
5	172	.048	.014	.006		.015	.037
	441	.022	.004	.006		.012	.054
7 **	9	.0080		.0015		.0075	.0075
	62	.0200		.0020		.0050	.0300
	119	.0170		<.0010		<.0010	.0900
9		.22		.19			.03
10	(***)	<.02	<.1				.16
11 *	?	.08	.036	.02			.007
	?	.07	.029	.02			.007
	?	.08		.02			.007
	?	.08		.02			.014

(* Reported as oxide; recalculated).

(** Reported as ppm).

(***) Dry milled and mixed sample of IEA # 1112, 1126, 1131, 1143, 1186 and 1196.

HIP SILICON CARBIDE

TABLE A8.

BULK CHEMICAL ANALYSIS (TRACE)

All concentrations in wt%.

Lab.#	Sample#	Al	B	Ca	Co	Cr	Fe
12	NAA 786	<.057		<.005	4.00E-7	2.40E-5	.00014
(**)	" 930	<.057		<.005	5.00E-7	2.70E-5	.00025
	" 1081	<.057		<.005	1.20E-5	2.37E-4	.01400
	" 1114	<.057		<.005	4.00E-7	2.40E-5	.00022
	" 1172	<.057		<.005	4.00E-7	2.40E-5	.00032
(***)	ICP-AES:Avg	.043	.04- .09(**)	.05- .56(**)		.007	.019
13	?	.037		.007			.10
(*)							
14	1200	.0060		.0004			<.0050
(**)	979	.0071		<.0001			<.0050
	1073	.0104		.0006			<.0050
	1017	.0079		.0025			<.0050
	1145	.0029		<.0001			<.0050

(*) Reported as oxide; recalculated.

(**) Reported as ppm.

(***) "Average" refers to a ground sample from 6 specimens with IEA # 814, 851, 858, 862, 967, 1003 for two weights and three analyses for each).

HIP SILICON CARBIDE

TABLE A9.

BULK CHEMICAL ANALYSIS (TRACE)

All concentrations in wt%.

Lab.#	Sample#	Mg	Mo	Ti	V	Zr	K
2	332	<.005		.04			
	700	<.005		.03			
	320			.01			
	363			.02			
3	243	<.001	.04	.008	<.005	.001	
	246	<.001	.04	.01	<.005	.001	
	305	<.001	.04	.008	<.005	.001	
	393	<.001	.04	.008	<.005	.001	
	446	<.001	.04	.008	<.005	.001	
	453	<.001	.04	.008	<.005	.001	
	492	<.001	.004	.01	<.005	.001	
	Average	<.001	.03	.009	<.005	.001	
5	172	.001		.025			
	441	.005		.019			
7	9					.0130	.0010
	62					.0100	<.0010
	119					.0100	<.0010
9			.1				
10	(***)	<.01					
11 (*)	?	.003		.03		.0150	.008
	?	.006		.03		.0060	.008
	?	.003		.03		.0100	.008
	?	.002		.02		.0060	.008

(*) Reported as oxides; recalculated.

(**) Reported as ppm.

(***) Dry milled and mixed sample of IEA # 1112, 1126, 1131, 1143, 1186 and 1196.

HIP SILICON CARBIDE

TABLE A10.

BULK CHEMICAL ANALYSIS (TRACE)

All concentrations in wt%.

Lab.#	Sample#	Mg	Mo	Ti	V	Zr	K
12	NAA 786		.0011	.0348	.0094	.0046	
(**)	" 930		.0012	.0392	.0092	.0053	
	" 1081		.0009	.0212	.0077	.0026	
	" 1114		.0011	.0357	.0090	.0045	
	" 1172		.0011	.0320	.0094	.0046	
	ICP-AES Avg.	.003	.003	.020	.008		.073
13	?	.01		.02			
(*)							
14	1200	<.0001		.0184			
(**)	979	<.0001		.0168			
	1073	<.0001		.0189			
	1017	<.0001		.0199			
	1145	<.0001		.0111			

(*) Reported as oxides; recalculated.

(**) Reported as ppm.

RESULTS.

A. HIP-SiC (ESK) MATERIAL

A.4 PHASE ANALYSIS.

TABLE A12.

Lab#	Major	Minor	Comments
1	6H	8H, β -SiC	1
2		(6H, 8H, β -SiC)	2
3	12H	8H(?)	3
4	6H	+ 4H or 8H	4
5	12H	8H	5
6	6H	4H + ?	6
8	6H	4H, 15R	8
9	(SiC)		9
10	6H	4H, 15R	10
11	(SiC)	(Si ₃ N ₄ - possible)	
12	6H	4H, 15R	12
13	6H	15R, 4H	13

Comments:

The following comments concerning the phase identification from the X-ray spectra were reported. The comments and points of discussion are published in this report either in abbreviated form (Lab.# 1) or in extenso (all others). For descriptions of sample preparation procedures and measurement conditions, when reported, see Section M.4 METHODOLOGY; Phase Analysis.

COMMENT 1.

Sample # 138 was examined both in bulk (as-received specimen surface) and in powdered form. The recorded spectra were (nearly) identical. One major and two minor phases (estimated at ca. 10 - 15% each) were identified. The identified phases accounted for all detected peaks.

A problem was encountered in connection with the JCPDS data base. Card 29-1128 (6H polytype) gives the best fit, but has been retracted /deleted from the data base, without replacement with an updated version. Card 29-1131 (also 6H; same crystal structure and space group as for 29-1128) is also a good fit, but recorded peaks at 2.00\AA and 1.68\AA are not given on this card, but are given in the "deleted" 29-1128 data.

The minor phases were identified by comparison of d-values and intensities with JCPDS Cards 29-1127 (8H-polytype) and 29-1129 (cubic β -SiC). In the case of the latter phase, a few peaks overlap the 6H-spectrum, thus complicating evaluation/intensity comparisons.

COMMENT 2.

This sample (IEA # 320) may contain two or possibly three forms of SiC because it has similarities to JCPDS Cards No. 29-1127, 29-1128 and 29-1129. A small amount of WC is also present from grinding. Similar results were obtained for sample IEA # 363.

COMMENT 3.

Major phase SiC 12H + trace amount of (possible) 8H.

COMMENT 4.

It was clear that there were at least two polymorphs of alpha-SiC present in all samples examined (IEA samples 199, 301, 325, 347, 376, 387). The primary phase was alpha-SiC Moissanite-6H (>95%).

With reference to minor phase(s) detected, a complementary comment - "4H or 8H, unable to identify" - has been given.

COMMENT 5.

Surface of bulk sample run. Major phase was SiC 12H with trace amount of SiC 8H.

COMMENT 6.

In a spreadsheet report dated 11 February 1988, spatial characteristics of the matrix were reported for IEA samples # 418, 614 and 202 as being 93.00 ± 3.00 % crystalline SiC, 5.00 ± 2.00 % "phase B" and 2.00 ± 1.00 % "phase C". SiC major phase is 6H polytype (JCPDS# 29-1129) with frequent faulting (c. 40/micron). Phase B is the 4H polytype of SiC (JCPDS# 29-1127). Phase C is carbon in the form of graphite (JCPDS# 23-64). Non-crystalline phase percentage was reported as 0.00 %.

In a spreadsheet report dated 9/14/87, spatial characteristics of the matrix were reported for the same, above-mentioned samples as being 99.50 % crystalline SiC and 0.50 % crystalline "Phase B". SiC matrix is 6H polytype with frequent faulting (c. 40/micron). Phase B is carbon in the form of graphite. Non-crystalline phase percentage was reported as 0.00%. Percentage of graphite and grain size distributions are based on TEM micrographs and are therefore semi-quantitative at best.

In a separate, detailed report on the spatial characteristics of the grain boundaries of the HIP-SiC material, the authors compare TEM and X-ray diffraction results. The TEM studies confirm the identification of the major 6H polytype phase and the presence of a high concentration of stacking faults which in turn give rise to the presence of 4H, and possibly other polytypes. Quoting the authors: "If we assume that each fault produces a 1 nm region of another polytype (other than 6H) (such as 4H), the fraction of the second polytype by this crude estimate is about 5%, which compares well with the X-ray diffraction data".

COMMENT 8.

Semi-quantitative results were reported for IEA specimens # 654, 278, 276, 699, 562, 636, 583, 690, 680, and 671. All specimens showed only one phase, namely SiC. The 6H polytype was the major phase with low amounts of 4H and 15R as is typical.

COMMENT 9.

In the X-ray diffraction analysis, only SiC was detected.

COMMENT 10.

The following data were reported;

(Mat. $\leq 100 \mu\text{m}$)

$\alpha / \beta = 93/7$

$6\text{H} > 4\text{H} > 15\text{R}$

COMMENT 12.

HIP-SiC (ESK) consists of α -SiC with the major modifications 6H (dominant), 4H and 15R: identical results for specimens # 1081 and # 1172, examined in bulk as received.

COMMENT 13.

Quantitative results were reported for the polytypes;

	15R (α)	6H (α)	4H (α)	3C (β)
Vol. %	5-10	90	≤ 5	0

The determination was carried out according to the method given in "The quantitative calculation of SiC-polytypes from measurements of X-ray diffraction peak intensities." J.Ruska et al., Journal of Mat. Sci. 14 (1979) 2013 - 2017.

RESULTS.

A. HIP-SiC (ESK) MATERIAL

A.5 MICROSTRUCTURE.

TABLE A13.

Grain Size Distribution

The table below shows the grain size distribution (median and standard deviation) and aspect ratio as reported in the Lotus spreadsheet for spatial characteristics, or in similar condensed form.

Lab.#	Sample#	Grain Size Median	Distribution Std.Dev.	Aspect Ratio	Comment
1	152/1	2.75	0.86	1.33	A
	/2	2.71	0.75		
	/3	2.89	0.78		
	/4	3.04	0.81		
	/5	2.93	0.77		
6	202	3	1	3:2	B
	418	2	1	3:2	
	614	2	1	3:2	
8	654	2.18	1.46	1.64	C
	278	2.22	1.51	1.66	
	276	2.24	1.66	1.65	
	699	2.17	1.42	1.64	
	562	2.28	1.59	1.68	
	636	2.44	1.67	1.70	
	583	2.22	1.57	1.66	
	690	2.24	1.54	1.66	
	680	2.11	1.51	1.65	
	Average	2.23		1.66	
Std. Dev.	0.09		0.02		
9	825	(1 - 5 micron)			D
	837				
	889				
10		(2 - 3 micron)			E
11					F
12	876	2.51		1.59	G
	930	2.59		1.54	
	1114	2.15		1.56	
	Average	2.39		1.56	
	Std. Dev.	1.13			

COMMENT A.

Grain sizes are equivalent circular diameter (in microns). In the above table, the sample identifications 155/1 to /4 relate to IEA specimen #155 and AC Spark Plug micrographs 8753/1 - 4. Designation 155/5 is identified at AC as micrograph 8754. Micrographs 8753 and 8754 are parallel and perpendicular surfaces respectively. Two hundred (200) grains measured in each micrograph.

In the "Grain Size Distribution" table of the Lotus spreadsheet, 15 classes with medians ranging from 0.75 to 7.75 microns, and with a class width of 0.25 microns are reported. (The reported class width is actually one half of the difference between two adjacent median values. Class width is therefore 0.5 microns. Ed.). Frequency count is reported in %-values.

COMMENT B.

Grain size distributions are based on TEM micrographs. All grains are elongated normal to the c-axis with the aspect ratios shown. Grain boundary thickness is reported to be < 0.0015 microns.

COMMENT C.

Average grain size was the average of the longer dimension. In the "Grain Size Distribution" table of the Lotus spreadsheet provided for detailed class data, 15 classes with medians ranging from 0.495 to 4.785 microns, and with a class width of 0.33 microns are reported. Total frequency count is 8970, of which 429 or 4.8% are reported as having a diameter > 5 microns. (It is assumed that the total frequency count is the sum of all observations made on the 9 identified specimens reported in the table above. Ed.).

COMMENT D.

Grain size obtained from SEM micrographs : 1 - 5 microns with occasional grains 15 microns. Grain morphology is essentially equiaxed.

COMMENT E.

Microstructure is reported as being quite homogeneous and equiaxed; average grain diameter 2 - 3 microns; average pore diameter 1 micron with some pore diameters as large as 2 microns; fracture mechanism essentially trans-crystalline, with some small degree of inter-crystalline fracture.

COMMENT F.

The microstructure is homogeneous, with grains up to max. 5 microns. The pore size is below 2 microns. No fracture origins could be identified with any great degree of certainty.

COMMENT G.

Structural analysis was carried out using an automatic image analyser (IBAS 2/ Kontron). Methodology and results are given in considerable detail, see section M.5 MICROSTRUCTURE and FIG.3. For specimens IEA# 876, 930 and 1114, the grain counts were 691, 642 and 916 respectively. Reported averages of grain area, max. grain length, ellipse form factor (b/a) and porosity (area%) are thus based on 2249 observations.

The reported grain size data are **arithmetic mean values** instead of median values. For comparison of reported aspect ratio data, the original values reported from this laboratory have been inverted.

**International Energy Agency : Annex II.
Co-operative Programme on Ceramics for Advanced
Engines and Other Applications.**

SUBTASK 3 : CERAMIC CHARACTERIZATION

RESULTS

FOR

MATERIAL "B".

HOT-ISOSTATICALLY PRESSED SILICON NITRIDE

Test material provided by ABB Cerama,(formerly ASEA Cerama), Sweden.

- B.1 Density
- B.2 Porosity
- B.3 Chemical Analysis
- B.4 Phase Analysis
- B.5 Microstructure

RESULTS

B. HIP-Si₃N₄ (ASEA CERAMA) MATERIAL

B.1 DENSITY.

All reported values for the geometric and immersion densities (in water and toluene) are presented in tables B2 to B4.

In table B1, these results are presented in condensed form as average values and standard deviations for each method and participating laboratory. For the sake of clarity, all averages have been rounded off to three decimals. (A "5" in the fourth decimal is rounded upwards, a "4" down). Standard deviations are given with two significant figures. (In case a third significant figure 0 > was reported, the second significant figure has been rounded upwards).

The column "n" gives the number of determinations. This is generally, but not always, equal to the number of specimens examined by that laboratory.

HIP-Si₃N₄ BULK DENSITY (g/cm³)

TABLE B1.

Lab#	Geometric	Immersion		n
		Water	Toluene	
1		3.200 ± 0.001	3.219 ± 0.001	10
2	3.174 ± 0.007	3.194 ± 0.007	3.204 ± 0.008	10
3	3.187	3.202	3.204	3
4	3.172 ± 0.034	3.225 ± 0.049		10
6	3.182 ± 0.007			10
7		3.200	3.204	2
8		3.206 ± 0.013	3.200 ± 0.036	10
9		3.23		10
10	3.185 ± 0.018	3.174 ± 0.008	3.177 ± 0.016	5
11		3.19		?
12		3.190 ± 0.002		10
16		3.202 ± 0.004		9
Avg.	3.177 ± 0.020	3.205 ± 0.023	3.201 ± 0.018	
n	33	57	56	

HIP SILICON NITRIDE TABLE B2.
BULK DENSITY (g/cm³)

Lab. #	Sample #	Geometric	Immersion		
			Water	Toluene	
1	409		3.1998	3.2188	
	612		3.2008	3.2189	
	10		3.2004	3.2194	
	1115		3.2016	3.2191	
	250		3.2018	3.2200	
	660		3.2001	3.2186	
	869		3.1991	3.2172	
	39		3.1994	3.2183	
	316		3.1993	3.2175	
	514		3.2009	3.2192	
		Average		3.2003	3.2187
		Std. Dev.		.0009	.0008
2	82	3.1826	3.1909	3.2061	
	531	3.1625	3.2007	3.2081	
	353	3.1755	3.1936	3.2104	
	790	3.1776	3.1954	3.2058	
	193	3.1772	3.1862	3.2050	
	204	3.1714	3.1979	3.2074	
	553	3.1619	3.1867	3.2052	
	155	3.1760	3.1938	3.1912	
	62	3.1750	3.2071	3.1904	
	598	3.1764	3.1908	3.2089	
		Average	3.1736	3.1943	3.2039
	Std. Dev.	.0066	.0064	.0071	
3	577	3.191	3.201	3.205	
	1027	3.187	3.201	3.200	
	265	3.182	3.204	3.207	
		3.187	3.202	3.204	

HIP SILICON NITRIDE

TABLE B3

BULK DENSITY (g/cm³)

Lab.#	Sample #	Geometric	Immersion	
			Water	Toluene
4	18	3.257	3.204	
	417	3.157	3.210	
	378	3.166	3.214	
	527	3.154	3.210	
	925	3.199	3.362	
	753	3.164	3.217	
	929	3.128	3.216	
	835	3.166	3.210	
	179	3.167	3.211	
	857	3.164	3.195	
	Average	3.172	3.225	
	Std. Dev.	.034	.049	
	6	256	3.174	
526		3.180		
115		3.172		
795		3.191		
456		3.179		
1015		3.183		
426		3.182		
587		3.192		
510		3.176		
642		3.187		
Average		3.182		
Std. Dev.		.007		
7		696		3.2002
	1026		3.1990	3.2015
	Average		3.200	3.204
8	130		3.195	3.223
	537		3.199	3.129
	368		3.225	3.223
	689		3.188	3.186
	941		3.200	3.145
	299		3.211	3.192
	506		3.225	3.227
	338		3.207	3.223
	729		3.212	3.224
	951		3.196	3.224
	Average		3.206	3.200
	Std. Dev.		.013	.036

HIP SILICON NITRIDE TABLE B4.
BULK DENSITY (g/cm³)

Lab.#	Sample #	Geometric	Immersion	
			Water	Toluene
9	Average (n = 10)		3.23	
10	Average (n = ?)		3.174	3.177
11	Average (n = ?)		3.19	
12	Average *	3.19		(Xylene)
	79			3.192
	144			3.193
	187			3.192
	212			3.190
	267			3.190
	745			3.191
	825			3.192
	878			3.190
	1159			3.192
	1166			3.191
	Average			3.191
	Std. Dev.			.001
	33			3.194
	38			3.192
	166			3.190
	386			3.191
	772			3.188
	849			3.189
	899			3.188
	989			3.193
	1040			3.189
	1042			3.190
	Average			3.190
	Std. Dev.			.002
16	241		3.1977	
	291		3.2019	
	913		3.2006	
	973		3.1982	
	241		3.2085	
	291		3.2031	
	913		3.2035	
	948		3.2037	
	973		3.2017	
	Average		3.202	
	Std. Dev.		.003	

RESULTS.

B. HIP-Si₃N₄ (ABB CERAMA) MATERIAL

B.2 POROSITY.

TABLE B5.

Lab#	Spec.#	Porosity (vol%)	Note
2	82	0.088	Max. value = 0.254%
	531	0.254	
	353	0.165	Min. value = 0.088
	790	0.216	
	193	0.205	
	204	0.090	
	553	0.228	
	155	0.165	
	62	0.202	
	598	0.102	
	Average	0.172	
	Std. Dev.	0.057	
4	417	0.82	Method ASTM Standard E 562-83 (Area porosity)
	527	0.6	
	929	0.64	
		Average	0.69
6	256	0.813	Based on theoretical density = 3.2 g/cc
	526	0.625	
	115	0.875	Max. value = 0.875 Min. value = 0.250
	795	0.281	
	456	0.656	
	1015	0.531	
	426	0.563	
	587	0.250	
	510	0.750	
	642	0.406	
	Average	0.575	
	Std. Dev.	0.202	

B.2 POROSITY.**TABLE B5.** (Contd).

Lab#	Spec.#	Porosity (vol%)	Note
8	130	0.62	Max. value = 0.70% Min. value = 0.01%
	537	0.01	
	368	0.09	
	689	0.43	
	941	0.25	
	299	0.45	
	506	0.15	
	338	0.29	
	729	0.70	
	951	0.52	
		Average	0.35
	Std. Dev.	0.22	
16	-	0.021	Open porosity - surface water film

RESULTS.

B. HIP-Si₃N₄ (ABB CERAMA) MATERIAL

B.3 CHEMICAL ANALYSIS.

HIP SILICON NITRIDE

TABLE B6

BULK CHEMICAL ANALYSIS (MAJOR / MINOR)

All concentrations in wt%.

Lab.#	Sample#	Major			Minor	
		Si	N	C	O	Y
2	193	(*)				3.
	204	(*)				3.
	531	(*)				3.
	553	(*)				3.
3	71				2.60	
	866			.48		
5	481			.54	2.29	2.0
	596			.53	2.35	2.0
7	31	56.55			1.92	1 (**)
	132	56.92			1.95	2 (**)
	135	56.38			1.87	2 (**)
9		56.54	36.24	.5	2.58	1.85
10	(****)		35.11	.68	3.39	1.40
12 (***)	849					2.2
	1042					2.1
	899					2.3
	772					2.1
	386					2.1
15	646					2.10
	683					1.94
	1039					1.94

(*) Reported as major element.

(**) Reported as 10000 and 20000 ppm resp.

(***) Reported estimated relative error 8%.

(****) IEA samples # 126, 452, 681, 1091 milled and mixed:
analyzed 3x.

HIP SILICON NITRIDE

TABLE B7.

BULK CHEMICAL ANALYSIS (TRACE)

All concentrations in wt%.

Lab.#	Sample#	Al	Ca	Cr	Fe	K	Mg	Na
2	193	.03	.1		.02		.005	
	204	.03	<.005		.02		.005	
	531	.03	.005		.02		.005	
	553	.03	.005		.02		.005	
3	1140		.006		.12		.003	
	469	.08						
	469			.003		.01	.0007	.05
5	481	.083			.054			
	596	.068			.071			
7	31	.012	.0010	.0015	.2000	.0060		
	132	.016	.0040	<.0010	.9000	.0080		
	135	.040	<.0010	<.0010	.0750	.0025		
9			nd		.05		nd	
10	(**)	.07			.09			
		.08			.12			
11	-	.15	.07		.04	.008	.005	.02
	-	.16	.08		.03	.008	.006	.02
	-	.16	.08		.03	.008	.007	.02
	-	.15	.07		.03		.005	
12 (*)	849	<.063	<.005	.00081	.0221	.0038		.0148
	1042	<.063	<.005	.00061	.0217	.0052		.0151
	899	<.063	<.005	.00065	.0242	.0057		.0152
	772	<.063	<.005	.00061	.0227	.0039		.0159
	386	<.063	<.005	.00086	.0236	.0041		.0160
15	646	.057	.0026		.023			
	683	.056	.0025		.023			
	1039	.057	.0026		.0026			

(*) From Neutron Activation Analysis (NAA); Al <0.063, >0.014

(**) IEA samples # 354, 377, 512, 616, 838 milled and mixed.

nd not detected

RESULTS.

B. HIP-Si₃N₄ (ABB-CERAMA) MATERIAL

B.4 PHASE ANALYSIS.

TABLE B8.

Lab#	Major	Minor	Samples
1	β-Si ₃ N ₄	Si ₂ ON ₂ ; Al ₂ Y ₄ O ₉ *	1115
2	β-Si ₃ N ₄	Si ₂ ON ₂ ; Al ₂ Y ₄ O ₉	193,204,531,553
3	β-Si ₃ N ₄	Si ₂ ON ₂ ;	577
5	β-Si ₃ N ₄	Si ₂ ON ₂ ;	-
6	β-Si ₃ N ₄	Si ₂ ON ₂ ; α-Y ₂ Si ₂ O ₇ ; +?	256,526,795
8	β-Si ₃ N ₄	Si ₂ ON ₂ ; Al ₂ Y ₄ O ₉	
9	β-Si ₃ N ₄	Si ₂ ON ₂ ; +?	
10	β-Si ₃ N ₄	Si ₂ ON ₂ ; Y ₂ Si ₂ O ₇	
11	β-Si ₃ N ₄	Si ₂ ON ₂ ; Si?	
12	β-Si ₃ N ₄	Si ₂ ON ₂ ; Y ₂ Si ₂ O ₇	386,1042

Comments:

The following comments concerning the phase identification from the X-ray spectra were reported. The comments and points of discussion are published in this report in abbreviated form in the case of Lab.# 1, and in extenso for all others.

For descriptions of sample preparation procedures and measurement conditions, when reported, see 5.4 METHODOLOGY; Phase Analysis.

Lab# 1.

The submitted Si_3N_4 bar (IEA# 1115) was examined both "as-fired" and after being ground to a fine powder. The two resulting diffraction patterns from these samples were nearly identical. The only difference in them is that the pattern resulting from the as-fired sample has sharper, more resolved peaks than that of the ground sample. Three phases were detected. The major phase is $\beta\text{-Si}_3\text{N}_4$. Two minor phases were detected as well: Si_2ON_2 , and $\text{Al}_2\text{Y}_4\text{O}_9$ or an unidentified phase.

Lab# 2.

In a summarizing table, minor phases are reported as Al_2ON_2 and $\text{Y}_4\text{Al}_2\text{O}_9$ for the four specimens examined (IEA# 193,204, 531,553). The total Al-content is reported to be 0.03%. Primary data from 1987-09-22 states "minor Si_2ON_2 " and "minor probable $\text{Al}_2\text{Y}_4\text{O}_9$ type structure (see cards 34-368 and 14-475)". All four spectra reportedly similar, which should imply no significant difference in phase composition and concentration.

Lab# 3.

The original spectrum, 2-theta $10\text{-}90^\circ$, for sample IEA# 577 was submitted. No information on equipment or measurement conditions. A copy of the same (?) spectrum, with 2-theta interval $10\text{-}50^\circ$, presents d-values and designates $\beta\text{-Si}_3\text{N}_4$ and $\text{Si}_2\text{N}_2\text{O}$ phases. (Two major peaks unidentified?).

Lab# 5.

No spectra appended to the original report.

Lab# 6.

Spectra appended original report; heading identifies equipment as Siemens Diffrac 500. Phase analysis is reported as being semi-quantitative, and crystalline phases are identified as $\beta\text{-Si}_3\text{N}_4$ (JCPDS# 33-1160) 94 ± 2 vol.%; Si_2ON_2 (JCPDS# 33-1162) $4 \pm 1\%$; $\text{Y}_2\text{Si}_2\text{O}_7$ (JCPDS# 21-1457) $2 \pm 1\%$.

Lab# 8.

Ten samples were analyzed (IEA# 130,537,368,689,941,299,506, 338,729,951). In the spreadsheet report, all ten specimen results were given the same notation, i.e. "major", "low", "low" for the three phases identified. This could conceivably be construed as implying that no significant differences were noted with respect to phase composition and relative concentrations. The report comments that the identification of $Y_4Al_2O_9$ phase is based on four diffraction lines only.

Lab# 9.

No information concerning equipment or measuring conditions reported. Samples were identified as IEA# 613,101,865,200, 711. Information on sample preparation implies that all samples were combined and milled for chemical and X-ray diffraction analyses. Results of XRD analysis reported as β - Si_3N_4 87% ; Si_2ON_2 4.1%. Some diffraction lines of low intensity were not identified.

Lab# 11.

No instrumental data, sample preparation procedure or sample identification reported. Phases identified ; Si_3N_4 ; Si_2ON_2 ; Si (possible).

Lab# 12.

Two specimens (# 386, # 1042) were examined in bulk as received. The original report states that; "Three crystalline phases were identified: β - Si_3N_4 ; Si_2ON_2 ; $Y_2Si_2O_7$; the two latter phases are minor in content".

RESULTS.

B. HIP-Si₃N₄ (ABB CERAMA) MATERIAL

B.5 MICROSTRUCTURE.

Grain Size Distribution

TABLE B9.

The table below shows the grain size distribution (median and standard deviation) and aspect ratio as reported in the Lotus spreadsheet for spatial characteristics, or in similar condensed form.

Lab.#	Sample#	Grain Size Median	Distribution Std.Dev.	Aspect Ratio	Comment
1	612	0.76	0.43		A
	612	0.63	0.36		
	250	0.68	0.54	1.96	
2	155	0.951	0.118		
6	256	0.7	0.2	1:1	B
	795	0.5	0.15	1:1	
	614	2	1	3:2	
9		0.5 - 2			C
10		ca. 1			D
11					E
12	35	1.04	0.72	2.27	F
	472	1.04	0.77	2.33	
	940	1.14	0.83	2.22	
	Average	1.07	0.77	2.27	

COMMENT A.

Grain sizes are equivalent circular diameter (in microns). In the above table, the specimen identifications IEA #612 and 250 are related to Lab.#1 micrographs 8798-1,2 and 8796-1 respectively. A minimum of one hundred (100) grains measured in each micrograph. In the "Grain Size Distribution" table of the Lotus spreadsheet, 17 classes with medians ranging from 0.1 to 1.7 microns, and with a class width of 0.05 microns are reported. (The reported class width is actually one half of the difference between two adjacent median values. Class width is therefore 0.1 microns. Ed.). Frequency count is reported in %-values.

COMMENT B.

Grain sizes determined from TEM micrographs.
Grain boundary thickness reported to be 0.001 microns.

COMMENT C.

IEA specimen # are given as 881, 272, 1007, 508 and 751.
Grain size obtained from SEM micrographs.
Diameter (cross-sectional) 0.5 - 2 microns, length up to 15 microns. Regular (even, narrow distribution?) cross-sectional (diameter) with elongated grains.

COMMENT D.

Microstructural characteristics;

- rather homogeneous crystallite size, ca. 1 micron.
- almost pore-free.
- single (individual) pores up to 2 micron diameter.
- three different phases.
- homogeneous Al-additive distribution.

COMMENT E.

Microstructure is homogeneous. A finely-distributed secondary phase is observed besides the small pores. The grain size of this phase and the pores is < 2 microns.

COMMENT F.

Structural analysis was carried out using an automatic image analyser (IBAS 2/ Kontron). Methodology and results are given in considerable detail, see section M.5 MICROSTRUCTURE and fig. 5. For specimens IEA# 35, 472 and 940, the grain counts were 516, 522 and 404 respectively. Reported averages of grain area, max. grain length, ellipse form factor (b/a) and porosity (area%) are thus based on 1442 observations.

The grain size data reported are arithmetic mean values. For comparison of aspect ratio, the values given in the original laboratory report have been inverted.

International Energy Agency : Annex II.

**Co-operative Programme on Ceramics for Advanced
Engines and Other Applications.**

SUBTASK 3 : CERAMIC CHARACTERIZATION

RESULTS

FOR

MATERIAL "C".

SINTERED SILICON NITRIDE SNW-1000

Test material provided by GTE Wesgo, USA.

- | | |
|-----|-------------------|
| C.1 | Density |
| C.2 | Porosity |
| C.3 | Chemical Analysis |
| C.4 | Phase Analysis |
| C.5 | Microstructure |

RESULTS.

C. Sintered-Si₃N₄ (GTE) MATERIAL

C.1 DENSITY.

All reported values for the geometric and immersion densities (in water and toluene) are presented in tables C2 to C5.

In table C1, these results are presented in condensed form as average values and standard deviations for each method and participating laboratory. For the sake of clarity, all averages have been rounded off to three decimals. (A "5" in the fourth decimal is rounded upwards, a "4" down). Standard deviations are given with two significant figures. (In case a third significant figure > 0 was reported, the second significant figure has been rounded upwards).

The column "n" gives the number of determinations. This is generally, but not always, equal to the number of specimens examined by that laboratory.

Sintered-Si₃N₄ BULK DENSITY (g/cm³)

TABLE C1.

Lab#	Geometric	Immersion		n
		Water	Toluene	
1		3.311 ± 0.012	3.330 ± 0.012	10
2	3.298 ± 0.014	3.309 ± 0.005	3.308 ± 0.006	10
3	3.290	3.302	3.307	3
4	3.352 ± 0.002	3.324 ± 0.003		10
6	3.293 ± 0.007			10
7			3.32	2
8		3.251 ± 0.043	3.329 ± 0.010	10
9		3.21		6
10		3.240 ± 0.015	3.248 ± 0.013	5?
11		3.21		?
12			3.310 ± 0.008	10
16		3.319 ± 0.007		9
Avg.	3.312 ± 0.034	3.302 ± 0.034	3.317 ± 0.017	
n	33	53	46	

SINTERED SILICON NITRIDE

TABLE C2

BULK DENSITY (g/cm³)

Lab. #	Sample #	Geometric	Immersion	
			Water	Toluene
1	613		3.3157	3.3343
	514		3.3084	3.3257
	60		3.3222	3.3407
	1356		3.3183	3.3379
	776		3.3140	3.3323
	1411		3.3170	3.3360
	547		3.3104	3.3295
	1749		3.3228	3.3419
	938		3.2956	3.3149
	968		3.2882	3.3073
		Average		3.3113
	Std. Dev.		.0113	.0113
2	179	3.2798	3.3078	3.3065
	248	3.3006	3.3170	3.3102
	307	3.3024	3.3122	3.3183
	339	3.3181	3.3136	3.3139
	527	3.2825	3.3030	3.3003
	789	3.3164	3.3116	3.3031
	985	3.3003	3.3064	3.3021
	1274	3.2907	3.3046	3.3118
	1320	3.3061	3.3091	3.3083
	1621	3.2811	3.3072	3.3035
		Average	3.2978	3.3093
	Std. Dev.	.0139	.0043	.0058
3	512	3.288	3.304	3.314
	964	3.277	3.278	3.281
	267	3.305	3.323	3.327
		Average	3.290	3.302

SINTERED SILICON NITRIDE TABLE C3.

BULK DENSITY (g/cm³)

Lab.#	Sample #	Geometric	Immersion	
			Water	Toluene
4	132	3.346	3.325	
	173	3.284	3.322	
	808	3.361	3.324	
	587	3.342	3.321	
	240	3.408	3.330	
	1058	3.317	3.326	
	896	3.329	3.307	
	739	3.390	3.317	
	246	3.386	3.334	
	30	3.352	3.330	
	Average	3.352	3.324	
	Std. Dev.	.037	.008	
	6	701	3.292	
1731		3.289		
341		3.306		
1608		3.279		
130		3.289		
1486		3.295		
747		3.292		
1684		3.301		
202		3.291		
467		3.292		
Average		3.293		
Std. Dev.		.007		
7	1382			3.32
	1433			3.32
8	781		3.265	3.328
	865		3.184	3.317
	895		3.233	3.316
	289		3.244	3.348
	1309		3.357	3.332
	702		3.238	3.326
	312		3.241	3.345
	46		3.225	3.330
	763		3.285	3.328
	548		3.241	3.320
	Average		3.251	3.329
	Std. Dev.		.045	.011

SINTERED SILICON NITRIDE

TABLE C4.

BULK DENSITY (g/cm³)

Lab.#	Sample #	Geometric	Immersion	
			Water	Toluene
9		(n = 6)	3.21	
10		(n = ?)	3.240	3.248
11		(n = ?)	3.21	
				(Xylene)
12	29			3.316
	54			3.314
	152			3.312
	681			3.306
	884			3.293
	1135			3.310
	1218			3.304
	1297			3.319
	1374			3.312
	1385			3.313
	Average			3.310
	Std. Dev.			.007
16	10		3.3198	
	223		3.3145	
	249		3.3231	
	1258		3.3243	
	10		3.3238	
	223		3.3161	
	249		3.3262	
	661		3.3144	
	1258		3.3250	
	Average		3.3208	
	Std. Dev.		.0047	

RESULTS

C. Sintered Si₃N₄ (GTE) MATERIAL

C.2 POROSITY.

TABLE C5.

Lab#	Sample#	Porosity (vol%)	Comments
2	179	0.1537	A
	248	0.1144	
	307	0.2302	
	339	0.1145	
	527	0.1025	
	789	0.1923	
	985	0.1283	
	1274	0.1649	
	1320	0.1533	
	1621	0.0642	
	Average	0.132 (8)	
	Std. Dev.	0.043 (1)	
4	132	7.38	B
	240	7.60	
	1058	8.25	
	Average	7.74	
	Std. Dev.	0.45	
6	Average	2.894	C
	Std. Dev.	0.214	
8	Average	1.78	D
	Std. Dev.	0.59	
12	529	1.94 ± 0.46	E
	666	1.66 ± 0.39	
	1739	2.15 ± 0.53	
	Average	1.92 ± 0.49	
16	-	0.028	F

COMMENT A.

The results given in the table above are reported in the Lotus spreadsheet column; "Porosity in volume %". The reported data are apparent porosity data obtained from ASTM procedure C-373.

COMMENT B.

Porosity results were determined on polished samples using ASTM Standard E 562-83, "Standard Practice for Determining Volume Fraction by Systematic Manual Point Count".

COMMENT C.

The laboratory reports "geometrical" density only for this material. Comments given in the Lotus spreadsheet; "Porosity results based on the theoretical density for silicon nitride 3.2 g/cc. This is obviously not the theoretical density of this material because of the large fraction of yttrium oxide sintering aid it contains. To recalculate the porosity using a more accurate value of density, simply change value of cell O37" - (in the Lotus spreadsheet).

COMMENT D.

"The porosity is the apparent porosity as per ASTM".

COMMENT E.

Area % - Image Analyzer IBAS 2/Kontron.

Ten measurements on each specimen.

COMMENT F.

Open porosity - surface water film.

RESULTS

C. Sintered Si₃N₄ (GTE) MATERIAL

C.3 CHEMICAL ANALYSIS.

SINTERED SILICON NITRIDE

TABLE C6.

BULK CHEMICAL ANALYSIS (MAJOR / MINOR)

All concentrations in wt%.

Lab.#	Sample#	Major			Minor		
		Si	N	C	O	Y	
2	179	(*)				10.	(***)
	339	(*)				10.	(***)
	985	(*)				10.	(***)
	1320	(*)				10.	(***)
3	146				5.47		
	987			.030			
	416					10.22	(**)
5	220			.036	5.47	10.80	
	1094			.036	5.31	10.40	
9		48.71	31.71	0.36	5.63	10.2	
10	(****)		31.09	.307	6.61	6.91	(AAS)
						8.39	(XRF)
11	-					6.13	(**)
	-					6.13	(**)
	-					6.17	(**)
12	1739					10.7	
	666					10.1	
	280					8.9	
	529					10.3	
	1363					9.3	
17						11.4	

(*) Reported as major element.

(**) Reported as oxide; recalculated.

(***) Reported as 100000 ppm.

(****) IEA samples # 807, 1122, 1456, 1730 milled and mixed.

SINTERED SILICON NITRIDE
BULK CHEMICAL ANALYSIS (TRACE)

TABLE C7.

All concentrations in wt%.

Lab. #	Sample#	Al	Ca	Fe	Mg	
2	179	2.0	.005	.005	.005	
	339	1.0	.005	.005	.005	
	985	0.8	.004	.005	.005	
	1320	0.7	.004	.005	.005	
3	206		.005	.59	.001	
	416	1.11				(*)
5	220	1.2				
	1094	1.1				
9	(**)	1.77	nd	.04	nd	
10	(***)	1.13		.22		(AAS)
		1.10		.18		(XRF)
11	-	2.17				
	-	2.15				
	-	2.13				
12	280	0.82	<.005	.0039	.0194	
	529	0.82	<.005	.0040	<.0200	
	666	0.82	<.005	.0042	<.0200	
	1363	0.82	<.005	.0042	<.0200	
	1739	0.82	<.005	.0041	<.0200	
17		0.69	0.004	0.01	0.03	

(*) Reported as oxide; recalculated.

(**) IEA samples # 1494, 1123, 261 milled and mixed.

(***) IEA samples # 234, 554, 1064, 1067, 1456 milled and mixed; analyzed 3x.

nd = not detected

RESULTS.

C. Sintered Si₃N₄ (GTE) MATERIAL

C.4 PHASE ANALYSIS.

TABLE C8.

Lab#	Sample#	Major	Minor	Comments
1	547	β-Si ₃ N ₄	Y ₂ SiO ₅ + ?	A
	1749	β-Si ₃ N ₄	Y ₁₀ Al ₂ Si ₃ O ₁₈ N ₄	
2	179	β-Si ₃ N ₄	mixture	B
	339	"	"	
	985	"	"	
	1320	"	"	
3	1113	β-Si ₃ N ₄	Y ₂ Si ₂ O ₅	
5	–	β-Si ₃ N ₄	Y ₂ SiO ₅ , Al ₂ O ₃	C
6	130	β-Si ₃ N ₄	Y ₁₀ Al ₂ Si ₃ O ₁₈ N ₄ , YSiO ₂ N, α-Si ₃ N ₄ + trace phases + non-crystalline	D
	701			
	1731			
8		β-Si ₃ N ₄	Y ₂ SiO ₅ , Y ₃ Si ₃ O ₆	E
9		β-Si ₃ N ₄	YSiO ₂ N, Y ₂ O ₃	F
10		β-Si ₃ N ₄	YSiO ₂ N, Y ₁₀ Al ₂ Si ₃ O ₁₈ N ₄	
11		β-Si ₃ N ₄		
12	843	β-Si ₃ N ₄	YSiO ₂ N, Y ₂ SiO ₅	G
	1332	"	" "	
	1728	β-Si ₃ N ₄	Y ₁₀ Al ₂ Si ₃ O ₁₈ N ₄	
17		β-Si ₃ N ₄	Y ₂ SiO ₅	

Comments:

Of the minor phases, Y_2SiO_5 and $YSiO_2N$ were most frequently identified, (four labs. each). $Y_{10}Al_2Si_3O_{18}N_4$ was identified by three laboratories. Seven participants reported a mixture of minor phases consisting of at least two phases.

The following specific comments concerning the phase identification from the X-ray spectra were reported. For descriptions of sample preparation procedures and measurement conditions, when reported, see 5.3 METHODOLOGY; Phase Analysis.

COMMENT A.

The two sets of submitted Si_3N_4 bars were examined both as-fired and after being ground to fine powders. The two resulting diffraction patterns from each of these sets of samples were nearly identical. The only difference in them is that the patterns resulting from the as-fired samples had sharper, more resolved peaks than those of the corresponding ground samples. (?) in the above table = unidentified phase.

COMMENT B.

"Mixture" in the above table is reported as "probable mixture of $Y_2Si_3O_3N_4$, $YSiO_2N$, $Y_4Al_2O_9$, Y_2O_3 phases".

COMMENT C.

Al_2O_3 phase reported as "very minor".

COMMENT D.

Semi-quantitative results were reported for the X-Ray phase analysis. For all three specimens analyzed, IEA# 130, 701 and 1731, the following volume percentages were given;

β - Si_3N_4	$70 \pm 5 \%$
$Y_{10}Al_2Si_3O_{18}N_4$	$15 \pm 5 \%$
$YSiO_2N$	$6 \pm 3 \%$
α - Si_3N_4	trace
Non-crystalline	$5 \pm 3 \%$

Not all X-Ray peaks accounted for; unidentified trace phases present. Grains are elongated parallel to the c-axis with an aspect ratio of 5 to 6:1.

COMMENT E.

This laboratory reports semi-quantitative data which indicate a possible variation in the relative concentrations of the minor phases.

The identified phases are given in the table above. An additional comment states -"Y₂SiO₇ and Y₂O₃ cannot be ruled out due to diffraction line coincidences. There are broad diffraction humps in the regions for the major Y₂SiO₅ lines for specimens 865, 702, 548 and 763 suggesting the presence of a glass phase which may crystallize to Y₂SiO₅ later".

COMMENT F.

β-Si₃N₄ concentration is reported as 79%

Lines from the phases YSiO₂N und Y₂O₃ were also detected.

COMMENT G.

The three specimens investigated were chosen so as to represent low, medium and high fracture strength values. IEA specimen# 1728, 1332 and 843 had been found to have strength values of 576, 660 and 742 MPa, respectively.

In the medium and high strength specimens, the identified phases were β-Si₃N₄, YSiO₂N and Y₂SiO₅. The content of the two minor phases was estimated to be appreciably higher in the high-strength specimen, roughly by a factor of two. In the low-strength specimen, only two phases were identified, namely β-Si₃N₄ and Y₁₀Al₂Si₃O₁₈N₄. The two other above mentioned Y-containing phases were absent in this sample or below detection limits.

Together with evidence from microprobe analyses, this laboratory draws the conclusion that the production parameters for this material were not the same for all samples.

RESULTS

C. Sintered Si₃N₄ (GTE) MATERIAL

C.5 MICROSTRUCTURE.

Lab#	Spec.#	Grain Size Distribution (Microns)		Aspect Ratio	Comment
		Median	Std.Dev.		
1	1411	0.228	0.1	1.41	A
	968	0.231	0.08		
2	556	0.688	0.088		
6	130	0.5	0.1	6:1	B
	701	0.4	0.1	5:1	
	1731	0.4	0.1	6:1	
9		(0.5 - 2 microns)			C
10					D
11					E
12	529	1.03	0.94	2.56	F
	666	1.00	0.84	2.56	
	1739	0.91	0.97	2.63	
Average		0.98	0.93	2.59	

COMMENT A. (AC Spark Plug)

Grain sizes reported are equivalent circular diameter (in microns). Minimum of 100 grains measured in each micrograph. Micrograph 8794 = IEA# 1411, 8792 = IEA# 968)

In the "Grain Size Distribution" table of the Lotus spreadsheet, 11 classes with medians ranging from < 0.05 to > 0.9 microns, and with a class width of 0.05 microns are reported. (The reported class width is actually one half of the difference between two adjacent median values. Class width is therefore 0.10 microns. Ed.). Frequency count is reported in %-values.

COMMENT B.

Grains elongated parallel to the c-axis with aspect ratios as shown. Grain size data refer to grain cross sections, and are based on TEM. Grain boundary thickness reported as 0.001 microns.

COMMENT C.

Grain size determined from SEM micrographs: Cross-section 0.5 - 2 microns; length up to 20 microns; in some cases exaggerated grain growth - aggregates. Grain morphology - apart from medium needle growth, a few giant crystallites.

COMMENT D.

Microstructural characteristics;

- numerous pores and low density areas with a diameter up to 2 microns.
- elongated crystallites \approx 3 microns long and 0.3 - 0.5 microns in diameter (in cross-section).
- a few large "bars"; 15 microns in length, 2 microns in diameter.
- quite homogeneous additive distribution (Y,Al).

COMMENT E.

The microstructure is extremely fine-grained; grain size in region < 5 microns. One or two needle-shaped crystallites of length up to 20 microns were observed. The pore structure shows signs of remnant press-granule structure. The pore structures of this type reach a diameter of up to 50 microns.

Concerning fracture initiation, it is commented that it was difficult to localize or detect exactly. One or two pores of up to 15 microns size are thought to derive from spaces between press-granules.

COMMENT F.

Structural analysis was carried out using an automatic image analyser (IBAS 2/ Kontron). Methodology and results are given in considerable detail, see section M.5 MICROSTRUCTURE and fig. 7. For specimens IEA# 529, 666 and 1739, the grain counts were 608, 618 and 705 respectively. Reported averages of grain area, max. grain length, ellipse form factor (b/a) and porosity (area%) are thus based on 1931 observations.

The grain size data reported are arithmetic mean values. For comparison of aspect ratio, the values given in the original laboratory report have been inverted.

SECTION "M".

METHODOLOGY.

METHODOLOGY.

M.1 DENSITY.

Lab.# 1:

Experimental Method: Bulk and immersion density.

Equipment: Fowler Ultra-Cal II digital micrometer, Mettler AE-163 balance, HP-85B computer with density program.

Sample Preparation and Measurement Conditions:

HIP-SiC: Measured thickness/width/length of each bar with micrometer; cleaned in acetone/ultrasonic for 30 sec., weighed on Mettler balance, placed all samples in beaker with distilled water and evacuated for 15 min. in vacuum desiccator. Weigh suspended in distilled water at 22 °C.

HIP - Si₃N₄: Measured samples, weighed samples dry, put into individual sample bottles in distilled water and evacuated for 1 hour, weighed suspended (T = 23.5 °C), dried at 120 °C for 1 hour, taken out and cooled overnight, reweighed dry, put into individual bottles in toluene, evacuated for 1 min. and stored for 1 hour, weighed suspended (T = 24.5 °C).

SSN: As for HIP - Si₃N₄, but with T (water) = 24 °C, drying overnight at 100 °C, and T (toluene) = 25 °C.

Comments: Density values reported:

- according to ASTM C - 373 temperature, density of water, air not compensated.
- according to ASTM C - 373 with temperature and density of water, air compensated.
- according to ASTM C - 373 with temperature and density of toluene, air compensated.
- the HP-85B computer program used assumes that the samples are suspended in water (1.00 g/cm³). For changes in the temperature and/or the suspending medium, the calculated density was multiplied by the appropriate correction factor.
- Fisher toluene; density at 25 °C = 0.867 g/cm³

Lab.# 6 :

Comments:

Length, width and thickness of each individual test bar given in the original laboratory report.

Lab.# 8 :

Experimental Method:

Equipment:

Sample Preparation:

Measurement Conditions:

Comments:

- Immersion densities are the bulk density as per ASTM.
- The porosity is the apparent porosity as per ASTM.

Lab.# 9 :

Experimental Methods:

Displacement method (with distilled water).

- a) Archimedes
- b) Pycnometer

Equipment:

- a) Digital Analytical Balance 2400, Sartorius
 - b) Digital Analytical Balance 2400, Sartorius
- Pycnometer content of 50 ml according to DIN 12796 with ground glass stopper with a capillary.

Sample Preparation:

Cleaned samples are dried at a temperature of 110 °C until constant weight is reached.

Measurement Conditions:

- a) Saturation of samples with distilled water at room temperature according to DIN 51056. During weighing, the samples are placed in distilled water.
- b) Determination of the volume of the displaced liquid according to DIN 51057

Comments:

The number of determinations was 6, 10, and 6 for the HIP-SiC, HIP-Si₃N₄ and SSN respectively.

Lab.# 12 :

Experimental Method:

Equipment:

Sample Preparation:

Measurement Conditions:

Comments:

- a) The geometric density of HIP-Si₃N₄ and SSN was measured on two series of 60 samples by a sub-contracted laboratory.
- b) Immersion densities of HIP-Si₃N₄ and SSN were determined by the buoyant-force method (xylene) using series of 10 broken specimens. The work was carried out by Lab.# 12 itself.
- c) Immersion densities of HIP-SiC were measured for all 60 samples prior to mechanical testing.

Lab.# 14 :

Experimental Method: Displacement method (Archimedes) with water.

Equipment: Mettler A 30

Sample Preparation:

Measurement Conditions: Room temperature

Comments: The densities of 70 specimens 3.5 x 4.5 x 50 mm were measured prior to mechanical testing.

METHODOLOGY

M.2 POROSITY.

Lab# 2.

Porosity is the apparent or open porosity as determined by ASTM procedure C-373.

Lab# 4.

Porosity results were determined on polished samples using ASTM Standard E 562-83 "Standard Practice for Determining Volume Fraction by Systematic Manual Point Count".

Lab# 6.

Porosity results based on the theoretical densities of each material. Values used were for SiC 3.217 g/cm^3 , and for Si_3N_4 3.2 g/cm^3 .

In the case of HIP- Si_3N_4 , it is noted that : "The presence of sintering aid will affect the theoretical density and porosity results. To adjust results for corrected density, change value of cell M38". (Reference to Lotus spreadsheet).

In the case of SSN, it is noted that: "This (the value of 3.2 g/cm^3 for the theoretical density of Si_3N_4) is obviously not the theoretical density of this material because of the large fraction of yttrium oxide sintering aid it contains. To recalculate the porosity using a more accurate value of density, simply change the value of cell O37". (Reference to Lotus spreadsheet).

Lab# 8.

"The porosity is the apparent porosity as per ASTM".

Lab# 12.

Quoting the original laboratory report;

"Measurement Data for HIP - SiC (ESK)".

- Mean value D / standard deviation s
 $D = 3.192 \text{ g/cm}^3 / s = 0.001$

- Mean total porosity P_t :
Taking $D_{th} = 3.217 \text{ g/cm}^3$ as the value of the theoretical density of α -SiC, the mean total porosity P_t is calculated as

$$P_t = 0.78 \%$$

- Open Porosity P_o :

The open porosity is calculated from the weight increase of the test sample after vacuum impregnation with xylene. In general, individual nominal values of P_o were below 0.1%, this being roughly the value of the measurement accuracy, thus;

- $P_o < 0.1 \%$

METHODOLOGY.

M.3 CHEMICAL ANALYSIS.

Lab.# 1

Analysis of : **TRACE ELEMENTS**
Method : Emission Spectrometry
Equipment : Baird Atomic Spectroscope
Preparation : Sample ground in W mortar and pestle; mix with carbon powder at 1:1 ratio; pack in carbon cup; start DC arc at 10 amp for 45 sec; read plate.
Comments : All results reported were qualitative.

Lab.# 2

Analysis of : **TRACE ELEMENTS**
Method : Qualitative Spectroscopy
Equipment : DC Arc
Preparation : Samples were ground in a tungsten carbide mill. The cobalt and/or tungsten (detected) may be from the grinding process.
Comments : Major = major constituent (10% or greater). Values accurate to a factor of three.

Analysis of : **TRACE ELEMENTS**
Method : AAE/ICP
Equipment : ARL 4300 ICP
Preparation : KOH fusion 25 g / 250
Comments :

Analysis of : **CARBON** ("Total" and "Free")
Method : ?
Equipment : ?
Preparation : Samples ground in a Ni/Cr dish.
Comments : Free carbon by ANSI method.

Lab.# 3

Analysis of : **TRACE ELEMENTS**
Method : Semi-quantitative Emission Spectroscopy
Equipment : ?
Preparation : ?
Comments :

Analysis of : **CARBON ("Total")**
Method : Combustion / conductometric.
Equipment : ?
Preparation : ?
Comments :

Lab.# 5

Analysis of : **TRACE ELEMENTS**
Method : ICP spectrometry
Equipment : Jarrell-Ash Atom Comp 750 ICP
Preparation : SiC - Leached with 12:5 HF:HNO₃ + conc.
 HCl for 4 hours in teflon. Filtered by gravity with
 highly retentive filter paper.
 Si₃N₄ - Digested in Parr bomb, in 3:1 HF:HNO₃
 for 12 hours, in 150 °C oven. "Taken to dryness"
 3 times with conc. HNO₃, then a final time with conc.
 H₂SO₄. (The matrix is eliminated).
Comments : Values reported in ppm if < 1000 ppm,
 in wt% if > 1000 ppm.
 SiC - ± 10 % RSD
 Si₃N₄ - ± 5 % RSD

Lab.# 6

Analysis of :
Method :
Equipment :
Preparation :
Comments :

Lab.# 7

Analysis of : **TRACE ELEMENTS**
Method : Spark Source Mass Spectrometry
Equipment :
Preparation :
Comments : Visual estimate of line densities ; should be correct
 within a factor of two.

Values reported also for Si, C, O - are reported as being determined by "Standard Gravimetric Analysis", "Leco Combustion" and "Neutron Activation Analysis" respectively.

Lab.# 9

Analysis of : **CARBON ("free"), SiC, Si**
Method : DIN 51075
Equipment :
Preparation :
Comments :

Analysis of : **NITROGEN**
Method : Kjeldahl
Equipment :
Preparation : Digestion in pressure vessel with HF/HNO₃.
Comments :

Analysis of : **Al, Ca; Fe, Ti**
Method : Wet chemical
Equipment :
Preparation :
Comments :

Analysis of : **OXYGEN**
Method : High temperature extraction.
Equipment : Leybold Heraeus NOA 2003
Preparation :
Comments :

Lab.# 10

Analysis of : **TRACE ELEMENTS** (in Si₃N₄ - Y,Al,Fe)
(in SiC - B, Fe,Al, La, Na,Mg)

Method : AAS

Equipment : Perkin Elmer 4000

Preparation : Si₃N₄ - pressure bomb digestion HNO₃/HF.
SiC - carbonate digestion.

Comments : Milled and mixed samples (<100 μm).
Triplicate analyses.

Analysis of : **TRACE ELEMENTS**

Method : XRF (X-Ray Fluorescence Spectrometry)

Equipment : Siemens SRS 303

Preparation : Melt digestion in Lithium Tetraborate.

Comments :

Analysis of : **CARBON ("total" and "free"), OXYGEN, NITROGEN**

Method : High temperature extraction; detector

Equipment : Leco CS 244; TC 136; RC 412

Preparation : 5 samples milled (< 100 μm) and mixed.

Comments :

Lab.# 11

Analysis of : **TRACE ELEMENTS** (Al, Fe, Ti, Ca ,Mg, Zr)

Method : ICP

Equipment : Spectroflame ICP, Fa. Spectro; GMK-nebulizer with
peristaltic pump.

Preparation : Samples milled in WC-receptacle; fusion process for SiC
and Si₃N₄ with Na₂CO₃, dissolved in HCl 1:1.

Comments : Values reported as oxides (Ed.).

Analysis of : **TRACE ELEMENTS (Na,K)**

Method : AES (Air/acetylene flame)

Equipment : Instrumentation Laboratory, JL Video 11;
Allied Analytical Systems.

Preparation : Samples milled in WC-receptacle, decomposition with
H₂F₂ /H₂SO₄, dissolved in HCl

Comments : Values reported as oxides (Ed.).

- Analysis of** : **CARBON** ("Total" and "Free")
Method : Coulometric acc. to DIN 51 075, parts 2 and 3.
Equipment : See DIN 51075, part 2.
Preparation : According to DIN 51075, part 1.
Comments :
- Analysis of** : **SILICON** ("Free")
Method : Gas-volumetric acc. to DIN 51 075, part 4.
Equipment : See DIN 51075, part 4.
Preparation : DIN 51075, part 1.
Comments :
- Analysis of** : **BORON**
Method : Spectrophotometric with dianthrimide reagent.
Equipment : Perkin-Elmer, Lamda 5.
Preparation : Fusion process with Na_2CO_3 , dissolved in 2M H_2SO_4 .
Comments : Values reported as oxide (Ed.).

Lab.# 12

- Analysis of** : **TRACE ELEMENTS** (SiC analyses only)
Method : ICP-AES
Equipment : Spectrometer ARL-34000-ICP-Quantovac or 3580-ICP-Vacuum; grating 1080 lines/mm, blaze: 600 nm; ICP support, Henry generator 1250 kW; Ar/Ar torch, plasma gas 0.8 l/min, carrier gas ca. 1 l/min; Meinard spray diffuser with peristaltic pump.
Preparation : Samples milled in a WC vessel with Co bonding.
Free silicon is dissolved in boiling NaOH (25%), the filtrate neutralized (HCl) and analysed with ICP-AES; calibration with standard solutions.
Si and Traces in solution are measured with ICP-AES after a decomposition process for the SiC using Na_2CO_3 and gravimetric separation from SiO_2 if present. Calibration is achieved with standard solutions.

- Comments** : Total Si content includes the Si from SiC, the Si bonded to oxygen, and Si(free).
(Decomposition following "Handbuch für das Eisenhüttenlaboratorium", Vol.1, p.186; "free" Si method following DIN 51075).
- Analysis of** : **TRACE ELEMENTS** (SiC, Si₃N₄ grades)
- Method** : Neutron Activation Analysis (NAA)
Absolute "k₀-method" with results being calculated from the activities of the (n,gamma)-activation products, the neutron fluxes and the required nuclear parameters; computerized evaluation of the gamma-ray spectra, with detection limits specific for a given material and for actual experimental conditions; multiple measurements after two irradiation steps (5 min, 24 h, different decay times).
- Equipment** : Irradiation in nuclear research reactor FRJ-2 at KFA-Jülich using special devices and neutron flux monitors.
Thereafter gamma-ray spectrometry using HPGe detectors and multichannel analyzers connected to a central computer (micro Vax II of DEC).
- Preparation** : Bend specimens as received or broken pieces were taken for analysis. They were first individually cleaned in HNO₃ / HF (5 min at 90 °C), then irradiated twice (5 min, 24 h).
- Comments** : :

Analysis of : **CARBON** ("Total" and "Free")
Method : IR Spectrometry of CO₂ after combustion of sample in oxygen.
Equipment : Leco Model CS-344
Preparation : Use of ground SiC sample as for "Trace Elements", see above. Total C : 100 - 200 mg; free C : 1g for heat treatment etc.
Comments : "Free" carbon calculated from total-C and from carbon content of a sample after heat treatment at 750 °C taking into account its weight change. In case of weight increase due to partial oxidation of SiC, the method for free Si is applied to 500 mg of heat treated sample (giving Si and SiO₂ as a total). ("Free" carbon method following DIN 51075).

Lab.# 13

Analysis of : **TRACE ELEMENTS**
Method : XRF (X-Ray Fluorescence Spectrometry)
Equipment : Siemens SRS 200
Preparation : Dry milling in a tungsten carbide mill, powder tablet.
Comments : Values reported as oxides (Ed.).

Analysis of : **CARBON** ("Free")
Method : DIN 51075 at 840 and 700 ° C.
Equipment : Strölein Coulomat 701.
Preparation : According to DIN 51075
Comments :

Analysis of : **OXYGEN**
Method : High temperature extraction
Equipment : Leco TC-336
Preparation : Dry milling in a tungsten carbide mill.
Comments :

Analysis of : **SILICON ("Metallic")**
Method : Wet Chemical, according to DIN 51075.
Equipment : According to DIN 51075.
Preparation : According to DIN 51075.
Comments :

Lab.# 14

Analysis of : **TRACE ELEMENTS**
Method : Emission Spectroscopy / ICP
Equipment : ARL 3520 ICP
Preparation : A specimen 3.5 x 4.5 x 50 mm was milled to a powder of maximum grain size of 70 m.
 The following fusion process was done according to DIN 51079.
Comments : Values reported as ppm (Ed.).

Lab.# 15

Analysis of : **MINOR AND TRACE ELEMENTS**
Method : Atomic Absorption Spectroscopy
Equipment : Varian Spectra A30
Preparation : Test bars were milled in a rotating mill, type "Schwingmühle". The first bar milled was not analysed with consideration to possible contamination from the thoroughly cleaned mill. Milled samples were digested in acid (HF, HNO₃) in a Parr bomb.
Comments : Blank values and correction for these reported.

Lab.# 17

Analysis of : **MINOR AND TRACE ELEMENTS**
Method : X-Ray Fluorescence
Equipment : Siemens SRS300
Preparation : Polished surface of the sintered sample in an 8 mm sample cup.
Comments :

METHODOLOGY.

M.4 PHASE ANALYSIS.

Lab# 1: HIP-SiC

Experimental Method:

Equipment: X-ray diffractometer Diano 700 (Manual) with Cu target tube and graphite diffracted beam monochromator.

Sample Preparation: The largest bars were attached to a glass slide. Three smaller pieces were also attached to the slide. The small outer positioned pieces acted as shims to properly position the bars in the sample holder. The bars were positioned so that they all had the same thickness.

Measurement Conditions: 50 kV, 20 mA XRD tube power, 2° 2-theta per minute scan rate, recorded at 2° 2-theta per inch of chart paper with medium resolution optics. The diffractometer was calibrated; good alignment was verified using α -alumina.

Comments:

- a) No reportable differences were detected among the bulk and powdered samples.
- b) No non-crystalline material detected.

Lab# 1: HIP-Si₃N₄ and SSN

Experimental Method:

Equipment: Scintag PAD(V) automated X-ray diffractometer and Data General computer equipment.

Sample Preparation:

- a) Three pieces of the Si₃N₄ bars were mounted as fired in the diffractometer for analysis of the surface.
- b) Several small pieces of the Si₃N₄ bars were wet ground to a fine powder in a boron carbide mortar. The grinding fluid was ethanol. The dry powder was transferred to a glass slide and made into a slurry with collodion diluted with ethanol. The flattened slurry was allowed to dry in room air.

Measurement Conditions:

X-ray tube power : 45 kV, 41 mA. Goniometer run continuously at 2° 2-theta per minute from 4° to 80° , taking data every 0.04° .

Comments:

- a) Standard used : NBS SRM #640, silicon powder alignment standard.
 b) The peaks in the diffraction pattern for the ground samples were not as sharp and well resolved as those for the as-fired (surface) samples.

Lab# 5:

Experimental Method:

Equipment : Philips APD 3600 Diffractometer

Sample Preparation : As received surface of sample

Measurement Conditions : 2-theta, 10 - 70^o, 45 kV, 40 mA

Comments :

Lab# 6:

Experimental Method: Qualitative Analysis by Peak Scan

Equipment : Norelco Diffractometer

Sample Preparation : As received

Measurement Conditions: 2 - theta 20 - 70^o

Comments : No standards used. Phase identification based on JCPDS-ICDD Powder Diffraction File.

Lab# 9:

Experimental Method External standard method. Mass absorption coefficient was calculated using the data from the chemical analysis.

Equipment : Philips - Diffractometer Type PW 1710

Sample Preparation: The samples were ground to < 63 μm in a WC rotating "Schwingmühle" mill. No correction was made, in the chemical and X-ray diffraction analysis, for the presence of wear-contaminants from the mill.

Measurement Conditions: CuK α 40 kV 20mA; 2-theta 10^o - 70^o. For intensity measurements: 0.01^o 2-theta per second continuous scan.

Comments : Measured intensities were compared with intensities of pure standards using;

$$x = \frac{I_{\text{sample}} \cdot \mu_{\text{standard}}}{I_{\text{standard}} \cdot \mu_{\text{sample}}}$$

where x is the concentration in weight percent.

Lab# 12:

Experimental Method:

Equipment : Siemens Diffractometer type D500 and Siemens software DIFFRAC-11.

Sample Preparation : specimens examined as received.

Measurement Conditions: Cu-K α ; 40 kV, 40 mA; the measurement time was 20 sec for step scan with (2-theta) = 0.02^o.

Comments :

Lab# 17:

Experimental Method:

Equipment : Siemens Diffractometer type D500.

Sample Preparation : polished specimen surface.

Measurement Conditions:

Comments :

METHODOLOGY.

M.5 MICROSTRUCTURE.

Lab.# 1

Equipment:

SEM JEOL JSM-T300 & JEOL JXA-35

Optical Microscope Zeiss Axiomat

Buehler Electro-polisher

Sample Preparation:

SiC (ESK): Standard petrographic procedures; mounted sample in thermoplastic, diamond polished to 1 micron surface finish, photographs (optical) taken, electrolytically etched for 30 sec at 40% max. power in 10% HCl/90% H₂O saturated with NaCl, rinsed, photographed (optical and SEM).

Observations on sample preparation: HF, HF/HCl solutions tried at room temp. - no success. 2KOH:NaOH at 900°C for 1 hour - no success.

Si₃N₄ (ABB Cerama and GTE Wesgo): As above for preparation for optical microscopy. Etched for 3-4 min. at 400°F in NH₄F buffer/HF (1:1) in Pt crucible, rinsed with dist. water, photographs (SEM) taken. (NH₄F buffer = 18.6g NH₄F dissolved in distilled water to make 100 ml solution.)

Procedure:

Optical (for porosity) and SEM (for grain characteristics) micrographs were taken at various magnifications and analyzed. A Zidas system was used to quantitatively determine the mean grain size and distribution. The grain outlines were traced with a sensor pen. Two hundred (200) grains were measured for each micrograph. The values reported are for an equivalent circular diameter. Both parallel and perpendicular surfaces were analyzed.

The aspect ratio was determined by measuring the maximum and minimum diameters (at 90°) for ten (10) random grains on each micrograph. The ratio of max/min for each was then determined.

Lab.# 6

Equipment: TEM - type, model not specified.

Sample Preparation and Procedure: not reported.

Comment: In addition to reporting values in the Lotus spreadsheet format, separate appendices concerning the (transmission) electron microscopy and x-ray diffraction were contributed.

This high-resolution work resulted in excellent micrographs, and some interesting observations were reported, e.g. concerning graphite precipitates in multi-grain junctions in the HIP-SiC material.

Lab.# 7

No grain size or aspect ratio data were reported. Back-scattered electron SEM micrographs of the HIP-SiC (IEA sample # 76) and the HIP-Si₃N₄ (IEA # 333) materials are, however, included in the original laboratory report.

Lab.# 12

A. HIP-SiC (ESK).

Quantitative structural analysis with respect to grain area, maximum grain length, grain shape (ellipse form factor, E.F.: quotient of the principle diameters of the ellipse of area equal to the grain area) and the stereometric porosity was performed with an automatic image analyzer (IBAS 2/Kontron). Micrographs of three samples were evaluated. The porosity was evaluated from polished sections of the samples before etching. Etching was performed with a boiling, modified Murakami solution for some minutes.

The stereometric porosity (pore fraction of the measurement area) includes grains broken out during the preparation, and its value is, in general, greater than the porosity value calculated from the density.

B. HIP-Si₃N₄ (ABB)

Quantitative structural analysis was performed on three samples with low, medium and high fracture strength values, namely IEA bar #35; 493 MPa, #472; 650 MPa and #940; 704 MPa.

Since the grain was too fine for an evaluation by light microscopy, SEM-micrographs with a magnification of 6000x were prepared for the image analysis, which was performed with respect to the grain size (area, maximum length) and grain shape. The etched specimens were sputtered with a thin layer of gold. The etching was performed with a NaOH-melt at 450°C for 20 sec. The porosity is low and was not measurable on the unetched samples.

C. S-Si₃N₄ (GTE)

Quantitative structural analysis was performed on three samples with low, medium and high fracture strength values, namely IEA bar #1739; 375 MPa, #666; 641 MPa and #529; 724 MPa.

The sample preparation was the same as for HIP-Si₃N₄.

According to the report from this laboratory;

"a) Arithmetic mean values from the automatic micrograph evaluation are quoted, without taking into account the anisotropic grain shape.

b) For comparison (with other reported results in subtask 3), the inverse of the (original report's) quoted figures (b/a) should be taken as the "aspect ratio". The "aspect ratios" or "ellipse form factors" are **mean values** of evaluated micrographs including approximately 2000 grains or so. As a consequence, these mean values are not a good measure of the real aspect ratio since the longitudinal and diametral cuts of the grains are intermixed.

From the micrographs shown in (the original report) the measurable individual aspect ratio of a grain may be much higher, e.g. more than 10:1 in special grains. Thus, the figures quoted by the different laboratories (participating in the IEA work) reflect the different evaluation methods and are apparently not all comparable."

In an addendum to the original report, the author suggests the use of an alternative statistical treatment of grain size distributions. A geometric mean and dispersion coefficient, (the latter equal to the standard deviation of the respective logarithm of the observation values), are put forward as giving a better description of the microstructure than the arithmetic mean and the usual standard deviation. This addendum contains other valuable points of discussion, and should therefore be taken into consideration in any future work in this area.

Lab.# 16

The original laboratory report contains an appreciable number of back-scatter SEM micrographs. These have not been evaluated with regard to grain size and shape. Sample preparation for the silicon nitride materials was with boiling H₃PO₃ for 8-10 min. Thermal etching in a graphite furnace at 1450°C for 2 h in N₂ was also used. Silicon carbide specimens were prepared in boiling Murakami solution for 1 - 3 min.

International Energy Agency : Annex II
Co-operative Programme on Ceramics for Advanced
Engines and Other Applications.

SUBTASK 3 : CERAMIC CHARACTERIZATION

FIGURES

Fig. 1:	Grain Size Distribution;	HIP-SiC	(ESK)	;	Lab# 1
Fig. 2:	Grain Size Distribution;	"	"	;	Lab# 8
Fig. 3:	Grain Size Distribution;	"	"	;	Lab# 12
Fig. 4:	Grain Size Distribution;	HIP-SN	(ABB)	;	Lab# 1
Fig. 5:	Grain Size Distribution;	"	"	;	Lab# 12
Fig. 6:	Grain Size Distribution;	SSN	(GTE)	;	Lab# 1
Fig. 7:	Grain Size Distribution;	"	"	;	Lab 12
Fig. 8:	Bulk Density; Water immersion	HIP-SiC	(ESK)	;	All labs.
Fig. 9:	Bulk Density; Toluene	"	"	;	"
Fig. 10:	Bulk Density; Geometric	"	"	;	"
Fig. 11:	Bulk Density; Condensed statistics	"	"	.	"
Fig. 12:	Bulk Density; Water immersion	HIP - SN	(ABB)	;	All labs.
Fig. 13:	Bulk Density; Toluene	"	"	;	"
Fig. 14:	Bulk Density; Geometric	"	"	;	"
Fig. 15:	Bulk Density; Condensed statistics	"	"	;	"
Fig. 16:	Bulk Density; Water immersion	SSN	(GTE)	;	All labs.
Fig. 17:	Bulk Density; Toluene	"	"	;	"
Fig. 18:	Bulk Density; Geometric	"	"	;	"
Fig. 19:	Bulk Density; Condensed statistics	"	"	.	"
Fig. 20:	Porosity (vol%) for 1. HIP-SiC ; 2. HIP-SN; 3. SSN.				Lab # 2.

HIP-SiC (ESK)
Grain Size Distribution
Lab# 1.

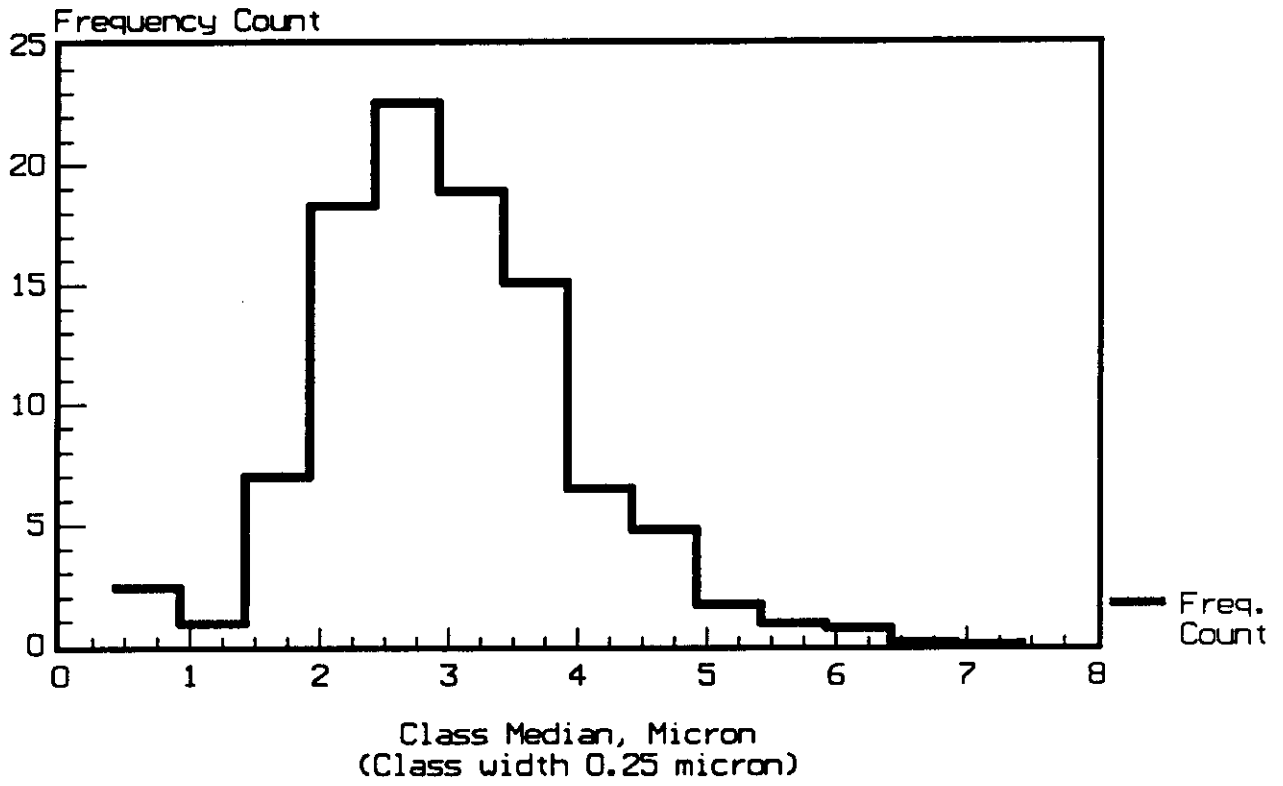


Fig. 1

HIP-SiC (ESK)
Grain Size Distribution
Lab# 8.

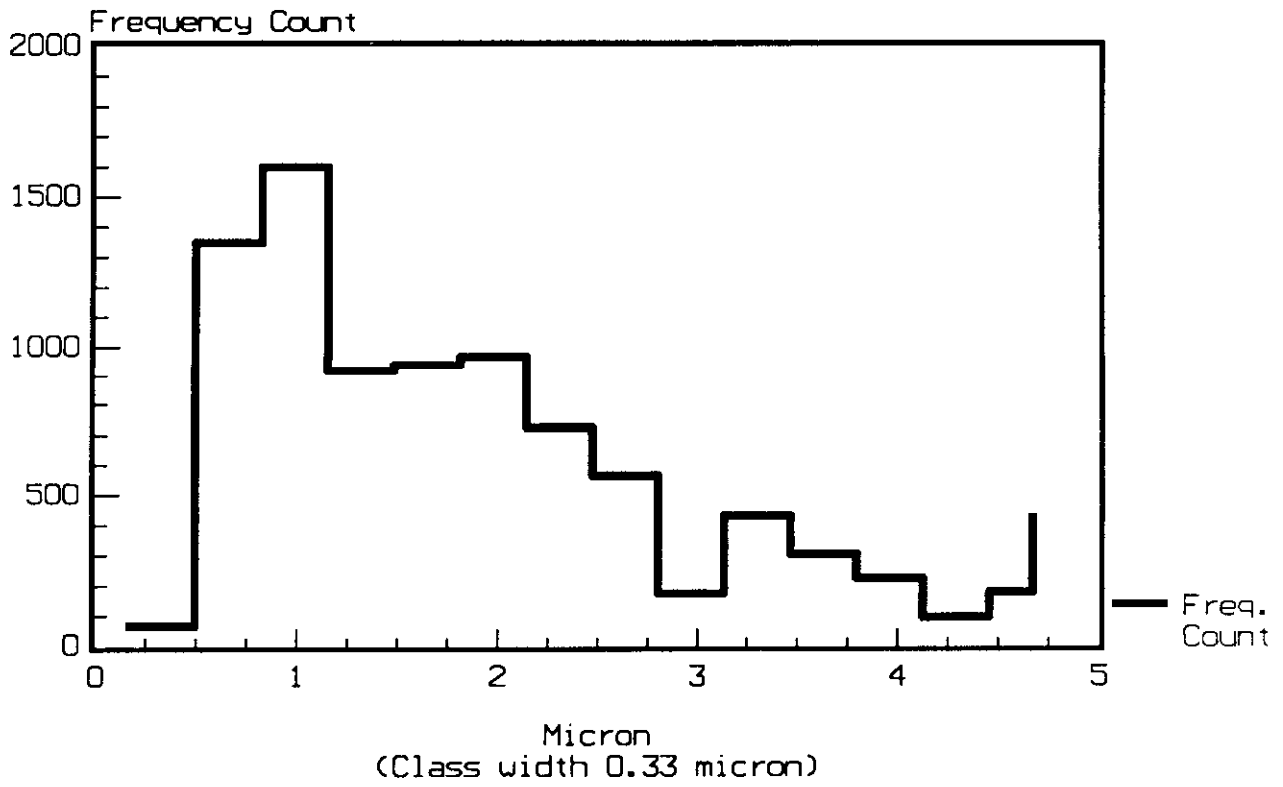
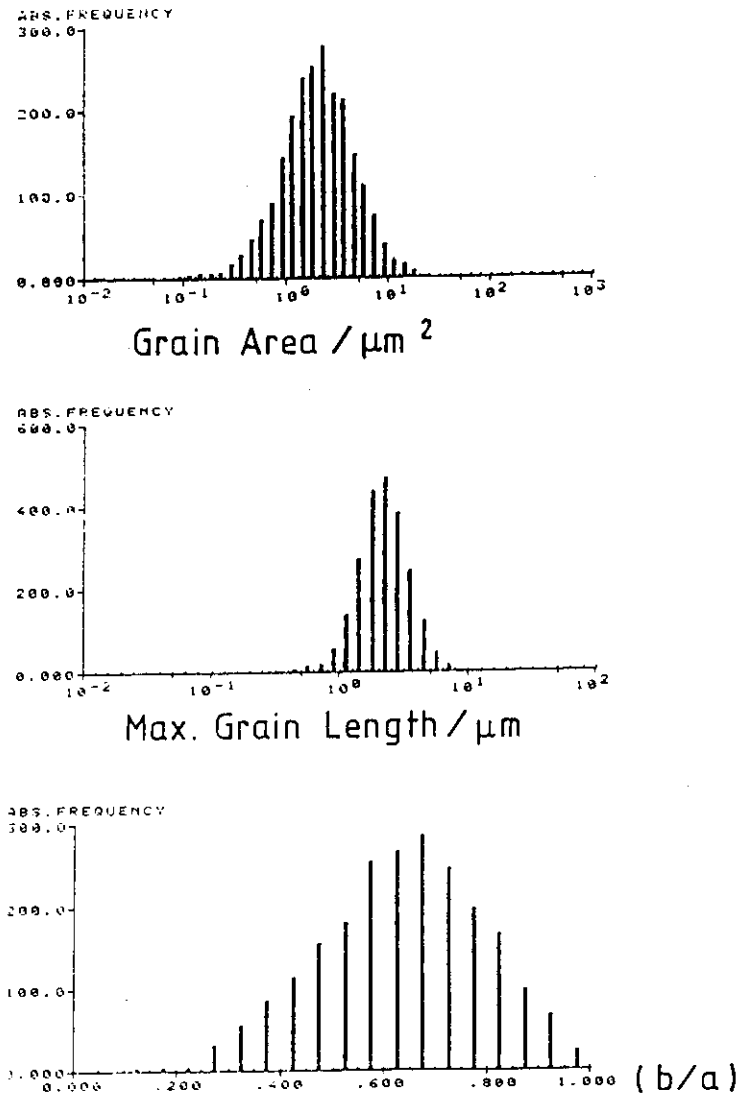


Fig. 2



Average Frequency Distributions of
Grain Area, Grain Length and
Ellipse Form Factor (b/a) for
HIP-SiC (ESK) -2249 Grains

Fig 3

HIP-SN (ASEA CERAMA)
Grain Size Distribution
Lab# 1.

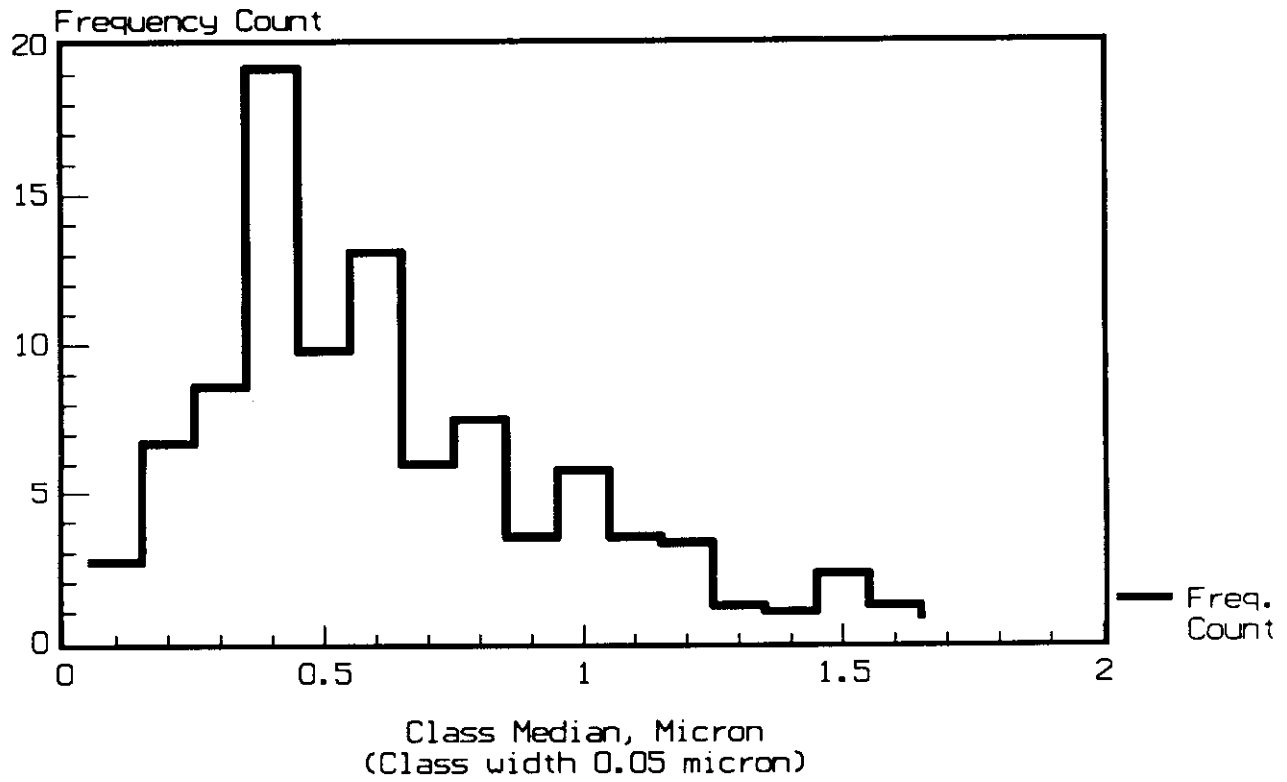
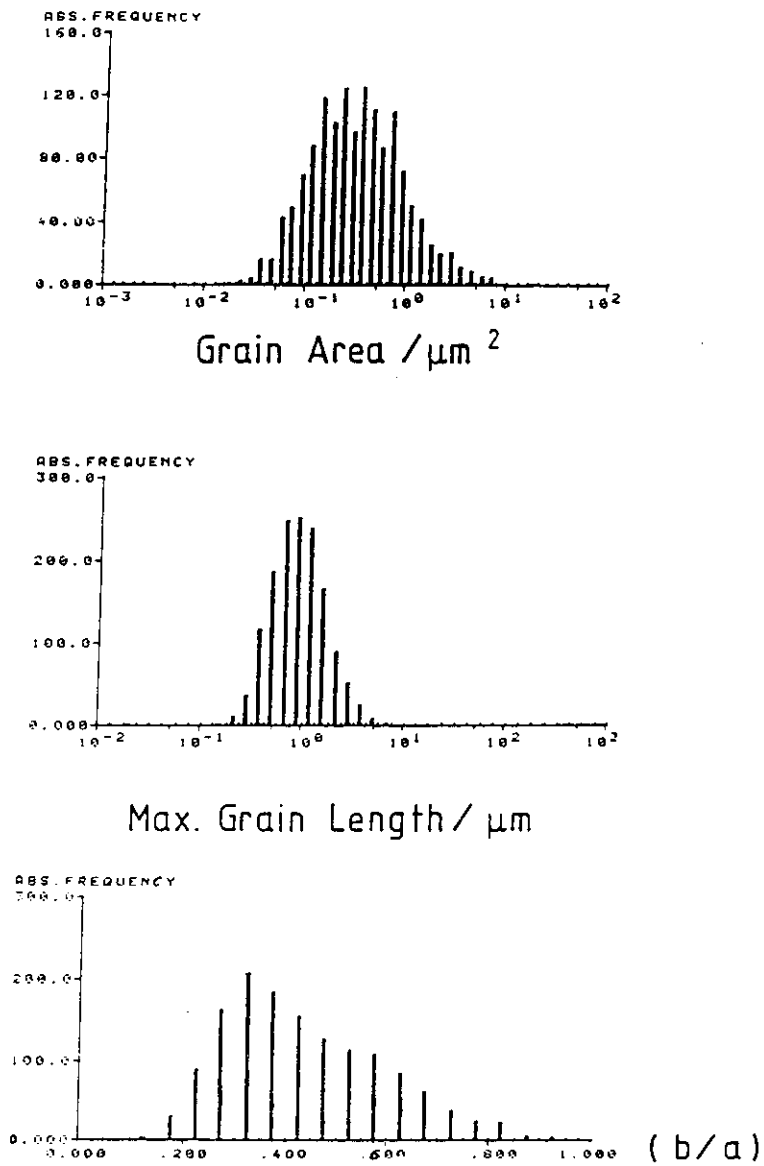


Fig. 4



Average Frequency Distributions of
Grain Area, Grain Length and
Ellipse Form Factor (b/a) for
HIP-Si₃N₄ (ASEA) - 1442 Grains

Fig 5

SSN (GTE)
Grain Size Distribution
Lab# 1.

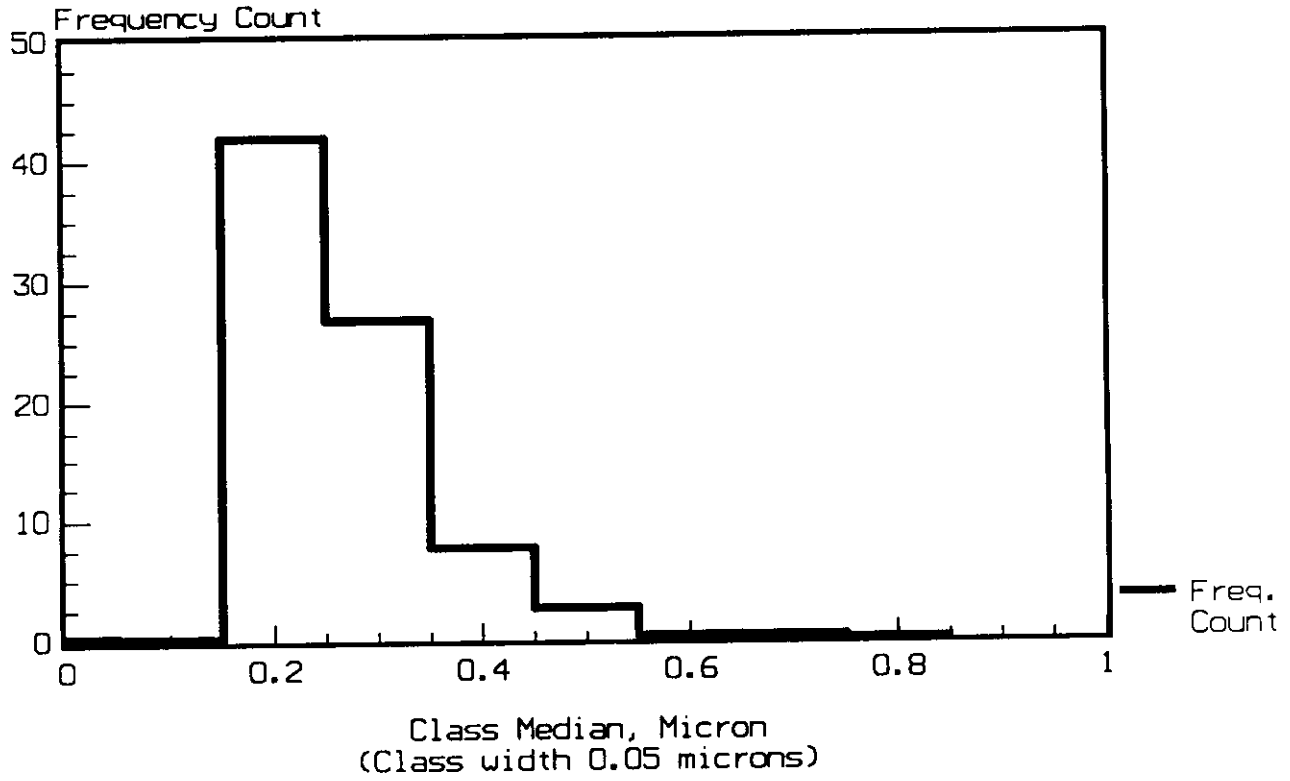
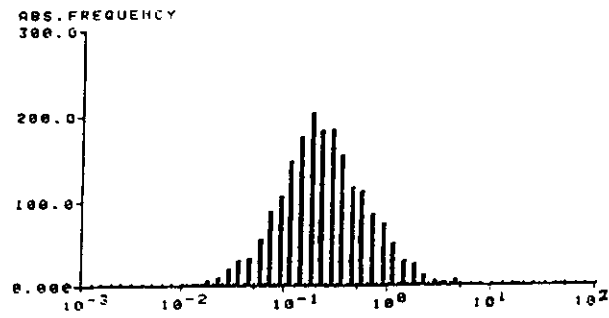
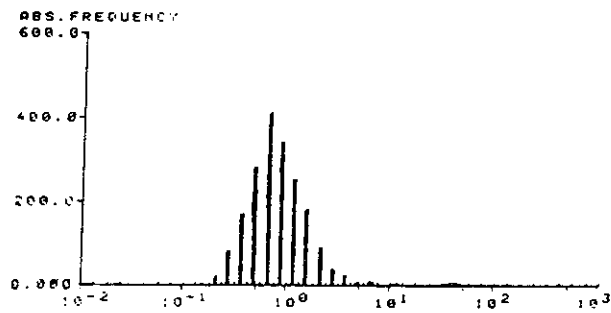


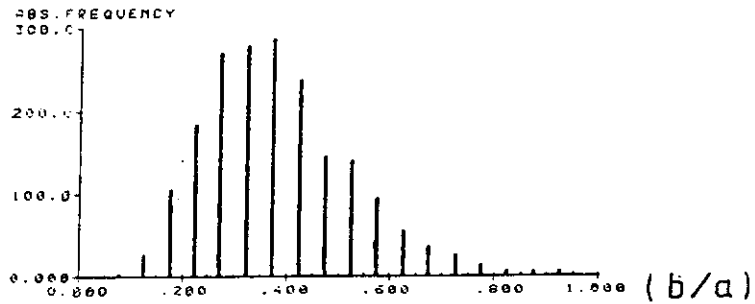
Fig. 6



Grain Area / μm^2



Max. Grain Length / μm



Average Frequency Distributions of
Grain Area, Grain Length and
Ellipse Form Factor (b/a) for
S-Si₃N₄ (GTE) - 1931 Grains

Fig 7

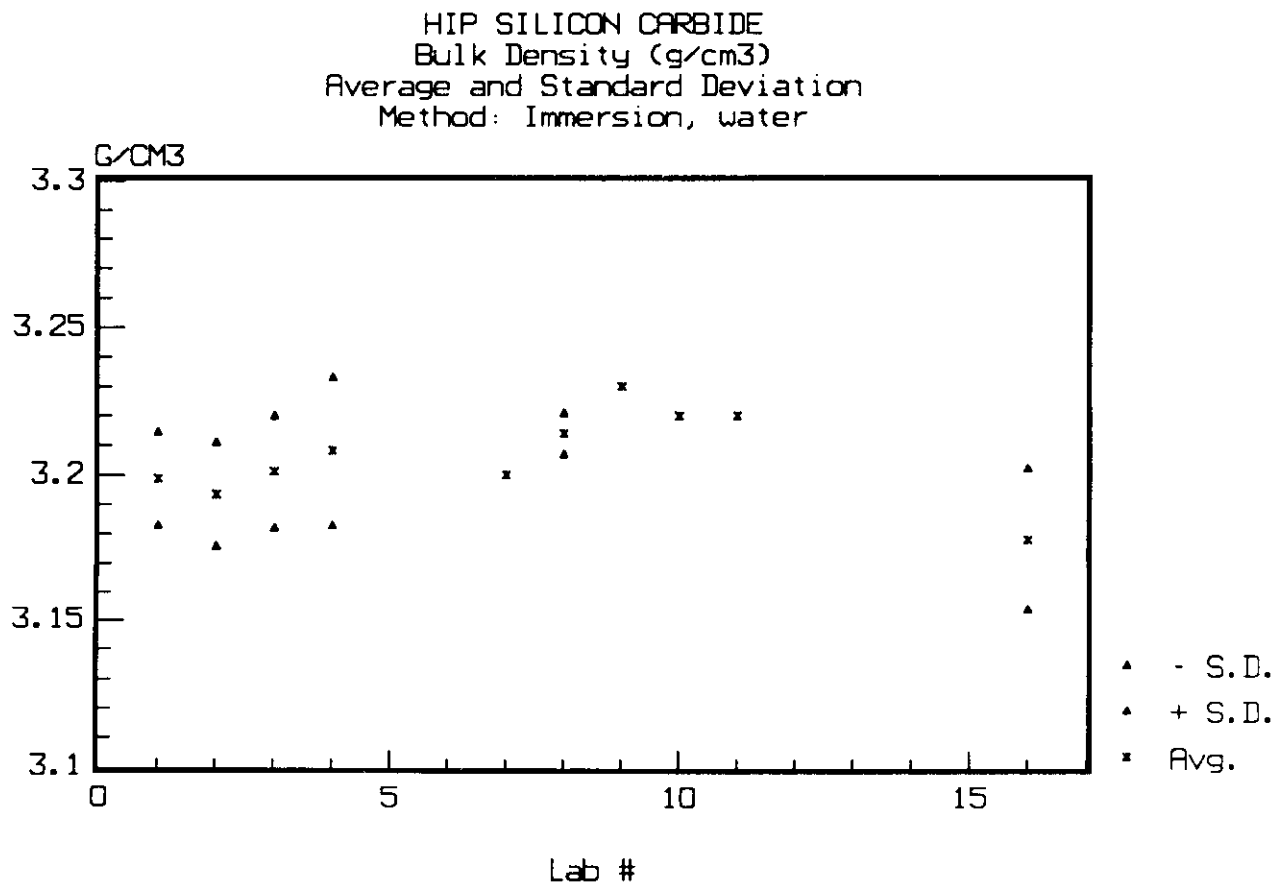


Fig. 8

HIP SILICON CARBIDE (ESK)
Bulk Density (g/cm³)
Average and Standard Deviation
Method: Immersion, toluene

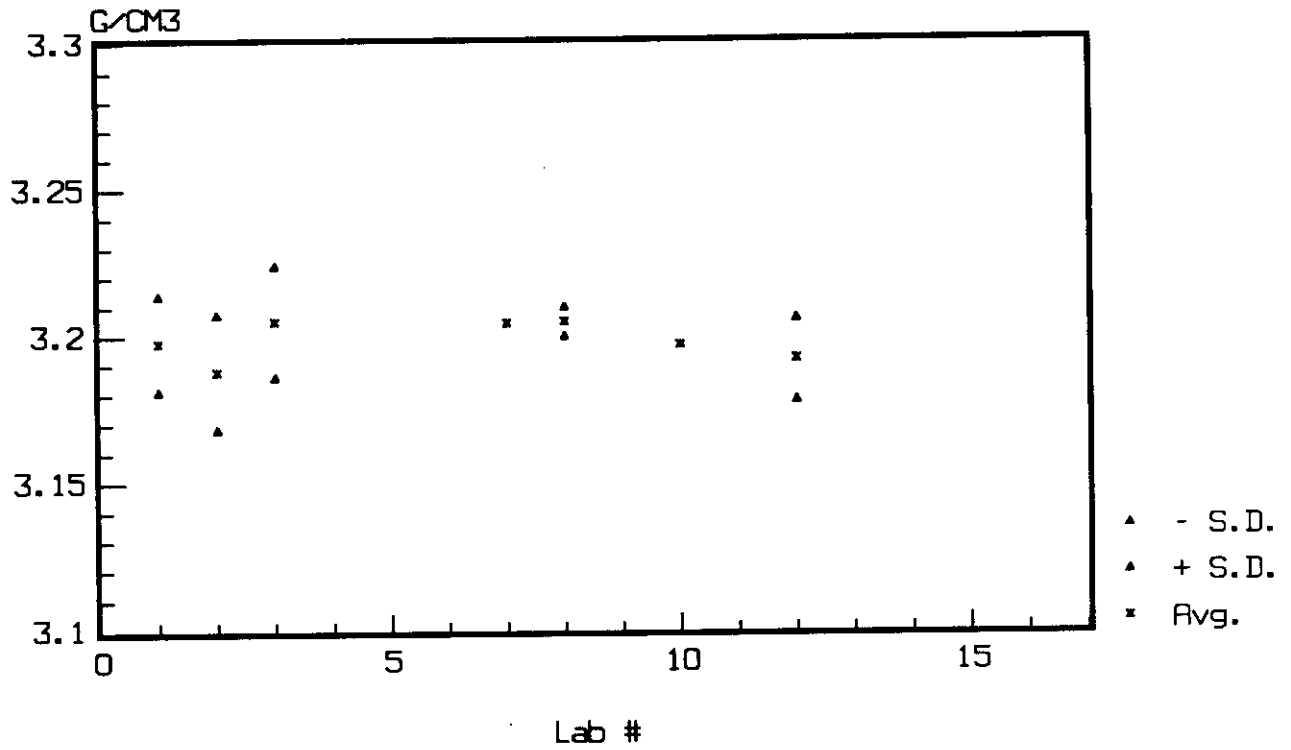


Fig. 9

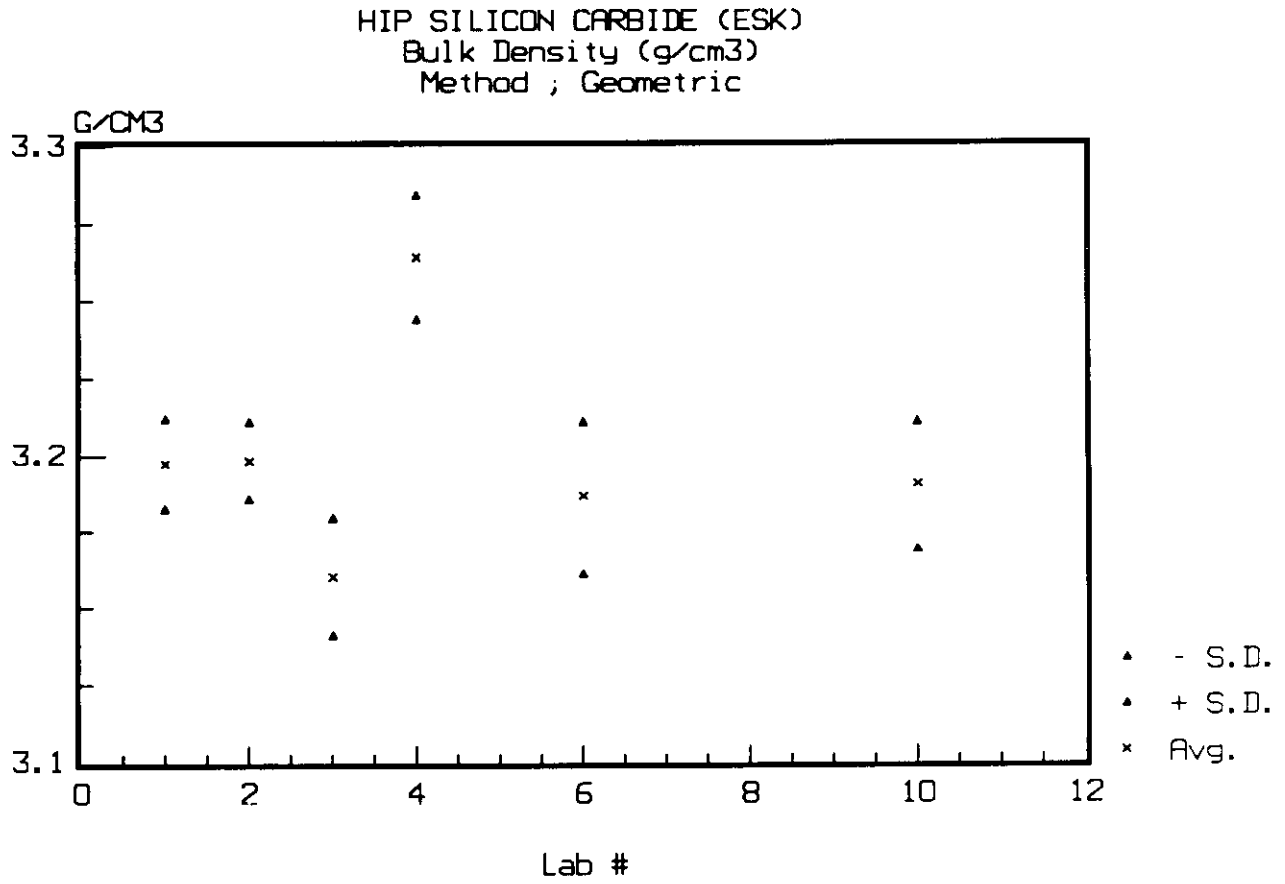


Fig. 10

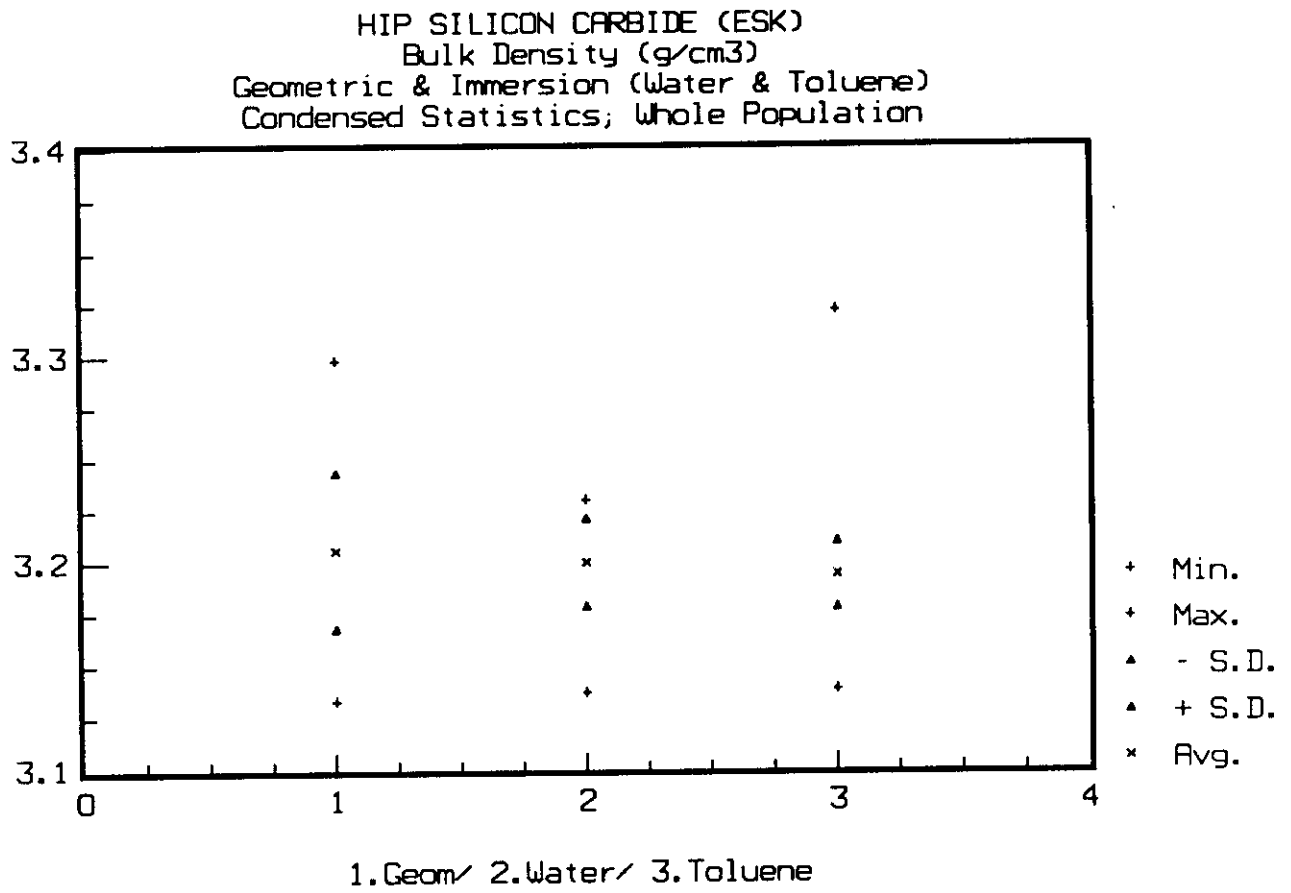


Fig. 11

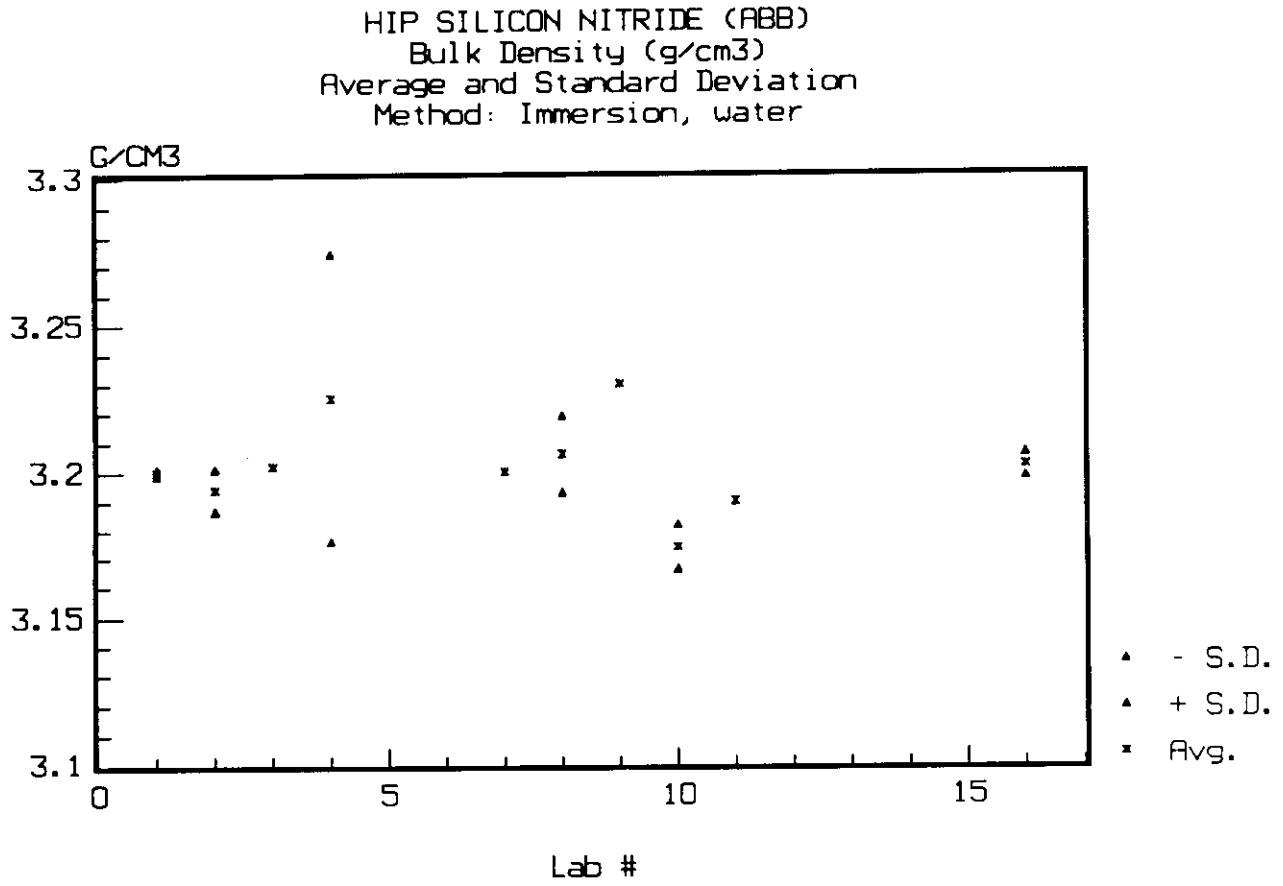


Fig. 12

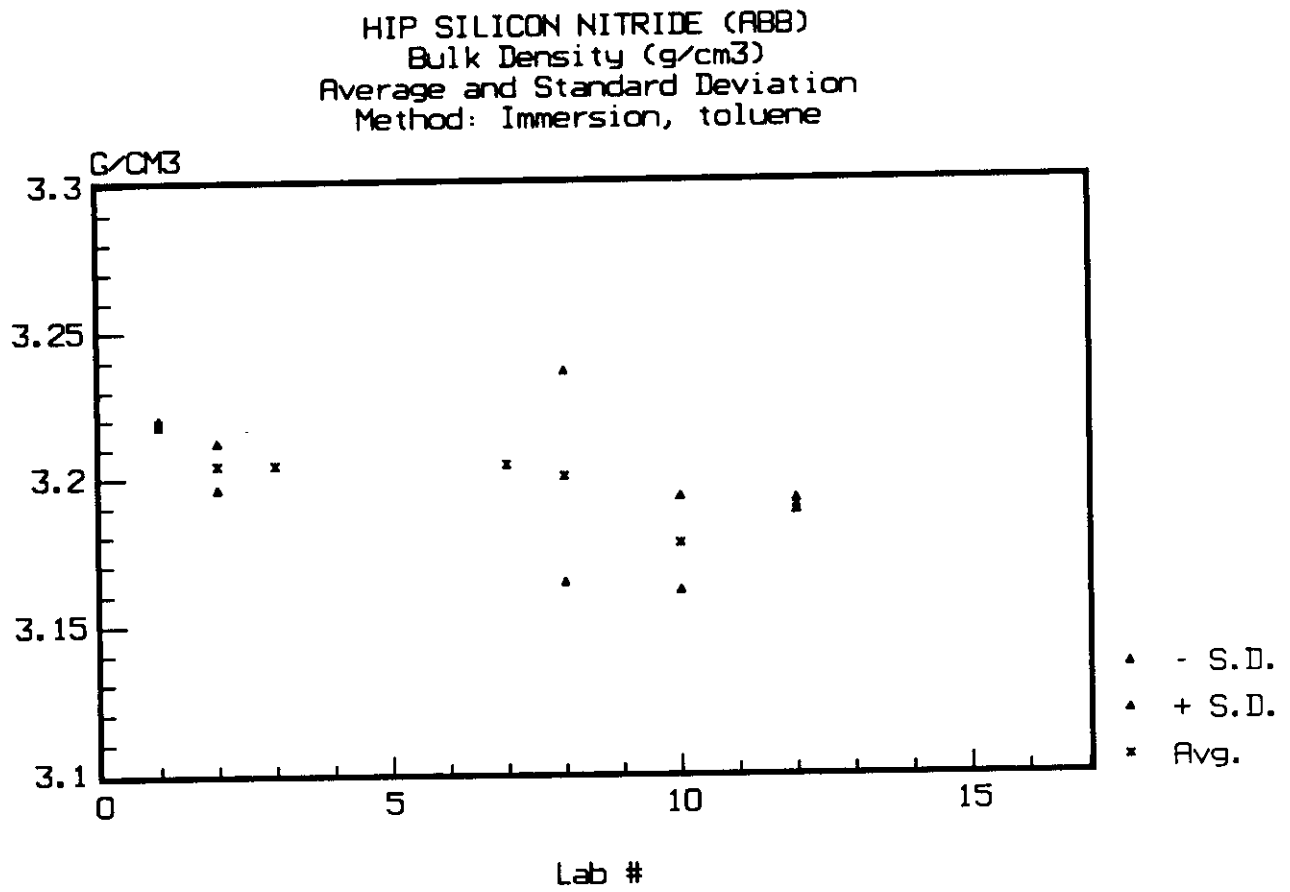


Fig. 13

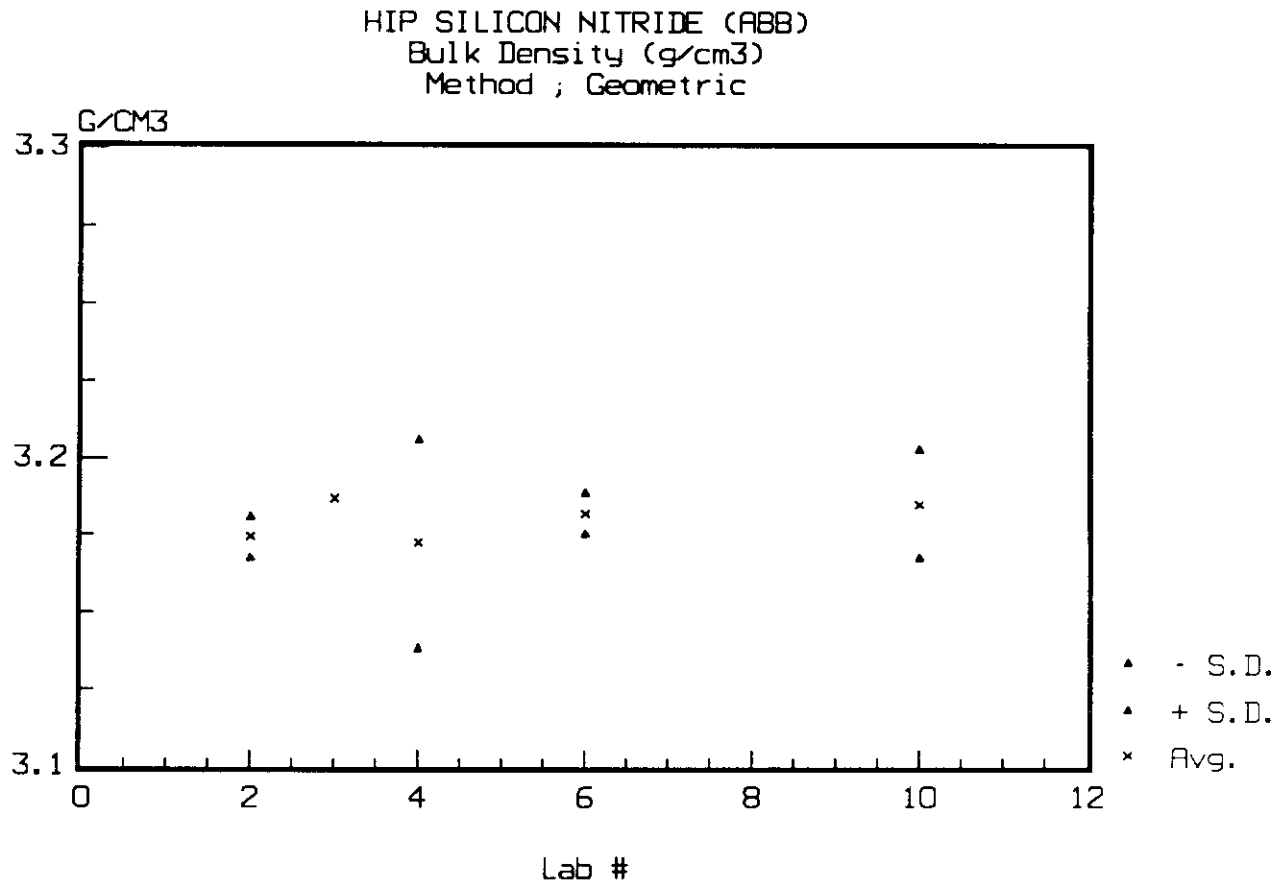


Fig. 14

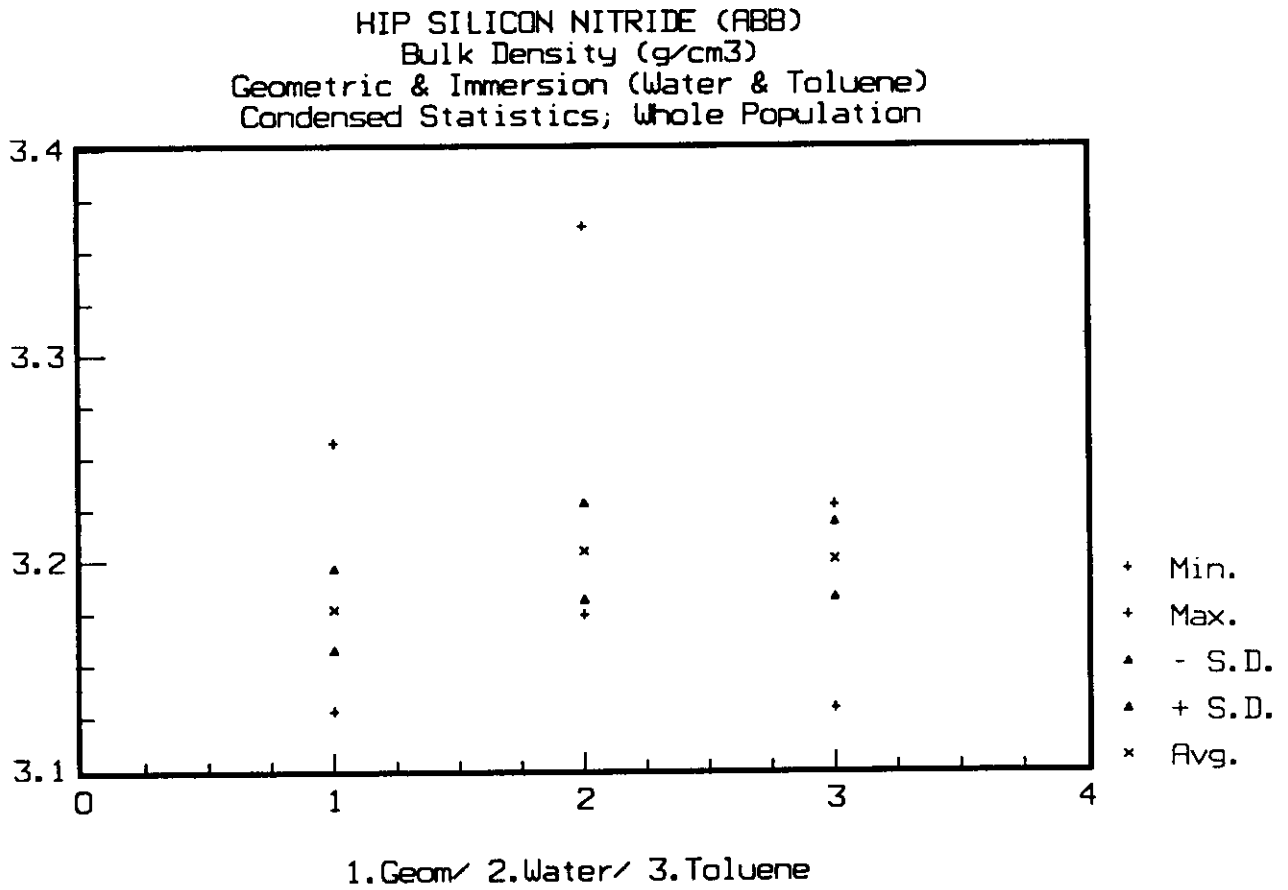


Fig. 15

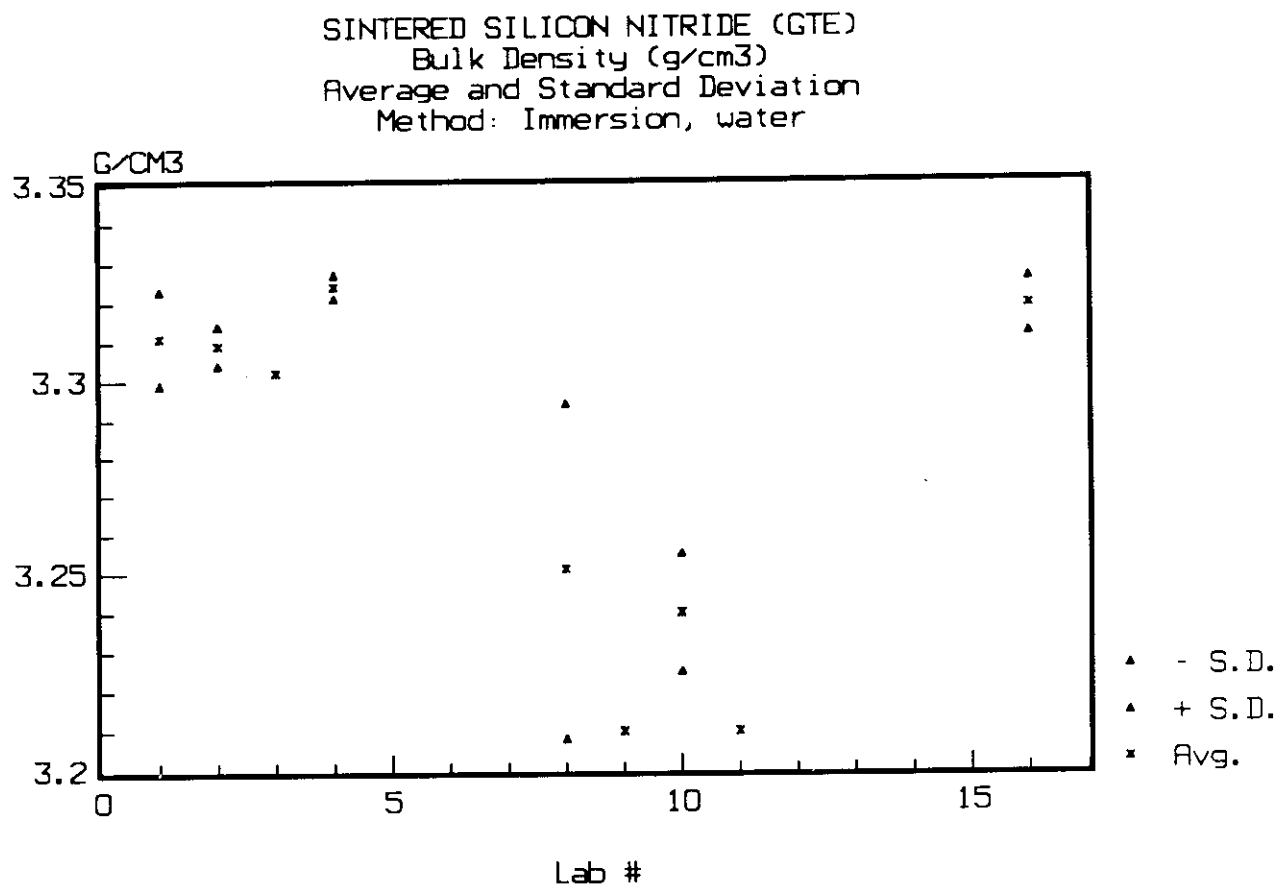


Fig. 16

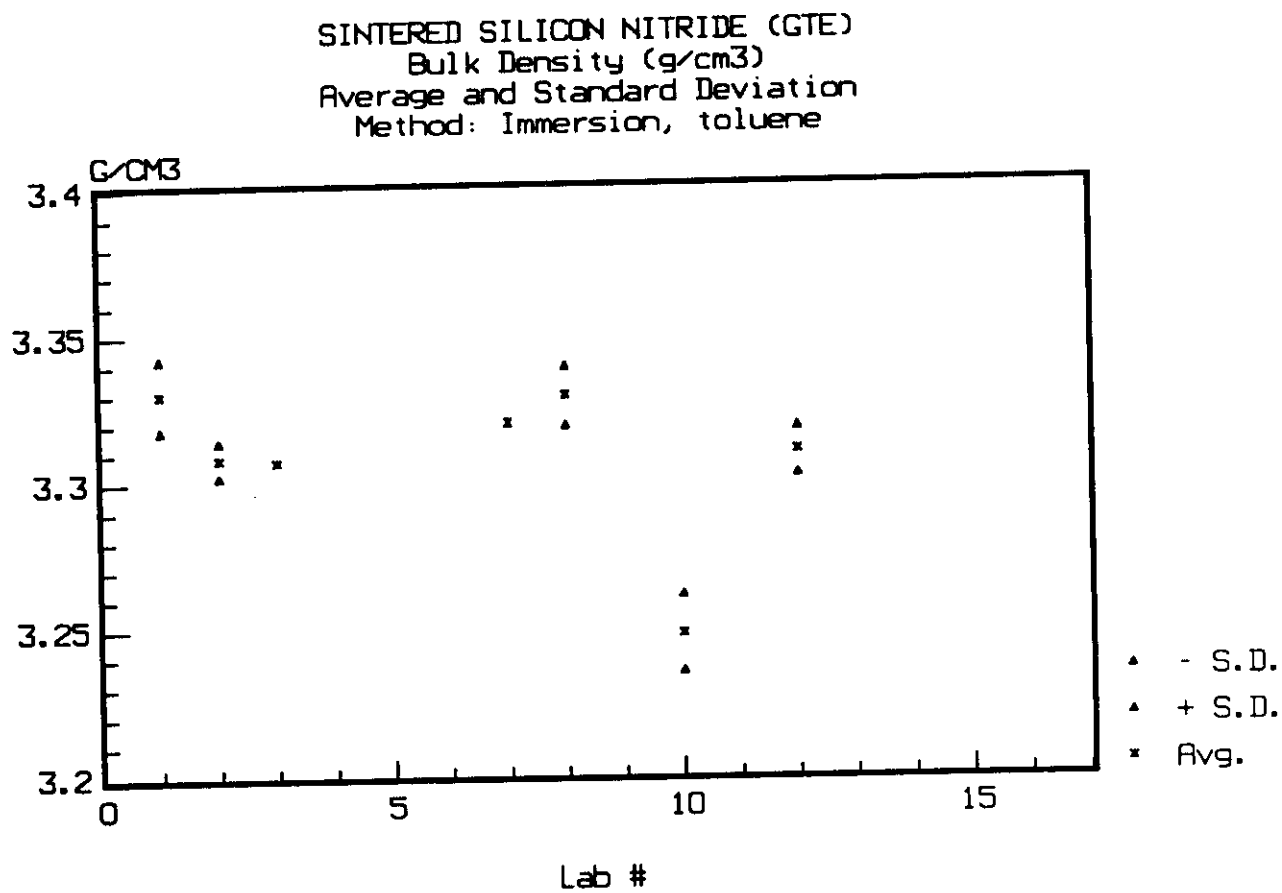


Fig 17

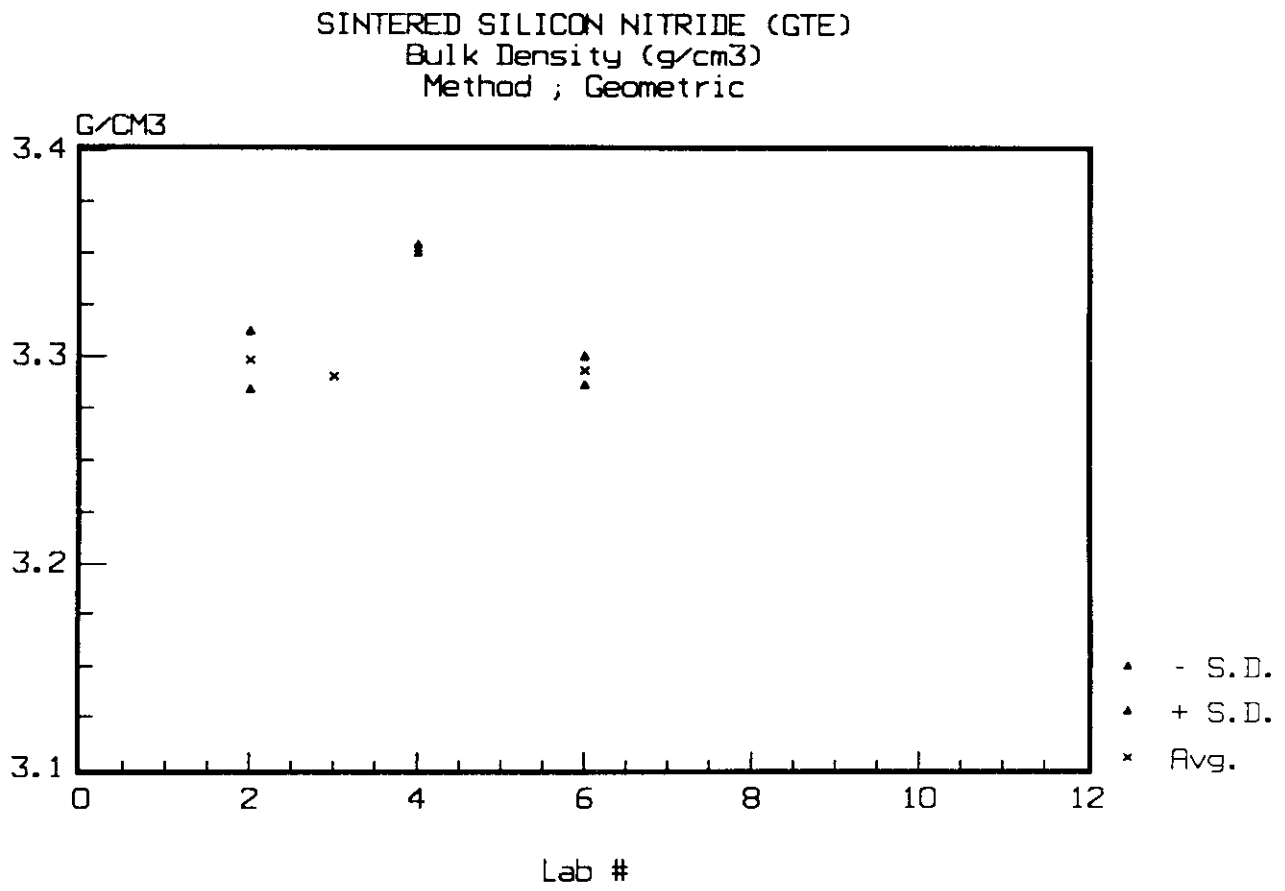


Fig 18

SINTERED SILICON NITRIDE (GTE)
Bulk Density (g/cm³)
Geometric & Immersion (Water & Toluene)
Condensed Statistics; Whole Population

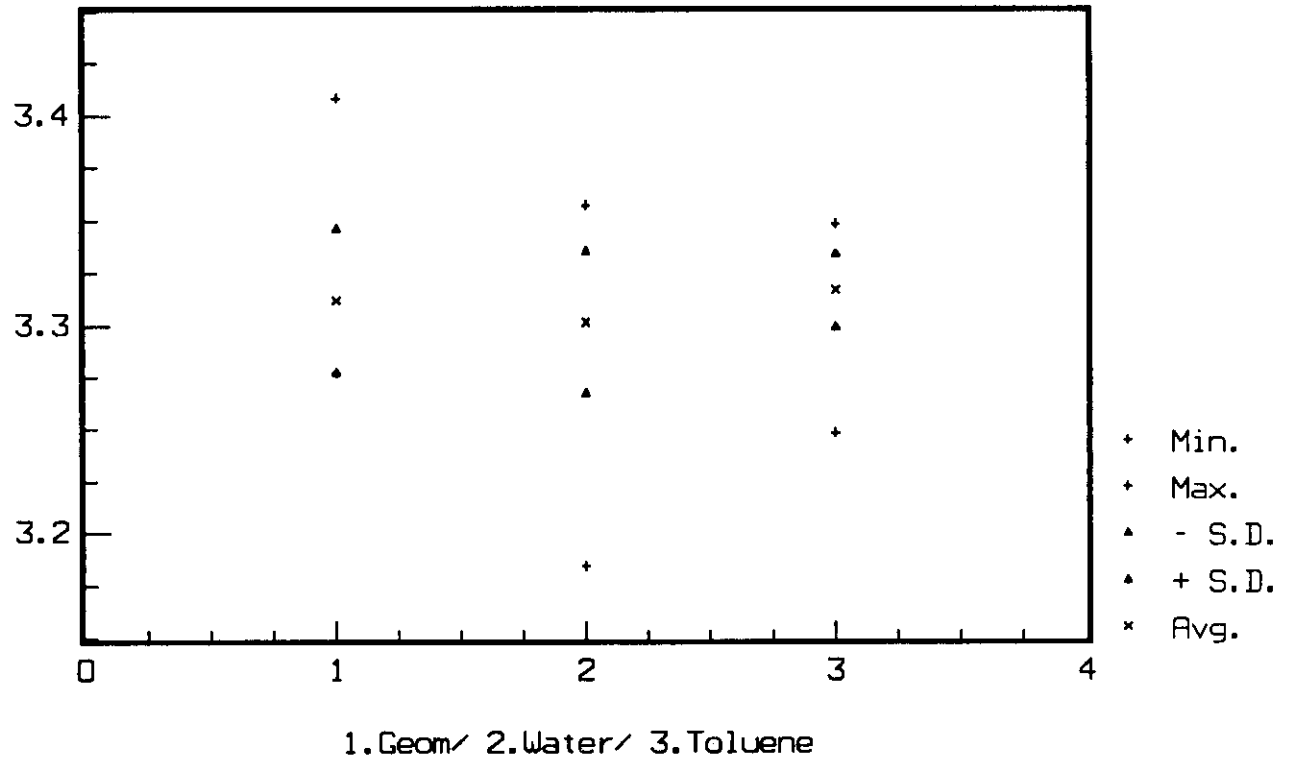


Fig 19

POROSITY (Vol%)
1. HIP SiC / 2. HIP SN / 3. SSN
Data : Lab # 2.
ASTM Procedure C-373.

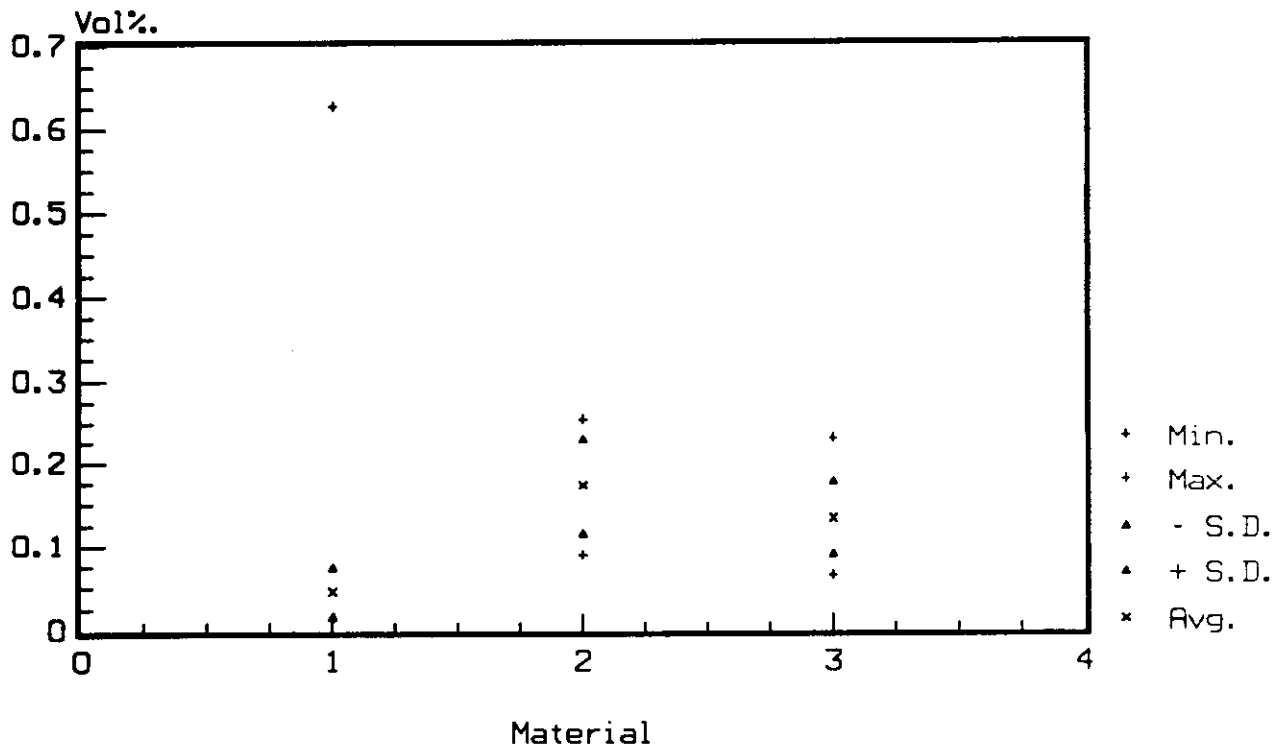


Fig. 20