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METAL AND SELF-BONDED SILICON CARBIDE

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FOREWORD

This report concerns the work of R. A. Alliegro, L. B. Coffin, Research Associates and J. R. Tinklepaugh, Project Director of the New York State College of Ceramics, Alfred University, Alfred, New York. The preparation of the report was largely the work of R. E. Wilson, Sr. Research Associate. The work was accomplished under the direction of W. G. Lawrence, Chairman, Department of Research, and M. Tuttle was a Consultant.

This report summarizes work on this project during the period 11 January 1953 to 10 January 1954 in which studies were continued on the metal-bonding of silicon carbide and the densification of self-bonded hot-pressed silicon carbide. Prior studies were reported in WADC Technical Report 53-5. This work is being continued and further reports will be issued as the research progresses. The work was accomplished under Contract AF33(038)-16190. It was administered under the direction of the Aeronautical Research Laboratory with Murray A. Schwartz as project engineer, and is identified under Task No. 70634, "Ceramic and Cermet Research."

ABSTRACT

Dense silicon carbide in the range of 95-97% of theoretical density was produced using various grain size mixes of alpha silicon carbide. When beta silicon carbide is used as the grain for hot pressing, uniform densities in the 97 to 98% range of theoretical density are obtained.

Hot pressed silicon carbide bonded by Cr:Mo (1:1) has a strength of 31,000 psi, modulus of rupture. This material is relatively stable at high temperatures in air, carbon monoxide and steam. Silicon carbide structures having porosities in the 35 to 40% range may be infiltrated by Hastelloy C under pressure. Chromium-nickel alloys and titanium metal will bond silicon carbide when sintered in vacuum.

PUBLICATION REVIEW

The publication of this report does not constitute approval by the Air Force of the findings or the conclusions contained therein. It is published only for the exchange and stimulation of ideas.

FOR THE COMMANDER:

Leslie B. Williams

LESLIE B. WILLIAMS
Colonel, USAF
Chief, Aeronautical Laboratory
Directorate of Research

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INTRODUCTION

The work reported here is a continuation of the investigation described in WADC Technical Report No. 53-5 issued in January 1953.

The primary objective of this work was to develop a metal bonded silicon carbide cermet having properties comparable to a typical nickel bonded titanium carbide cermet. Silicon carbide has not been bonded successfully previously by the transition metals and, therefore, the achievement of even moderate strengths in such compacts is a significant technical advancement in the high temperature field.

For applications in the aircraft power plant, exceptional high temperature strength is required. This goal has not been reached in the work reported here, and therefore, it will be necessary to continue the investigation of methods of fabrication, particularly infiltration.

This report is the result of several simultaneous investigations and is divided into four parts to facilitate preparation. Part I is concerned with the methods used to obtain extremely dense silicon carbide. Part II describes the various investigations in the fabrication of metal bonded silicon carbide. Parts III and IV pertain to the high temperature oxidation resistance of silicon carbide and the structure of the various silicon carbides as observed by x-ray diffraction techniques.

PART I

METHOD FOR PREPARING SELF BONDED SILICON CARBIDE OF HIGH UNIFORM DENSITY

I DISCUSSION

Previous work had produced thin pieces of silicon carbide having a density approximately 95% of the theoretical density. To do this, pressures of the order of 10,000 to 16,000 psi were required and the dense region extended only about 1/8" inward from the top and bottom surfaces of the samples. These extreme pressures and the high temperature (approaching the dissociation temperature) required imposed limitations on the forming of large pieces. To form large pieces of uniform density, the temperature and pressure required had to be reduced and this was attempted in the following ways:

(1) By the selection of proper grain size or combination using alpha silicon carbide.

(2) By hot pressing parts using the elements silicon and carbon.

(3) By forming beta silicon carbide from the elements and subsequently hot pressing this material during its inversion to alpha.

II. HOT PRESSING TECHNIQUES USING ALPHA SILICON CARBIDE

A. Temperature Calibration

Accurate temperature measurements of the specimens being hot pressed were difficult to obtain with either a radiation or optical pyrometer because of the presence of gases at high temperature and because of the large temperature gradients within the furnace. A method of calibrating the temperature indicated with the actual temperature of the piece being pressed was devised using a special calibration furnace and sight tubes purged with helium.

B. Hot Pressing Techniques

Silicon carbide specimens 3/4" diameter by 1" long were hot pressed from the top and bottom in cylindrical graphite molds 3" in diameter and 2 1/2" long. Specimens were prepressed cold and then hot pressed to a maximum temperature which was held for a short period of time. Experiments were conducted to determine the effect of; grain size, maximum temperature, prepressing pressure, hot pressing pressure, and length of time held at maximum temperature on the density and uniformity of the specimen.

(1) Prepressing Technique - By reinforcing the graphite die with a steel ring and using steel push rods, pressures up to 25,000 psi were applied to the cold die without causing failure. The following mix designated "Mix O" was used to

determine the effect of variations in cold pressing pressure on the final hot pressed density.

100 mesh	SiC	30.0%
240 "	"	45.0%
1200 "	"	25.0%

Mix O was prepressed cold to pressures ranging from 5000 to 25,000 psi in the steel reinforced graphite die and then hot pressed using 10,000 psi to as close to 4600°F as possible and held for 15 minutes. The bulk density of each specimen was determined and is listed in Table I.

TABLE I

Effect of Various Prepressing Pressures On The Final Hot Pressed Density

Cold Pressing Pressure psi	Hot Pressed Density g/cc	Temperature °F
5,000	2.75	4640
10,000	2.85	4645
15,000	2.90	4655
20,000	2.89	4670
25,000	2.85	4670
25,000	2.89	4665
25,000	2.76	4505

From Table I it is obvious that increasing the prepressing pressure from 5000 to 15,000 psi increased the final density and that higher pressures did not result in further increase. The specimens appeared to be fairly uniform in density throughout.

(2) Effect of Hot Pressing Temperature on Final Density - Specimens were cold pressed from Mix O at 5000 psi and then hot pressing using 10,000 psi holding various maximum temperatures for 10 minutes. The densities of the specimens are given in Table II.

TABLE II

Effect of Hot Pressing Temperature on Bulk Density

Temperature °F	Density g/cc
4305	2.66
4340	2.67
4415	2.66
4450	2.60
4500	2.70
4540	2.71
4590	2.71
4640	2.75

From the data obtained, it was evident that the density increases with temperature up to the highest temperature shown. Higher temperatures result in the dissociation of the silicon carbide into graphite and silicon vapor.

(3) Effect of Holding Time at Maximum Temperature - The length of time that the specimen was held at maximum temperature presented still another variable. A series of specimens were cold pressed at 25,000 psi and then hot pressed using 10,000 psi to about 4600°F for various lengths of time as shown in Table III. Mix 33 having the following composition was used for this work.

100	mesh	SiC	35.0%
240	"	"	40.0%
1200	"	"	25.0%

TABLE III

Effect of Time or Maximum Temperature on Density

Time at Temperature	Density g/cc	Temperature °F
0	2.70	4650
5	2.79	4655
10	2.96	4645
15	2.95	4600
20	2.74	4600

Maximum density was found to be obtained from a 10 to 15 minute holding period at maximum temperature.

(4) Effect of Variation of Hot Pressing Pressure - A very pure 1200 mesh silicon carbide was used for this work. Specimens were cold pressed at 20,000 psi and hot pressed to 4500°F for 15 minutes using various pressures as shown in Table IV.

TABLE IV

Effect of Hot Pressing Pressure on Density

Pressure psi	Density g/cc	Temperature °F
2500	2.34	4510
5000	2.43	4500
7500	2.75	4500
10,000	3.11	4500

The density was found to increase quite rapidly with pressure up to 10,000 psi.

(5) Effect of Grain Size Distribution on Density - Various grain sizes and mixtures of grain sizes were cold pressed using 15,000 psi and then hot pressed using 12,000 psi.

Densities were determined after cold pressing and after hot pressing and the results are given in Table V. The two, three and four component mixes were selected for their high cold pressed densities found in previous work. Each specimen was held for 15 minutes at the maximum temperature.

The greatest density was achieved using 1200 mesh silicon carbide. It was noted that the grain size compositions giving the highest cold pressed density, did not produce the highest final hot pressed density.

C. Discussion of Results

The formation of dense self bonded silicon carbide from alpha silicon carbide grain required 10,000 psi or higher and the dissociation temperature of silicon carbide had to be approached and the temperature maintained for ten to fifteen minutes. By cold pressing the alpha grain to 15,000 psi prior to hot pressing, specimens of greater density were obtained apparently as a result of greater uniformity. The high pressures and temperatures required to hot press dense parts from alpha silicon carbide make the formation of large pieces by this method impractical.

TABLE V

The Effect of Grain Sizes and Compositions on Density

Mesh	Average Particle Size Wagners Micron	Mix 21 %	Mix 23 %	Mix 22 %	Mix 24 %	Mix 19 %	Mix 259 %	Mix 33 %	Mix 221 %	Mix 244 %
20	1015.0								40.0	39.0
100	132.0							35.0		26.0
240	49.0	100.0					68.0	40.0	35.0	
400	14.5		100.0							22.0
800	8.2			100.0						
1000	6.6				100.0					
1200	5.4					100.0	32.0	25.0	25.0	13.0
Temp. °F		4504	4515	4510	4510	4490	4535	4550	4565	4560
Cold Pressed Density gms/cc		1.92	1.89	1.73	1.67	1.64	2.19	2.36	2.42	2.52
Hot Pressed Density gms/cc		2.60	2.93	2.47	2.44	3.18	2.66	2.63	2.81	2.77

III THE FORMATION OF UNIFORM DENSE SILICON CARBIDE BY HOT PRESSING SILICON AND CARBON

A. Discussion

The purpose of this study was to determine the feasibility of using a mixture of carbon and silicon as the powder charge to hot press uniformly dense silicon carbide.

Loss of silicon from extrusion between the die and plunger or reaction with the graphite die were anticipated and, therefore, various ratios of silicon to carbon were used.

Spectrographic pure electrode carbon and a high purity silicon powder were used to make the charge. The hot pressing technique which was previously established for hot pressing silicon carbide was used.

B. Procedure and Results

Mixtures of silicon and carbon varying from 65 to 75% silicon were prepared and hot pressed to 4500°F. Specimens made from a mixture of carbon and silicon equivalent to the theoretical composition of silicon carbide (70% Si - 30% C) were hot pressed at different temperatures from 4450°F to 4650°F. The results are shown in Table VI.

TABLE VI

Temperature and Composition versus Density

Silicon %	Carbon %	Temperature °F	Bulk Density gms/cc	App. Density g/cc
70.0	30.0	4400	2.91	3.10
70.0	30.0	4500	2.41	3.19
70.0	30.0	4650	2.32	3.20
65.0	35.0	4500	2.68	3.12
68.0	32.0	4500	2.36	3.20
72.0	28.0	4500	2.17	3.27
75.0	25.0	4500	2.12	3.21

Note - The samples were prepressed at 16,000 psi and hot pressed at 10,000 psi. The maximum temperature was held for 10 minutes.

C. Discussion of Results

A rapid slump occurred between 2400°F and 2650°F when the silicon melted. Application of pressure through this temperature range had considerable effect upon the density of the specimen. Considerable reaction with the graphite die occurred at the high temperatures, as the ratio of silicon to carbon was increased past the theoretical composition (70.0% Si + 30.0% C).

The samples obtained from this technique were not as high in density as those obtained using the alpha silicon carbide grain. They were, however, uniform from top to bottom of the specimen.

IV THE FORMATION OF UNIFORM DENSE SILICON CARBIDE FROM BETA SILICON CARBIDE

A. Discussion

As a variation of the method described above in which silicon carbide was hot pressed directly from the elements, it was attempted to first form beta silicon carbide without application of pressure. The beta could then be hot pressed to form a dense specimen of alpha taking advantage of the high state of reactivity resulting from the beta to alpha inversion. It was anticipated that this would reduce the temperature and pressure required for the formation of dense self bonded specimens.

B. Procedure and Results

Mixtures of fairly pure silicon and carbon (70.0% Si and 30.0%C) were fired at 3300°F to 3500°F to form beta silicon carbide. X-rays of this material after treating with acid showed the material obtained to be mostly beta silicon carbide. The beta silicon carbide was ground in a mortar to pass through a 200 mesh screen. It was then leached with HNO_3 and HF acid solution (50.0% - 50.0% by volume) to remove any excess silicon. The material was then washed to remove the acid and float out the carbon. After drying, it was passed through a 200 mesh screen and hot pressed. Two batches were prepared in this matter. The results of the hot pressing of this material are shown in Table VII.

TABLE VII

Hot Pressing of Beta Silicon Carbide

Batch No.	Temp. °F	Pressure psi	Bulk Density g/cc	App. Density g/cc	Percent Theoretical
1	4460	10,000	3.15	3.15	98.0
1	4460	10,000	3.11	3.11	96.5
2	4455	8,000	3.12		97.2
2	4455	6,000	3.08		95.9

Note - Specimens were cold pressed to 16,000 psi and the peak temperatures held 10 minutes.

C. Discussion of Results

Uniform, dense silicon carbide specimens were formed using beta silicon carbide. This method appeared to be the best of the methods tried. The lower pressure and temperatures required in forming dense specimens makes this method the most feasible for forming large shapes.

V. CONCLUSIONS

Alpha silicon carbide may be hot pressed forming specimens of a density approaching the theoretical. The following factors influence the density obtained.

(1) Mixes containing coarse grain fractions must be hot pressed to between 4550 and 4650°F. The use of only fine material reduces the hot pressing temperature.

(2) The length of time that the specimen is held at maximum temperature is critical with a holding time of 10 to 15 minutes being the optimum.

(3) Pressures of at least 10,000 psi must be used.

(4) The selection of the proper grain size distribution to give the most dense packing does not necessarily result in the most dense hot pressed specimen.

(5) Cold pressing the specimens to 15,000 psi before hot pressing increases the density obtained by improving the uniformity of the density distribution.

(6) Dense specimens of silicon carbide were not satisfactorily formed by hot pressing starting with the elements.

(7) Silicon carbide specimens of greatest uniform density were made by hot pressing the beta form during its inversion to alpha. Pressures as low as 6000 psi may be used to achieve densities of 96% of the theoretical at hot pressing temperatures between 4400 and 4500°F.

PART II

INVESTIGATION OF METHODS OF FORMING AND THE PROPERTIES OF METAL BONDED SILICON CARBIDE

I Discussion

The investigation of the bonding of silicon carbide by metals, as described in WADC Technical Report 53-5 has opened several fields of specific interest. Based on these findings further development of metal bonded silicon carbide has progressed.

It was apparent from the past work that the metals most suitable for bonding silicon carbide could be narrowed down to chromium, iron and a mixture (solid solution) of chromium and molybdenum (1:1) by weight. Therefore, an investigation involving these metals was undertaken to study the following: (1) the pressing conditions necessary to form dense, well bonded specimens; (2) the effect of additions of molybdenum and chromium on the iron bonded silicon carbide; (3) the strength (modulus of rupture) of the metal bonded specimens formed under varying hot pressing conditions; (4) the study using x-ray techniques of the effect of varying the additions of molybdenum on chromium bonded silicon carbide.

Stellite 21 (Vitallium) and Hastelloy C were also investigated as bonding agents for silicon carbide. Nickel by itself seemed to be too reactive with silicon carbide, but when alloyed with other metals such as chromium and molybdenum the activity was substantially decreased. This allowed for the use of alloys such as Hastelloy B and C because of their desirable high temperature properties.

The investigation of the behavior of metals and alloys with silicon carbide was undertaken using vacuum techniques. The melting ranges of several metals and alloys were determined by heating the metals on different materials, i.e. zirconia, graphite, etc. This was accomplished so that vacuum infiltration and sintering could be more easily carried out with the information derived. Infiltration and sintering under an atmosphere of helium and argon was also tried with the various metals.

Using techniques similar to those used in hot pressing, Hastelloy C has been successfully forced into pre-hot pressed silicon carbide skeletons. This technique allows for a more reactive metal or alloy to be forced into the silicon carbide structure at temperatures low enough to minimize and control the reaction products formed.

II HOT PRESSED METAL-SILICON CARBIDE MIXTURES

A. Hot Pressing Techniques

Iron, chromium and chromium-molybdenum (1:1) were selected as materials most likely to bond silicon carbide based on investigations taking into account the bonding zone studies, wettability of the metals on silicon carbide, and the x-ray investigation of reaction phases. A mixture of 50% - 400 mesh - 30% - 800 mesh and 20% - 1200 mesh silicon carbide grain was selected to be used with the metals under investigation. Varying percentages of the metals were mixed with the silicon carbide grain for a period of twenty four hours or more in glass jars attached to a ball mill frame.

The material was tamped into graphite dies which had previously been lightly coated with colloidal graphite to prevent excessive reaction with the mold and plungers. The mold was placed in the hot press shown in Fig. 1 and heated to temperatures ranging from 2450°F to 3700°F depending on the metal used, under a pressure of from 5000 - 10,000 psi. The mold diameter was one inch so that from the resultant specimen, two bars measuring approximately 7/8" x 3/16" x 1/8" could be cut and used for modulus of rupture tests.

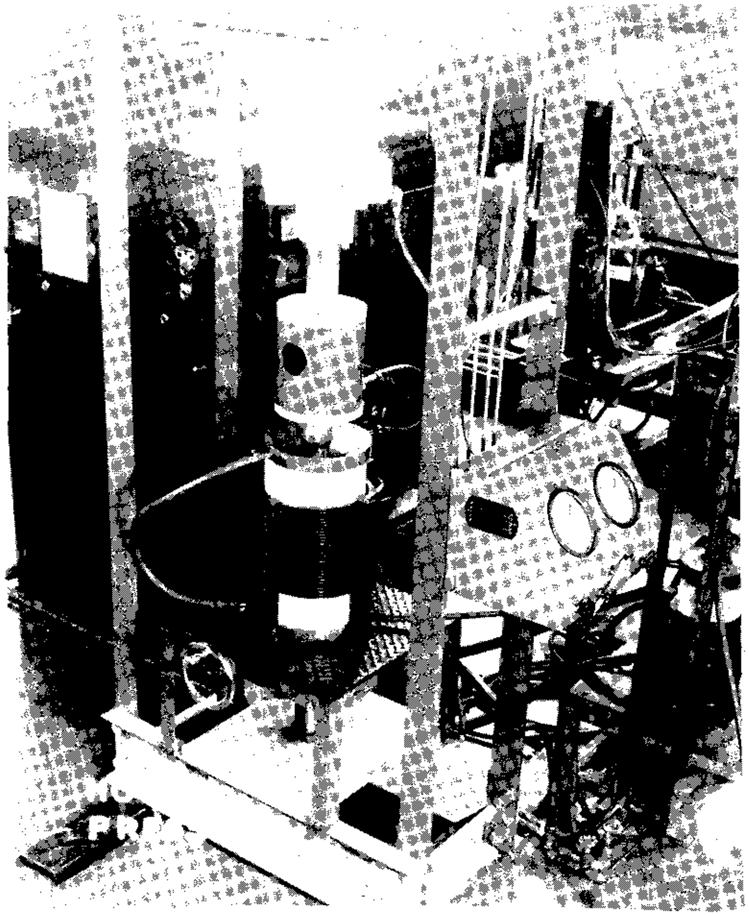


Fig. 1

Hot Press Furnace

(1) Hot Press Results - The results for the chromium, silicon carbide; chromium-molybdenum, silicon carbide; and iron-chromium-molybdenum, silicon carbide systems are shown in Tables VIII and IX.

It was apparent in many of the pressings that the metal had squeezed out from around the graphite plungers. Therefore, a series of firings were completed using mixtures having a much higher metal content and employing much lower pressures and temperatures than had previously been used. The results of this series are shown in Table X. Some of the specimens produced were of a sufficient size that bars 1-1/2" long could be cut from them. These bars were broken on a 1-1/4" span at 1800°F and 2000°F.

(2) Modulus of Rupture - The modulus of rupture unit used for the testing of these bars is shown in Fig. 2. The force for breaking the bars was transmitted by a silicon carbide indentor mounted in a silicon carbide refractory. The weight was applied to a lever (10.3:1) by means of a pail into which a stream of water was directed. The weight was measured by a spring-type scale. The results of the modulus of rupture tests are shown in Tables VIII, IX and X.

TABLE VIII

Silicon Carbide-Cr and Cr:Mo Bonded

Spec. No.	Composition	Vol. Ratio	Density	Porosity	Modulus of Rupture	Remarks
1	65% SiC - 35% Cr:Mo	85:15	3.82	2.0%	11,100	Slight cracks
2	↓	85:15	3.83	2.0%	23,700	Slight cracks
3		87:13	3.74	0.7%	27,000	
4		87:13	3.73	1.0%	31,600	
5		90:10	3.66	0.6%	25,000	
6		90:10	3.66	0.6%	22,000	
7	65% SiC - 30% Cr:Mo 5% Si	85:15	3.75	3.2%	18,000	Mold Broke
8	65% SiC - 35% Cr	87:13	3.55	3.8%	10,000	Slight cracks
9	↓	89:11	3.50	1.2%	13,700	
10		88:12	3.46	3.1%	15,000	
11		84:11	3.29	5.3%	17,300	
12		88:12	3.56	1.4%	12,100	

Note: Hot-pressed at 10,000 psi - Cr:Mo fired to 3600°F, Cr to 3500°F

TABLE IX

Hot Pressing Temperature-Pressure and Physical Data With Modulus of Rupture

Spec. No.	Composition	Firing Temp.	Pressure psi	Density	Porosity	Modulus of Rupture
13	65% SiC-20% Fe-15% Cr:Mo	3500°F	10,000	3.22	12.2%	14,100
14A	65% SiC-15% Fe-20% Cr:Mo	3500	10,000	2.86	20.2%	10,900
B	65% SiC-15% Fe-20% Cr:Mo	3500	10,000	2.78	20.3%	10,000
15A	70% SiC-20% Fe-10% Cr:Mo	3500	10,000	2.96	18.5%	12,950
B	70% SiC-20% Fe-10% Cr:Mo	3500	10,000	2.89	18.5%	12,850
16A	65% SiC-30% Fe-5% Cr:Mo	3500	10,000	2.84	17.9%	12,150
B	65% SiC-30% Fe-5% Cr:Mo	3500	10,000	2.84	17.5%	12,050
17	50% SiC-30% Fe-20% Cr:Mo	2700	7,000	3.30	10.3%	24,700
18A	50% SiC-30% Fe-20% Cr:Mo	2800	5,000	3.06	19.0%	18,800
B	50% SiC-30% Fe-20% Cr:Mo	2800	5,000	3.06	10.0%	18,100
19A	65% SiC-20% Fe-15% Cr:Mo	3150	10,000	2.84	19.4%	13,800
B	65% SiC-20% Fe-15% Cr:Mo	3150	10,000	2.84	19.2%	13,950
20A	65% SiC-15% Fe-20% Cr:Mo	3150	10,000	2.85	19.5%	13,850
B	65% SiC-15% Fe-20% Cr:Mo	3150	10,000	2.82	20.0%	14,700
21A	65% SiC-20% Fe-15% Cr:Mo	3750	3,000	3.08	19.1%	12,500

TABLE X

Modulus of Rupture and Physical Data of Hot Pressed Metal-Silicon Carbide Compositions

Spec. No.	Composition	Vol. Ratio	Temp. of testing	Temp. of forming	Density	Porosity %	Modulus of Rupture
22	45% SiC-55% Cr:Mo(1:1)		Rm. Temp.	2800°F	4.61	0.1	30,600 +
23A	35% SiC-65% Cr:Mo(2:1)	68:32	2000°F	2700°F	4.60	3.0	25,700
B	" "	"	"	"	"	"	24,100
24A	35% SiC-65% Cr:Mo(2:1)	65:35	Rm. Temp.	2800°F	4.76	1.2	24,800
B	" "	"	"	"	"	"	23,200
C	" "	"	"	"	"	"	22,600
D	" "	"	1800°F	"	"	"	30,300 +
25A	35% SiC-65% Cr:Mo(2:1)	64:36	Rm. Temp.	2775°F	4.58	5.8	22,400
B	" "	"	"	"	"	"	21,700
C	" "	"	"	"	"	"	21,300
D	" "	"	1800°F	"	"	"	30,000 +
26A	35% SiC-65% Cr:Mo(2:1)	63:37	Rm. Temp.	2730°F	4.87	1.0	22,000
B	" "	"	"	"	"	"	20,000
C	" "	"	"	"	"	"	18,200
D	" "	"	1800°F	"	"	"	25,000 +
27A	35% SiC-65% Cr:Mo(1:1)	61.39	Rm. Temp.	2670°F	5.10	1.0	22,600
B	" "	"	"	"	"	"	22,200
C	" "	"	"	"	"	"	21,500
D	" "	"	1800°F	"	"	"	23,100 +

TABLE X (con't.)

Spec. No.	Composition	Vol. Ratio	Temp. of testing	Temp. of forming	Density	Porosity %	Modulus of Rupture
28A	35% SiC-65% Cr:Mo(2:1)	60:40	Rm. Temp.	2800°F	4.96	1.2	20,600
B	" "	"	"	"	"	"	18,300
C	" "	"	"	"	"	"	18,100
D	" "	"	1800°F	"	"	"	29,200 o
29A	35% SiC-65% Cr:Mo(2:1)	60:40	Rm. Temp.	2730 °F	4.92	1.8	22,000
B	" "	"	"	"	"	"	20,000
C	" "	"	"	"	"	"	18,200
D	" "	"	"	"	"	"	25,000
30A	35% SiC-65% Cr:Mo(2:1)	53.47	Rm. Temp.	2735°F	4.67	14.0	16,700
B	" "	"	"	"	"	"	16,000
C	" "	"	"	"	"	"	15,500
D	" "	"	1800°F	"	"	"	27,200 †
31A	35% SiC-65% Cr:Mo(2:1)	53:47	Rm. Temp.	2800°F	4.98	8.0	18,500
B	" "		"	"	"	"	18,000
C	" "		"	"	"	"	17,500
D	" "		1800°F	"	"	"	31,800 †
32A	35% SiC-65% Cr:Mo(2:1)	53:47	Rm. Temp.	2770°F	4.80	11.0	16,500
B	" "	"	"	"	"	"	15,700
C	" "	"	"	"	"	"	12,400
33	65% SiC-35% Vitallium	----	Rm. Temp.	3450°F	3.18	4.4	20,600

Note: All specimens formed under 5000 psi

† Withstood 10 cycles from 1800°F to water (70°F) without failing
o Failed after 6 cycles from 1800°F to water (70°F) - one crack was evident

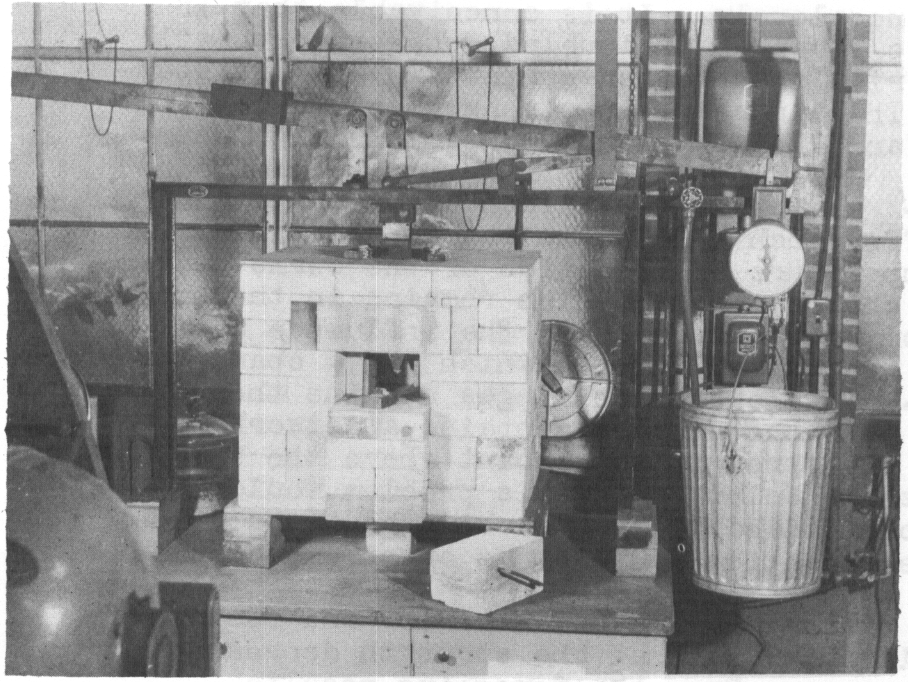


Fig. 2

Modulus of
Rupture Furnace

B. Discussion of Results

The results of the work described in Tables VIII, IX and X indicate that although the strengths of the cermets are low in most cases, there are many possibilities wherein the strength may be increased appreciably. The following discussion covers the results contained in the tables.

(1) Chromium-molybdenum - The preliminary modulus of rupture tests for the chromium-molybdenum, silicon carbide system are encouraging. Although the strength values are low when compared to titanium carbide, they are high compared to previously attained results using silicon carbide as a base material for cermets.

The highest room temperature value attained was 31,600 for a silicon carbide cermet low in metal content. An increase in the metal content seems to lower the strength value slightly but it is believed that the lower maturing temperature is the major cause for this strength decrease. This in turn is the result of using powders of both chromium and molybdenum instead of a single powder of the alloyed metals.

As Table X shows, the strengths of the molybdenum-chromium cermets of higher metal content increase almost twofold upon heating to 1800°F and 2000°F. This in itself is an important factor to consider. Whereas most titanium carbide base cermets have extremely high room temperature strengths and lower high temperature strength, this material appears to behave anomalously. It is conceivable that if the room temperature strength is doubled, the strength will be in a range that rivals the other cermets in the high temperature regions. This increase in strength should come with the procurement of an alloyed power of chromium-molybdenum.

(2) Chromium - The chromium-silicon carbide system does not seem to offer such promise in the cermet field. Chromium at the temperature of formation of the cermets, forms an amount of chrome carbide which remains in the body. Upon storage at room temperature under the influence of moisture, a gas is formed and emitted which has a characteristic carbide odor. This evolution of gas strains the body and in a matter of days the surface contains a network of cracks which lower the strength to a point where the body is useless. A possible solution to this problem would be the forming of chrome bonded silicon carbide bodies at temperatures below the formation temperature of chrome carbide.

The strengths of the bars tested were low and results appear conclusive in the face that the strength decreases as the density increases. From the foregoing results, chromium alone will not be considered any longer as a possible binder for silicon carbide.

(3) Iron - The addition of iron to the chromium-molybdenum, silicon carbide system did not appear to offer much in the way of increased strength. Although the bodies formed had strengths approaching those without any iron in them, the porosities of the bodies were much too high. It appeared that the iron had almost entirely been lost during the hot pressing cycle.

C. X-ray Investigation of Cr:Mo-SiC System

After completion of the x-ray investigation of the reaction products formed when a mixture of chromium, molybdenum and silicon carbide was hot pressed, it was decided to further investigate this system as the percentage of molybdenum was decreased to zero. The composition retained the metal-silicon carbide ratio of 30-70 but the chrome to molybdenum weight ratio was varied in five successive steps from 1:1 to 1:0. Each specimens was investigated to determine the following: (1) the reaction products formed; (2) the ratio of chromium to molybdenum in solid solution; (3) the shift (if any) in silicon carbide lines and; (4) the density and porosity of the buttons pressed.

(1) Experimental Procedure - The compositions were varied as shown in Table XI.

TABLE XI

Hot Pressed Specimen Composition - Density and Porosity

Spec. No.	Wt. % of Raw Material Cr	Mo	SiC*	Density	Porosity %
32	15	15	70	3.63	5.0
33	18	12	70	3.68	2.8
34	21	9	70	3.28	12.4
35	24	6	70	3.12	11.4
36	27	3	70	3.56	7.2
37	30	0	70	3.38	10.9

*SiC - had the following grain size distribution

50% - 400 mesh
30% - 800 mesh
20% -1200 mesh

The buttons were formed using the usual method of hot pressing, that is, pressing the material to shape in a graphite die heated to a high temperature by means of an induction coil. The temperature and pressure used was 3650°F and 10,000 psi respectively. The button thus formed was rough ground using a diamond wheel and polished on a lap using diamond paste as the polishing medium. The densities and porosities were determined and may be seen in Table XI.

Two x-ray diffraction patterns were taken of each button using a General Electric XRD-3 unit. The patterns were taken before and after the buttons were rotated 90° so that any orientation due to hot pressing could be observed. The buttons were then cut so that the one half could be saved and the other half ground to 200 mesh and a subsequent powder pattern made using the General Electric XRD-3 unit.

(2) Discussion of Results - In general, most of the silicon carbide lines remained ordered so that they are of no great importance in this study. The metal lines did change and fair correlation could be made of the effect molybdenum has on the reaction products formed.

The following discussion of results based upon x-ray data is more qualitative than quantitative since there is very little ASTM and National Bureau of Standards data on the systems studied. However, by comparing the patterns a definite correlation of results can be expressed as follows:

(a) The line at 2.86A$^{\circ}$ - 2.88A$^{\circ}$ was tentatively identified as a (Mo,Cr) Si$_2$ (compound) diffraction line. One of the strongest lines of MoSi$_2$ has a "d" value of 2.95A$^{\circ}$, therefore, it seems probable that a replacement of a definite amount of the Mo by Cr would give a "d" value in the neighborhood of 2.86A$^{\circ}$. The intensity also seems to indicate the presence of a compound since it decreases to zero as the amount of Mo in the specimen decreases to zero.

(b) Lines at 2.25, 1.86 and 1.15A$^{\circ}$ were identified as Cr-Si compounds with increasing amounts of Cr from Specimen 32-37, since the diffraction lines coincide with the strong lines of synthesized CrSi (1:1 atomic weight). The CrSi was synthesized since no x-ray patterns were available from outside sources.

(c) A line at 2.45A$^{\circ}$ was identified as chromium-molybdenum solid solution as based on a series of Mo:Cr which was synthesized. The calculated interplanar spacing based on the ratios of Mo and Cr used in the specimens agree to a certain extent with those obtained from the diffraction patterns. The intensities, however, do seem to indicate a series of solid solutions since the line does occur in Specimen 37, which contained no molybdenum.

(d) A line at 2.05-2.06A$^{\circ}$ is evidently caused by chromium in the silicon carbide since the "d" value for SiC was increased from 2.40 to 2.45A$^{\circ}$. This "d" value corresponds to the $10\bar{1}0$ plane. The line at 1.99A$^{\circ}$ was identified as chromium metal line.

No correlation between density and composition could be made because of the erratic results. These results are probably due entirely to difficulties in obtaining uniform conditions over the series of specimens. Uniform temperature and pressure conditions affect the attainment of uniform forming conditions to the greatest degree.

D. Effect of Mixing and Grinding for Two Metal-Silicon Carbide Systems

The effect of mixing vs. wet-grinding was studied for the chromium-molybdenum-silicon carbide system. A composition of 65% silicon carbide (made up of 50% - 400 mesh, 30% 800 mesh and 20% 1200 mesh grain) and 35% chromium-molybdenum (1:1 by weight) was selected as a representative case. One charge was mixed in a glass receptacle for a period of 24 hours on a ball mill frame, the other was placed in a steel ball mill to which was added 200 gms. of half inch balls and enough carbon tetrachloride to make a slurry. The mill was then rotated for a period of 24 hours during which time there was an iron pickup of less than one percent.

After drying both powders they were prepared for hot pressing and pressed at a pressure of 5000 psi over a temperature range from 2300 to 3500°F. The materials were tamped into graphite molds and hot pressed in the usual manner.

(1) Results - The plotted results of density and porosity vs. temperature may be seen in Fig. 3 and Fig. 4.

The same procedure for wet-grinding in carbon tetrachloride was carried out by replacing the 35% chromium-molybdenum with 35% Stellite No. 21 (Vitallium) powder. A similar hot pressing series was run, the results of which may be seen in Fig. 5.

(2) Discussion of Results - There seemed to be little difference in the results, between the dry-mixed and the wet milled materials. In both cases, density was low and porosity high, due in part to the relatively low pressure used. For the chromium-molybdenum, silicon carbide series there appeared to be an appreciable amount of metal lost as the temperature was raised even though the density increased. As was recognized in the past, pressures of from 8000 to 10,000 psi are desired for metal bonded silicon carbide shapes, the density and porosity depending directly on the pressure, but these pressures

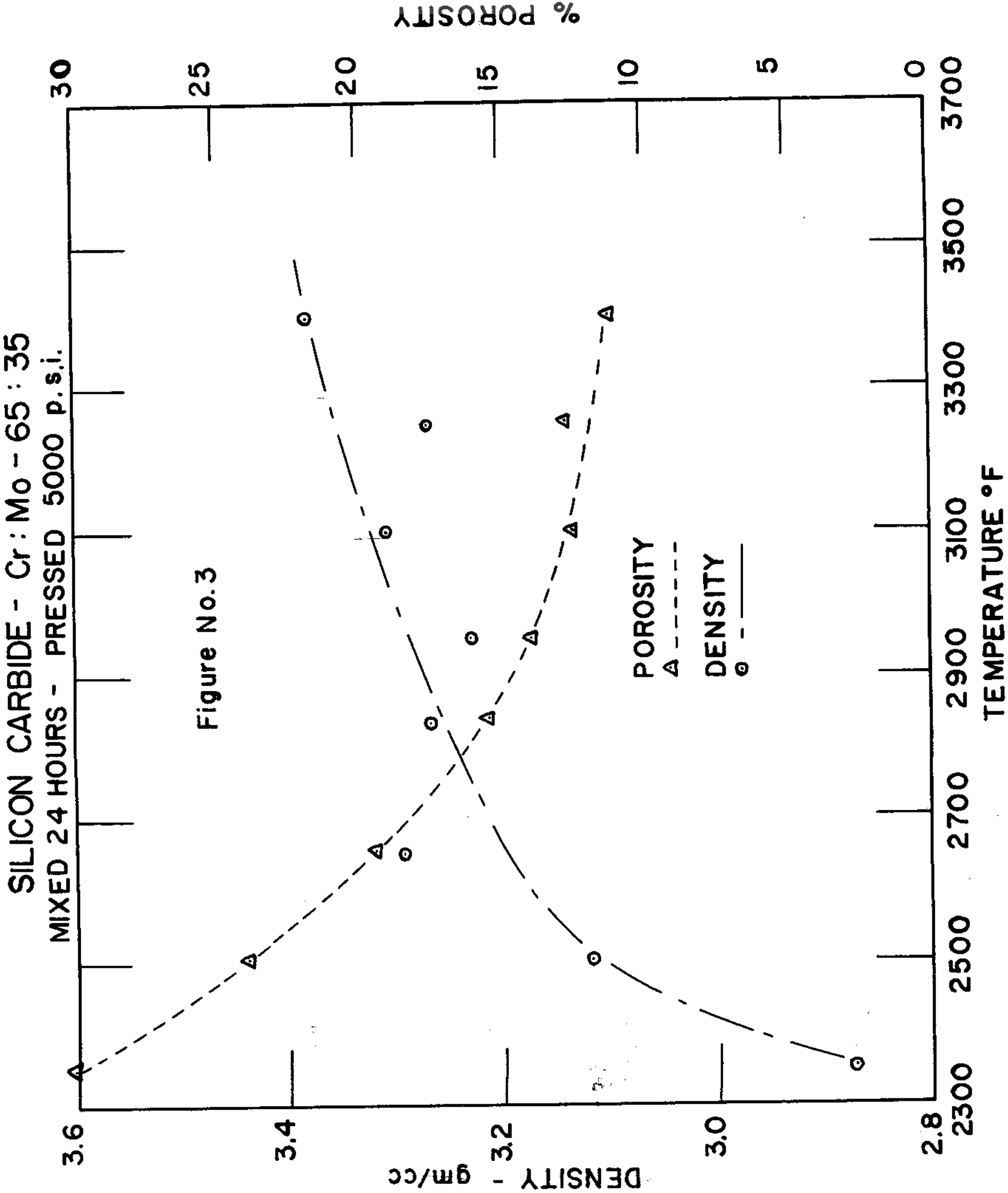


Figure No. 3

SILICON CARBIDE - Cr : Mo - 65 : 35

MIXED 24 HOURS - PRESSED 5000 p.s.i.

SILICON CARBIDE - Cr : Mo - 65 : 35

MILLED - 24 HOURS - STEEL BALLS - CCl_4 - PRESSED 5000 p.s.i.

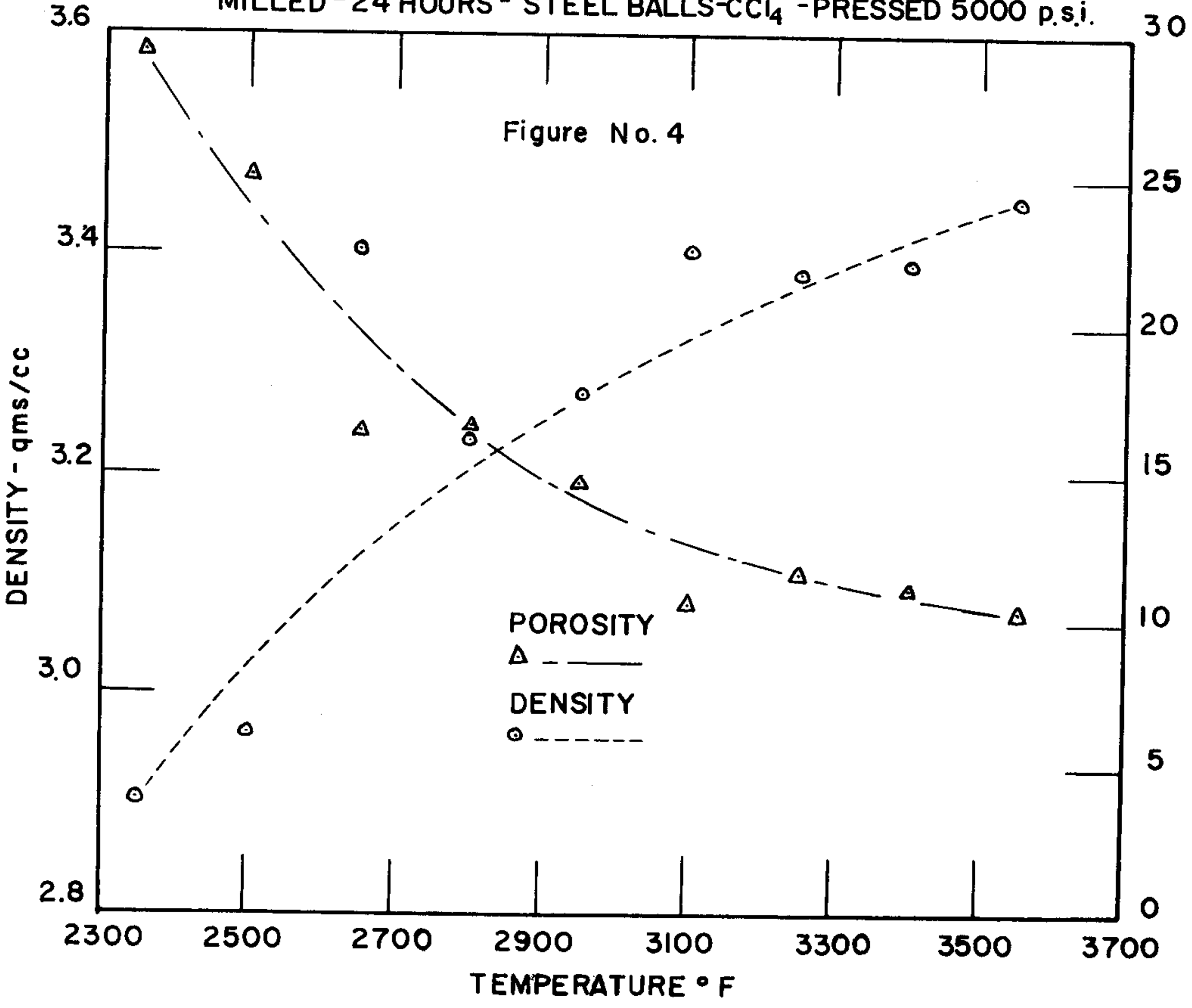


Figure No. 4

SILICON CARBIDE - VITALLIUM SERIES

65:35

5000 p.s.i.

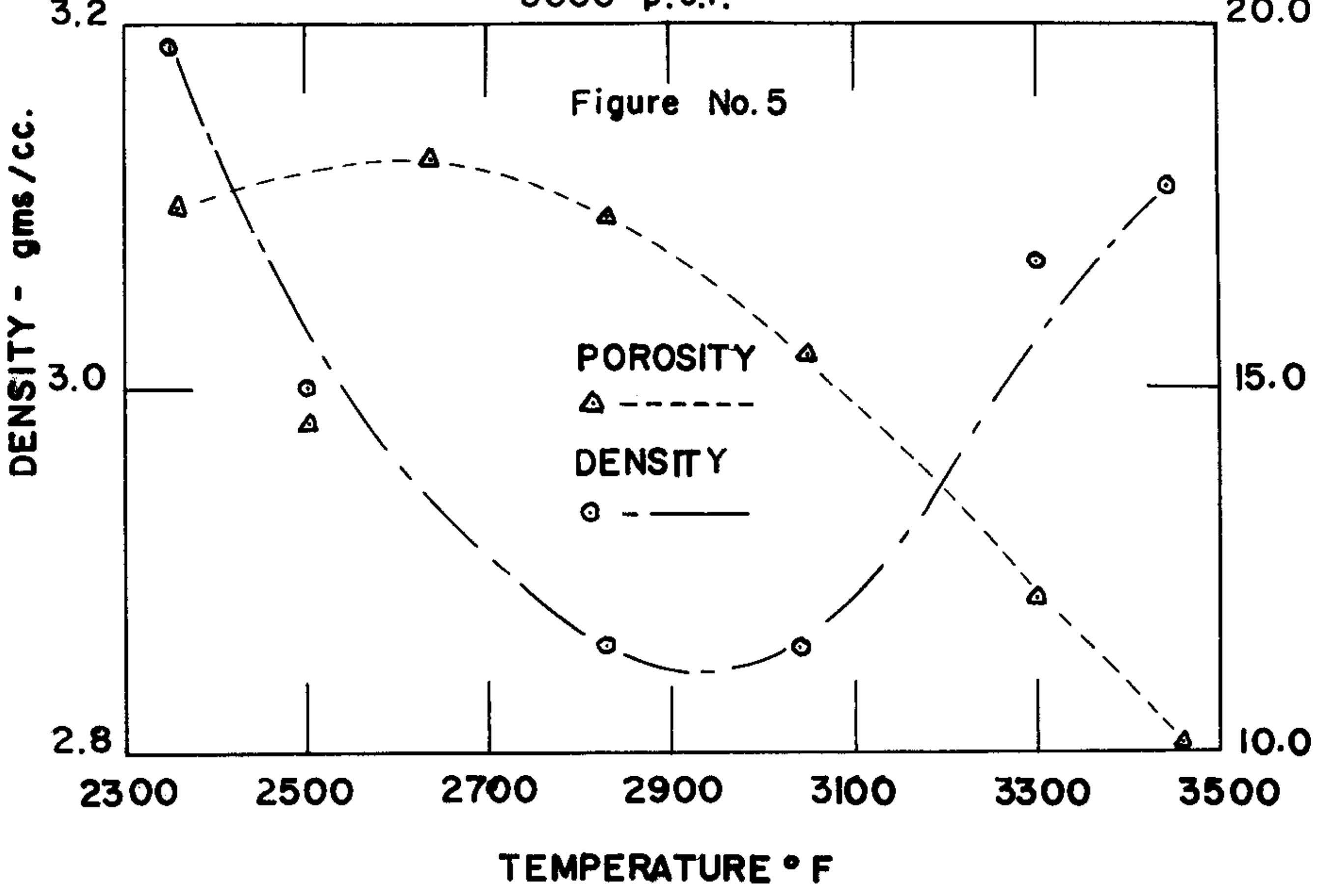


Figure No. 5

can only be used satisfactorily above 3200°F due to the decreasing strength of graphite at lower temperatures.

Vitallium, silicon carbide compositions seemed less desirable than the chromium-molybdenum, since porosities were higher and densities lower. From the composition of Vitallium as shown below, it might be predicted that it would not work well for bonding silicon carbides.

Analysis of Vitallium

Co - 62.0
Cr - 25.0 - 35.0
Mo - 4.50 - 6.50
Fe - 2.0 - max.
Ni - 1.50 - 3.50
C - 0.20 - 0.35

Density approx. 8.3 gm/cc.

As shown in past studies, cobalt reacts with silicon carbide forming cobalt silicide. While this would probably be advantageous for small amounts of cobalt, large amounts tend to weaken the structure.

III THE INVESTIGATION OF INFILTRATING TECHNIQUES AS APPLIED TO METALS AND SILICON CARBIDE

A. Determination of Melting Points

After a search of the literature for methods describing vacuum sintering and infiltration, a program was undertaken to determine the melting points and reactions of metals and alloys heated on different refractory slabs. The refractories used included zirconia, graphite and hot pressed silicon carbide. The metals and alloys to be studied were cold pressed in disc form under a pressure of 50 tsi. The discs were approximately one inch in diameter; large enough so that a hole one quarter in diameter could be drilled through the center. The hole in the center facilitated good measurement of the melting point as the metal disc melted and the hole collapsed,

(1) Experimental Procedure - The metals were placed on the refractory plates and put in the furnace chamber of the vacuum furnace shown in Fig. 6. A vacuum was then drawn and the heat applied gradually so as to prevent spalling of the zirconia crucible containing the charge. At a tempera-

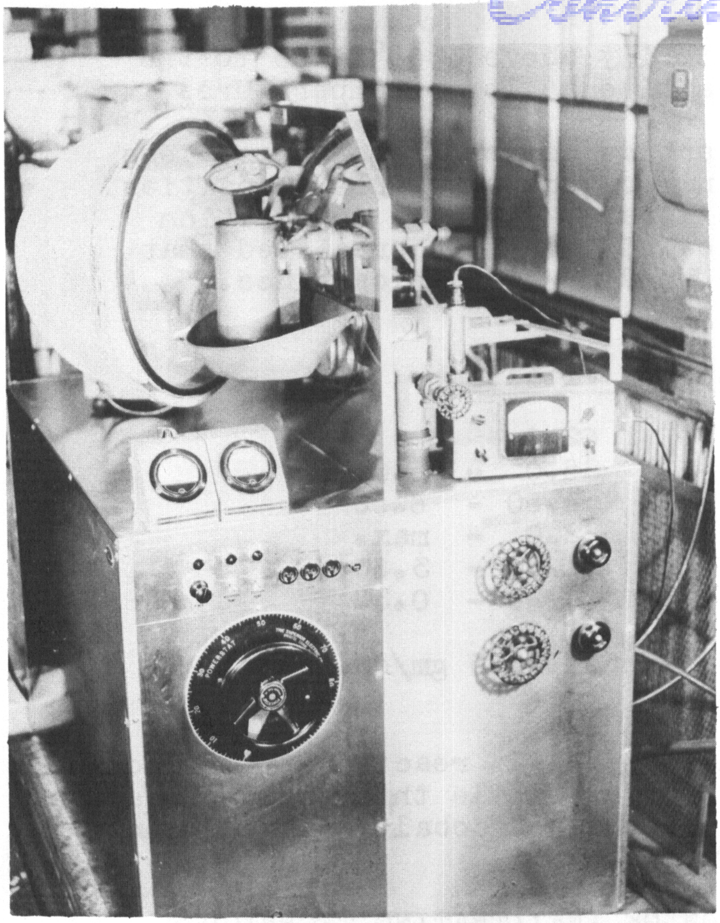


Fig. 6

Vacuum Furnace

ture of 1500°F, the furnace heating was delayed until a pressure of 0.1 microns of mercury was drawn. Then the heating cycle progressed as before until the melting point of the metal was observed. For chromium and alloys containing chromium, a partial vacuum was used so as not to lose the chromium through volatilization.

(2) Results - The data obtained from the melting point studies are shown in Table XII.

It was observed that the metals melted at different temperatures depending upon the refractory on which they were melted. The brief summary of the melting characteristics follows:

(a) Nickel melted consistently in the same temperature range. It did not appear to have wetted the zirconia slab.

(b) Iron melted on the zirconia, wetting it and forming a slag type of substance around the periphery of the button.

(c) Chromium and molybdenum behaved very erratically since the observed melting point ranged from 3000 to above 3600°F. When the metals were melted on either silicon carbide or graphite there seemed to be enough carbon present to react and form carbides

TABLE XII

Melting Points of Metals and Alloys on Refractory Materials

Metal	Temperature °F	Book Temp. (STP)	Vacuum (mm Hg)	Refractory Slab
Nickel (a)	2635	2650	0.0001	Zirconia
Nickel (b)	2675	2650	0.032	"
Iron	2520	2795	0.0001	"
Cr-Mo	3595 (no melting)	----	0.0500	"
Cr-Mo (pre sintered)	3290	----	0.1610	Graphite
Cr-Mo	3000	----	0.1200	"
Cr-Mo	3040	----	0.100	Silicon Carbide
Chromium	2895	2940	0.200	Graphite
Chromium	2885	2940	0.054	Silicon Carbide
Vitallium	2580	----	0.044	" "
Silicon	2625	2590	0.0001	" "
Hastelloy B	2590	----	0.0550	Zirconia
Cr-Silicon	2700	----	0.0650	Silicon Carbide

of the metals. The molten metal flowed completely around the graphite slabs showing its excellent wetting properties. It did not melt on zirconia, however, even at 3600°F.

(d) Chromium reacted in much the same manner as chromium and molybdenum with the exception that it formed long bronze colored crystals of chromium carbide in a bronze colored matrix, whereas chromium and molybdenum had a silvery appearance. Chromium also wet the graphite slab and flowed around it.

(e) Vitallium wet silicon carbide but reacted with it, apparently to form cobalt silicide.

(f) Silicon wet and adhered to silicon carbide, but did not react with it.

(g) Hastelloy B melted but did not wet or react with zirconia.

(h) Chrome-silicon wet silicon carbide and seemed to have infiltrated it to some extent. No visible reaction was noted.

B. Vacuum Infiltration of Metals Into Silicon Carbide

(1) Discussion - The need for additional methods for fabrication of metal-silicon carbide parts arose because of the rather difficult hot pressing technique when pressures exceeding 8000 psi are desired. The one method which particularly seemed to apply to silicon carbide was the infiltration technique whereby a porous skeleton was filled with a continuous matrix of metal. This in theory would give a product which exhibits the properties of each of the phases since both would be continuous.

(2) Experimental Procedure - Infiltration of silicon carbide with alloys and metals was begun with the investigation of technique and firing conditions as principal considerations. It was necessary to limit the silicon carbide grain size from 36 to 100 mesh since finer grain hot pressed at low temperatures and pressures would not permit infiltration. This was caused by the smallness of the channels through which the metal had to flow and also because of the small grains, higher surface energy and hence ease of reaction with highly reactive metals. To minimize this reaction, this study has been confined to the use of four grain sizes 36, 60, 80 and 100 mesh silicon carbide. A

finer grain size silicon carbide (240 mesh was also investigated but results indicated that the pores were too small for many of the metals used.

The silicon carbide used was hot pressed at temperatures ranging from 3600-4400°F under a varying pressure not exceeding 2500 psi. This resulted in a bonded structure containing 30 to 45% pore of sufficient size to permit the entry of metals and alloys. The bonded silicon carbide was removed from the mold, cleaned of any graphite on the surface and prepared for vacuum sintering in the following manner.

The silicon carbide was placed in the firing chamber of the vacuum furnace shown in Fig. 6. An alumina tube containing the powdered or sintered metal was placed above this sample. A vacuum was then drawn and heating begun at a rate so as not to destroy the vacuum by an evolution of too much adsorbed or absorbed gas. For those mixtures of metals or alloys that contained chromium, an argon atmosphere of 300 mm. of mercury pressure was admitted. This prevented the sublimation of chromium over the temperature range covered.

(3) Results - Using the above procedure, metals and alloys such as Cr-Si, Mo-Cr, Cr-Mo-Si, Cr-Mo-Ni-Si-W, and Hastelloy C were used to infiltrate silicon carbide. Table XIII contains the data accumulated for the various infiltration runs.

The results obtained were not conclusive enough to establish whether or not vacuum sintering is satisfactorily a replacement for hot pressing. For some applications where the size of the grains used is not of extreme importance, vacuum sintering techniques could be used. However, small parts would not have the proportionate strength of the large parts due to the larger grain size, whereas the hot pressed material would tend to exhibit equal properties whether the part were large or small.

(4) Discussion of Results - The metals that seem to work best with silicon carbide include Cr-Si, Cr-Mo-Si and Ni-Cr-Si-Mo-W. It is felt that these combinations of metals can be used to form a dense, low porosity body. However, none of these combinations appear to react with silicon carbide and as a result some small particles are lost on

TABLE XIII

Vacuum Infiltration of Silicon Carbide Structures

No.	Metal Phase	SiC	Temp. °F	Density	Porosity	Remarks
1	Cr-Si (1:1)	36 mesh	2900	3.34	8.2%	Contained localized pore area
2	Hastelloy C	"	2850	4.65	12.0%	Porosity due to reaction products formed
3	Cr-Mo-Si(2:1:1)	"	3000 3200*	---	---	Bonded - but macro-pores present
4	Cr-Mo-Ni-Si-W (8:4:4:4:1)	"	3090	---	---	Very hard - macro-pores present
5	" " "	"	3000	4.2	7.3	Very dense at surface - localized pores
6	Ni-Cr-Mo-Si-W (8:4:4:4:1)	"	2850	---	---	Very porous
7	Hastelloy C	"	2825	---	---	Bonded - but porous
8	Ti-Si-Cr (2:1:1)	100	3000	---	---	No infiltration
9	Mo-Cr (1:1)	"	3130 3000*	---	---	" "
10	Hastelloy C	"	2620	---	---	" "
11	Hastelloy C	"	3015 2700*	---	---	" "
12	Hastelloy C	"	2800	---	---	Well bonded but contained localized unbonded areas

* Successive fillings (repeats)

TABLE XIII (con't.)

No.	Metal Phase	SiC	Temp. °F	Density	Porosity	Remarks
13	Cr-Si(1:1)	80 mesh	2785	3.6	7.25%	Good bonding - some macro-pores
14	Cr-Si	"	2800	3.57	7.3	" " "
15	Hastelloy C	"	3100	----	---	No infiltration
16	Si-Cr (1:1) (pre-alloyed)	"	2800 3000*	3.72	5.0	Bonded well - few pores present
17	Cr-Mo-Si(2:1:1)	"	3220	3.96	4.2	Slightly porous throughout
18	Cr-Mo(1:1)	"	3180	----	---	No infiltration
19	Cr:Mo:Ni:Si:W (8:4:4:4:1)	"	2910	3.83	11.5	Well bonded - macro-pores present
20	" "	"	"	3.96	8.5	One porous area through center - otherwise very good bonding
21	Ni:Cr:Mo:Si:W (8:4:4:4:1)	"	2940	----	---	Bonded - contained localized unbonded areas.
22	" "	"	3000	4.35	4.1	Slightly porous - good bond
23	Ni:Cr:Si:Mo:W (6:6:6:1:1)	"	2880 2990*	----	---	Porous specimen

*Successive fillings (repeats)

polishing, indicating that the degree of wetting, hence the bonding, is not great. Hastelloy C reacts freely with silicon carbide at the temperatures used producing a silicide of nickel which seems to bond the structure together. Very few pullouts are evident when a Hastelloy C bonded silicon carbide body is polished. However, the high temperature needed for infiltration of Hastelloy C permitted too much reaction phase to form. For this reason, a program was initiated of pressure infiltration at lower temperatures, the results of which are contained further on in this section.

The grain size that seems to be best for this type of forming is 80 mesh, while 100 mesh grain can be used for some of the metals such as Cr and Si which wet silicon carbide to a greater degree than others. Examples of the types of structures derived from the method of infiltration using various grain sizes is shown in 1, 2, 3, and 4 of Fig. 7. Micrograph 1 shows 36 mesh silicon carbide bonded by Cr-Mo-Ni-Si-W (8:4:4:4:1). Micrograph 2 shows 36 mesh silicon carbide bonded by Hastelloy C. Note the extensive reaction areas. Micrographs 3 and 4 show 80 mesh silicon carbide bonded by Cr:Mo:Si (2:1:1) and Cr:Ni:Mo:Si:W (8:4:4:4:1) respectively. The black areas present are voids due mainly to pullouts during polishing. The finer the grain gets the more likely a pullout is to occur. As can be seen from the four micrographs, Hastelloy C is the only metal combination that actually reacts with the silicon carbide to form a bonding phase. The others seem to exhibit quantities of isolated metal particles. On the macroscale, however, all the bodies appear to be well bonded when cut with a diamond cut-off wheel although the Hastelloy C bonded silicon carbide is a little tougher. These may be compared with Part 6 of the same figure which is a micrograph of hot pressed chromium-molybdenum bonded silicon carbide having a density of 3.80 and a porosity of 1.0%. Here again the voids are mainly caused by pullouts.

C. Pressure Infiltrated Silicon Carbide

Another method of forming metal-bonded silicon carbide was also investigated. It involved the forcing of a metal under high pressure into a silicon carbide structure using the hot press technique.

(1) Experimental Procedure - Silicon carbide cylinders were hot pressed in a manner similar to those in Section B above, that is under a pressure of from 500-2500 psi and a temperature of from 3600-4200°F. This process left the cylinders with about 35-45% pore volume, enough to permit

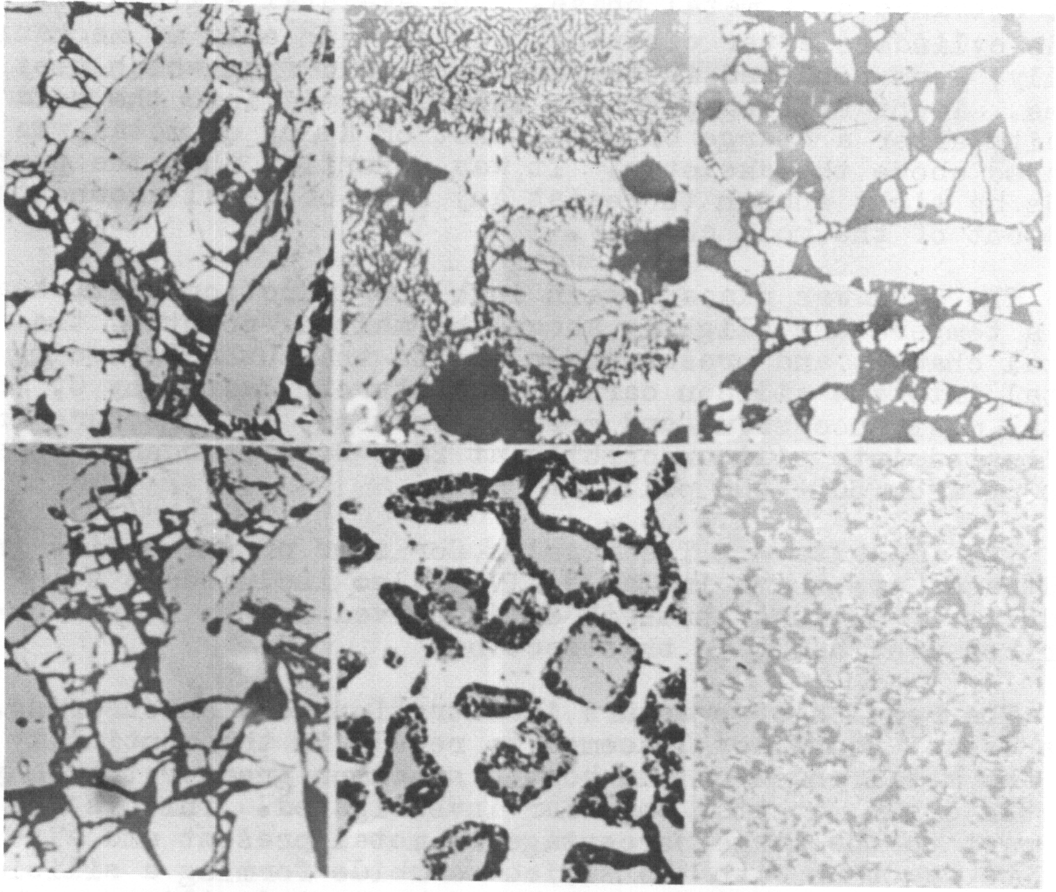


Fig. 7
(75x)

Metal-Bonded Silicon Carbide Bodies

1. Cr:Mo:Ni:Si:W (8:4:4:4:1) - 36 mesh grain - vac. infil.
2. Hastelloy C - 36 mesh grain - vac. infil.
3. Cr:Mo:Si (1:1:1) - 80 mesh grain - vac. infil.
4. Cr:Ni:Mo:Si:W (8:4:4:4:1) - 80 mesh - vac. infil.
5. Hastelloy C - 100 mesh - pressure infil.
6. Cr:Mo (1:1) 400, 800, 1200 mesh grain - hot pressed

Gray - Silicon Carbide
White - Metal
Black - Pullouts and Pores

the entrance of a metal phase. The skeletal silicon carbide cylinders after cleaning, either with acid or mechanically, were replaced in the graphite mold from which they came. Tight fitting pushrods were inserted into the mold cavity after a charge of metal shot or a slug of metal was placed above the skeleton. It was essential that the pushrods be tight enough to resist any flow of metal around them and out of the mold chamber.

The mold was placed again into the induction unit, heated to a temperature slightly above the melting point of the metal charge, and pressure applied to the pushrod forcing the metal into the silicon carbide structure. Hastelloy C, the metal most successful and most often used, was pressure infiltrated into silicon carbide at 2300-2400°F under a pressure of from 500-2500 psi.

(2) Results - The results for some of the bodies infiltrated are shown in Table XIV. Also included is some modulus of rupture strength data derived in the manner described previously in this section.

The results of pressure infiltration were encouraging. The use of Hastelloy C seemed to result in the continuity of the metal phase of the bonded specimen greater than any of the other material thus far investigated. This is due in part to the large percentage of metal present and also to its reaction with the silicon carbide forming a silicide which ties the metal in with the non-reacted silicon carbide grain. The relatively low pressure requirements would aid in the production of large parts, much larger than could be made by hot pressing directly.

A micrograph of 100 mesh silicon carbide pressure infiltrated with Hastelloy C may be seen in Part 5 of Fig. 7. The reaction phase can be seen around the grains. The degree of reaction can be regulated by regulating both the temperature and time at maximum temperature.

(3) Discussion of Results - The strength values shown in Table XIV indicate that as a whole the structure of Hastelloy C infiltrated silicon carbide is low. This is due in part to the large grain size silicon carbide used and the small bar which was used for test purposes. The high temperature strength, however, does increase over twofold at 1800°F, giving a value of around 18,000 psi.

TABLE XIV

Pressure Infiltration of Silicon Carbide Structures

No.	Composition	Vol.%	Temp.°F	Density	Porosity	Mod. of Rup.	Remarks
34A	Hastelloy C 60 mesh SiC	36:64	2325	5.12	3.0%	10,300	Hard Well Bonded Structure
B	" "	"	"	"	"	8,500	
C	" "	"	"	"	"	8,300	
D	" "	"	"	"	"	8,200	
35	Hastelloy C 100 mesh SiC	39:61	2300	5.45	1.2%	11,000	Hard - Well Bonded
36	Hastelloy C 100 mesh SiC	----	2325	5.25	3.0%	-----	Hard - Well Bonded
37	Hastelloy C 80 mesh SiC	----	2400	4.66	9.3%	-----	Uniform -but slightly porous
38	" "	-----	"	4.72	7.4%	-----	" " "
39	Ni:Cr:Mo:Si 36 Mesh SiC 40:20:20:20	-----	2800	----	----	-----	No complete infiltration
40A	Hastelloy C 100 mesh SiC	33:67	2400	4.67	9.0%	11,400	Slightly porous
B	" "	"	"	"	"	9,600	
C	" "	"	"	"	"	7,400	
D	" "	"	"	"	"	18,400*	

*Strength at 1800°F - Withstood 10 cycles from 1800°F to water at 70°F without failure.

TABLE XIV (con't.)

Pressure Infiltration of Silicon Carbide Structures

No.	Composition	Vol.%	Temp.°F	Density	Porosity	Mod. of Rup.	Remarks
41A	Hastelloy C 60 mesh SiC	30:70	2400	4.64	5.3%	6,700	Bars small for size of grain used
B	" "	"	"	"	"	6,500	
C	" "	"	"	"	"	6,400	
D	" "	"	"	"	"	6,000	
42A	Hastelloy C	37:63	2400	5.08	4.8%	15,200	Same as above
B	" "	"	"	"	"	12,500	

*Strength at 1800°F - Withstood 10 cycles from 1800°F to water (70°F) without failing

It should be realized that these preliminary tests are in no way conclusive. The strength of Hastelloy C infiltrated silicon carbide with a refinement in forming and an increase in uniformity, plus proper heat treatment, should be as great if not greater than the values obtained for the hot pressed material.

(4) Conclusions:

(a) Modulus of rupture strengths in the neighborhood of 31,000 psi are characteristic of the chromium-molybdenum bonded silicon carbide.

(b) Iron and chromium alone do not appear to be satisfactory metals for the bonding of silicon carbide.

(c) Cermets containing higher than 35% metal (Cr:Mo) appear to bond silicon carbide very well, however, the strength of the cermets do not exceed the values for the 35% metal- 65% silicon carbide cermets.

(d) Modulus of rupture strengths of Cr-Mo, SiC specimens appear to increase as much as 100% upon heating to 1800°F and 2000°F.

(e) X-ray studies revealed that a series of solid solutions were formed when chromium and molybdenum in varying proportions were hot pressed with silicon carbide.

(f) Low densities and high porosities are characteristic of the 35% chromium-molybdenum bonded silicon carbide when pressed at pressures lower than 8000 to 10,000 psi. Whether or not the batch was milled or just mixed did not seem to effect the results greatly.

(g) High densities and low porosities are characteristic of the 65% chromium-molybdenum bonded silicon carbide when pressed at pressures in the order of 5000 psi.

(h) Vitallium bonded silicon carbide did not show any desirable properties when hot pressed.

(i) Metals melted under vacuum and partial pressures of helium and argon demonstrate erratic melting points depending upon the refractory slab used as a support.

(j) Mixtures of molybdenum and chromium and silicon and chromium appear to work satisfactorily for infiltration of silicon carbide skeletons as long as porosities of 35% or more are characteristic of the skeletal material.

(k) Hastelloy C is too reactive when used to infiltrate silicon carbide using vacuum techniques. However, it can be satisfactorily infiltrated using the hot pressing technique.

(l) Strengths at present for Hastelloy C pressure infiltrated silicon carbide are low but higher strengths are expected when the infiltration process is perfected.

IV SINTERING OF METALS WITH SILICON CARBIDE

A. Discussion

Although most carbides have been successfully sintered with binder metals, silicon carbide does not lend itself to such treatment because it is not wet by most of the common binder metals. It has been noted that silicon carbide reacts with iron, cobalt, nickel, and chromium at sintering temperatures. Infiltration and hot pressing studies have shown that some combinations of metals such as Cr:Mo do bind silicon carbide to some degree. This study was made to determine which metals or combination of metals might be used in binding silicon carbide using a sintering process.

B. Experimental Procedure

The weighed compositions were mixed for 24 hours in glass jars and then cylindrical specimens 1/2" in diameter and 1/2" long were dry pressed to 50,000 psi.

Sintering was accomplished in a vacuum furnace with the specimen seated on a graphite block inside an alumina crucible. All specimens were heated to 2000°F and out gassed to one micron of mercury for 10 minutes. At this point, the sintering procedure was adapted to the particular composition being sintered. Compositions containing metals with high vapor pressures at the sintering temperature were sintered in argon at 300 mm. pressure. Along with variations in composition there were several other variables considered such as sintering temperature, sintering time, atmosphere and pressure, and grain size of the silicon carbide.

C. Results

Visual observations of the sintered specimens noting diffusion of the metal to the surface and the porosity was used as the main criteria. In Table XV is listed the compositions and sintering procedure along with the visual observations made.

D. Discussion of Results

Without exception, every metal sintered with silicon carbide showed some diffusion of the metal to the surface of the specimen and this effect became more pronounced with increased sintering time. The titanium-silicon carbide system showed the least diffusion and produced the soundest structure of the systems investigated. A composition containing equal volumes of carbide and metal (about 60% Ti by weight) produced the soundest specimens.

The micrograph in Fig. 8 shows the sintered structure of the 40% SiC60% Ti composition. The light phase is titanium while grey has not been identified. Silicon carbide appears as the darkest of the three phases.

Although titanium bonds to silicon carbide, its strength at high temperature and poor resistance to oxidation makes it of questionable value as a binder. It may be possible, however, to employ the titanium as a bond between the silicon carbide and a strong metal.

The system Ni-Cr-SiC also showed little diffusion of the metal to the surface of the specimen. It was observed in this system also that equal volumes of metal and carbide produced the soundest specimens.

E. Conclusions

1. Titanium and silicon carbide form a strong bond when sintered together in vacuum or in argon.

2. Chromium, nickel and silicon carbide form a bond when sintered together in an argon atmosphere.

3. The best sintering was obtained when equal volumes of metal and carbide were used.

TABLE XV

Results of Sintering Metal-Silicon Carbide Mixes

Composition	Sin. Press.	Sin. Time	Sin. Temp.	Results Noted
A-1 60% SiC (1200 mesh) 20% Cr 20% Mo	.100 mm. air	3 min.	$2950^{\circ}F$	Porous specimen -no sintering evident.
	.100 mm. air	3 min.	3200	Melting of metal evident, some diffused to surface little sintering.
A-2 50% SiC (400) 25% Cr 25% Mo	300 mm. argon	20 min.	$3000^{\circ}F$	Pronounced diffusion of metal.
	" "	40 min.	"	Increasing diffusion of metal.
A-3 35% SiC (1200) 32.5% Cr 32.5% Mo	300 mm. argon	20 min.	$3000^{\circ}F$ $2900^{\circ}F$	Metal diffused to the surface of the specimen, coating the entire surface
A-4 35% SiC (400) 40% Cr 25% Mo	300 mm. argon	5 min.	$2950^{\circ}F$	Metal diffused to the surface and ran out
A-5 28% SiC (400) 44% Cr 28% Mo	300 mm. argon	5 min.	$2950^{\circ}F$	Metal diffused to the surface. Specimen was porous & soft

TABLE XV (con't.)

Composition	Sin. Press.	Sin. Time	Sin. Temp.	Results Noted
A-6 23% SiC (400) 47% Cr 30% Mo	300 mm. argon	5 min.	2950°F	Metal diffused to the surface. Some metal sintered within the specimen but no bond occurred with the SiC
A-7 35% SiC (400) 65% Fe	.0001 mm. air	20 min.	2450°F	Metal collected in small contractions, showing no obvious wetting of the SiC
A-8 35% SiC (400) 32.5% Cr 32.5% Si	200 mm. helium	20 min.	2630°F	Metal diffused to surface. No evidence of metal-SiC bond
A-9 35% SiC (400) 32.5% Ni 32.5% Si	.0001 mm. air	5 min.	1880°F	Metal diffused to surface. No evidence of a metal-SiC bond.
A-10 50% SiC (100) 20% Cr 10% Ni 10% Si 10% Mo	300 mm. argon	3 min.	2700°F	Slight evidence of bonding. However, specimen showed some diffusion and was extremely porous

TABLE XV (con't.)

Composition	Sin. Press.	Sin. Time	Sin. Temp.	Results Noted
A-11 50% SiC (400) 50% Ti (Hydride)	.0001 mm. air 100 mm. argon 300 mm. argon	5 min. 15 min. 1 min.	3080°F 3000 3100	All specimens appeared about same. Some sintering evident, but metal lost in diffusion. Porosity 20%
A-12 50% SiC (100) 50% Ti (Hydride)	300 mm. argon	1 min.	3100	This specimen appeared much the same as A-11; the coarser SiC had no noticeable effect.
A-13 45% SiC (400) 55% Ti (Hydride)	300 mm. argon	1 min.	3100	Porosity 14.2%. Sintering improved, metal diffusion evident.
A-14 40% SiC (400) 60% Ti (Hydride)	300 mm. argon	1 min.	3100	Porosity 2.4%; Specimen showed good sintering with little diffusion evident.
A-15 35% SiC (400) 65% Ti 'Hydride)	.066 mm. air	1 min.	3100	Good sintering - considerable shrinkage; argon atm. most desirable. Por. 1.5%.
A-16 50% SiC (400) 25% Ti (Hydride) 25% Ni	.0004 mm. air	30 min.	2960	Some sintering, a great deal of metal diffusion evident.

TABLE XV (con't.)

Composition	Sin. Press.	Sin. Time	Sin. Temp.	Results Noted
A-17 50% SiC (100) 30% Ti (Hydride) 20% Ni	300 mm. argon	1 min.	3100°F	Some sintering, porous structure. Metal diffusion evident
A-18 50% SiC (400) 25% Ti (Hydride) 25% Cr	.050 mm. air 100 mm. argon	30 min. 15 min.	3029 3000	Both specimens appeared similar; loss of metal due to diffusion was evident. Porosity appeared high
A-19 29% SiC (400) 27.5% Ti (Hydride) 43.5% Cr	300 mm. argon	3 min.	3100	Porosity - 13% Sintering appeared good, no metal diffusion evident.
A-20 40% SiC (400) 46% Cr 14% Ni	300 mm. argon	5 min.	2500	Porosity - 4.3% Very porous specimen with little bonding evident.
A-21 35% SiC (400) 40% Cr 25% Ni	300 mm. argon	5 min.	2550	Some sintering, however the specimen was quite porous. Metal formed lakes in the structure

TABLE XV (con't.)

Composition	Sin. Press.	Sin. Time	Sin. Temp.	Results Noted
A-22 35% SiC (80) 40% Cr 25% Ni	300 mm. argon	3 min.	2700°F	Little sintering was evident; coarse material decreased strength of bond
A-23 30% SiC (400) 53% Cr 17% Ni	300 mm. argon	5 min.	2500	Porosity 26.0% little diffusion evident, sintered bond not strong
A-24 25% SiC (400) 57% Cr 18% Ni	300 mm. argon	3 min.	2800	Porosity 20.0% Specimen showed good sintering, bond was not strong
A-25 22.5% SiC (400) 58.7% Cr 18.8% Ni	300 mm. argon	15 min.	2750	Porosity 11% - good sintering, no metal diffusion, specimen appeared strong
A-26 20% SiC (400) 61% Cr 19% Ni	300 mm. argon	5 min.	2500	Porosity .55%, strong bond, well sintered continuous metal phase
A-27 25% SiC (400) 75% Hastelloy C	300 mm. argon	3 min.	2300	Sintering appeared good. Metal-SiC bond was present. No continuous phase was evident.

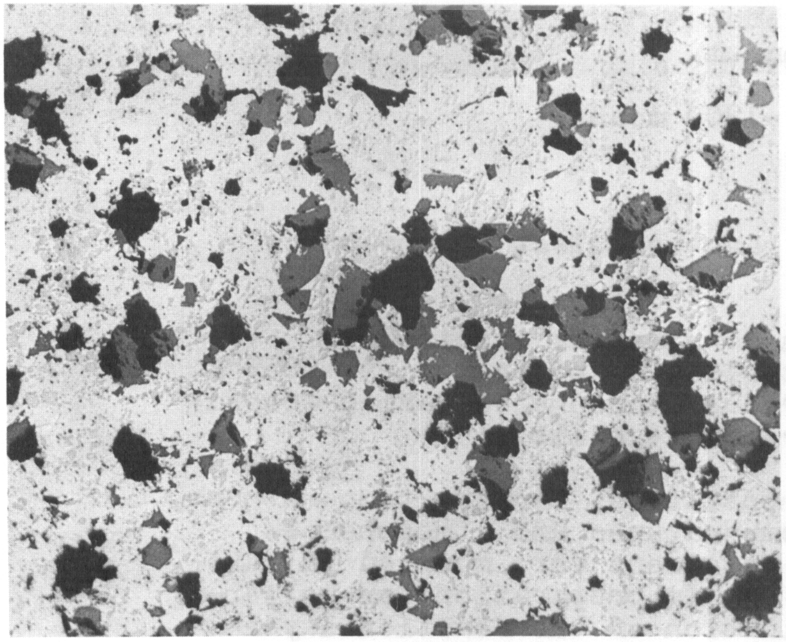


Fig. 8

Micrograph of 60% Ti
40% SiC
Sintered at 3100°F for
one minute
(125x)

PART III

HIGH TEMPERATURE STABILITY OF SELF BONDED AND CR-MO BONDED SILICON CARBIDE IN VARIOUS ATMOSPHERES

I DISCUSSION

Most of the anticipated use for both metal bonded and self bonded silicon carbide require stability in the presence of air, carbon monoxide and water vapor at high temperature. A study of the chemical stability of these materials as indicated by weight change in these gases was undertaken. The automatically weighing and recording balance described in Report No. 45, Contract No. W33(038) ac-14233 was used for the studies in air and water vapor. A horizontal tube furnace and periodic weighing was resorted to for studies using carbon monoxide since it provided a tighter, closed system.

II EXPERIMENTAL PROCEDURE

All of the specimens tested were hot pressed cylinders 1/2 inch in diameter and 3/8 inches long. Methods used for hot pressing are described in Parts I and II of this report. Self bonded silicon carbide specimens were made from both the alpha and beta forms.

Silicon carbide specimens bonded by a chromium-molybdenum mixture were made by hot pressing and oxidized in the three atmospheres at 1832°F. The composition hot pressed was as follows:

23%	Molybdenum
42%	Chromium
28%	SiC - 400 mesh
7%	SiC -1200 mesh
100%	

Some of the metal phase may have been lost in the hot pressing operation.

The self bonded silicon carbide was oxidized in steam and carbon monoxide at 1832°F and in air at 2552°F. Time of oxidation in the various atmospheres varied according to the time it took to reach stability.

Table XVI lists the compositions, forming temperatures, physical data and testing temperatures and atmospheres. After testing, the oxidized specimens were mounted in bakelite and cut with a diamond saw in preparation for polishing and metallographic examination of the reaction layers.

III RESULTS

The weight changes occurring in self bonded silicon carbide when exposed to air, water and carbon monoxide, at high temperatures are shown in Fig. 9. Weight changes are expressed in milligrams per square centimeter of original surface area of the specimen.

Fig. 10 shows the effect of these atmospheres on chromium-molybdenum bonded silicon carbide.

Metallographic examination of the polished sections of the oxidized specimens revealed no reaction layers on the surfaces of either the self bonded or metal bonded material.

IV DISCUSSION OF RESULTS

The automatically weighing and recording apparatus in general have reliable results but in using atmospheres of water and CO, several complications occurred. A carbon monoxide atmosphere could not be used in this apparatus because a tight seal against air could not be made. In using water vapor, the steam generator caused strong up-drafts and water condensed on the chain holding the specimen giving false weights. Sudden up-drafts were reduced by placing glass beads in the steam generator and condensation was reduced by heating the chain but considerable

TABLE XVI

Effect of Various Atmospheres on Self Bonded and Cr-Mo Bonded Silicon Carbide at High Temperatures

Spec. No.	Composition	Hot Press. Temp. °F	Bulk Den. g/cc.	Porosity %	Test Temp. °F	Atmosphero
43	1200 mesh SiC	4500	3.09	0.59	2552	air
66	" " "	"	3.12	0.11	2772	"
13	" " "	"	3.18	---	1832	CO
6	Beta SiC	4450	3.0	---	1832	steam
4	35% SiC 65% Cr-Mo	2700	4.90	2.10	1832	CO
5	35% SiC 65% Cr-Mo	2700	5.16	2.66	1832	CO
3	35% SiC 65% Cr-Mo	2700	4.95	1.36	1832	air
10	35% SiC 65% Cr-Mo	2700	4.46	1.37	1832	steam
11	35% SiC 65% Cr-Mo	2670	4.80	1.52	1832	air

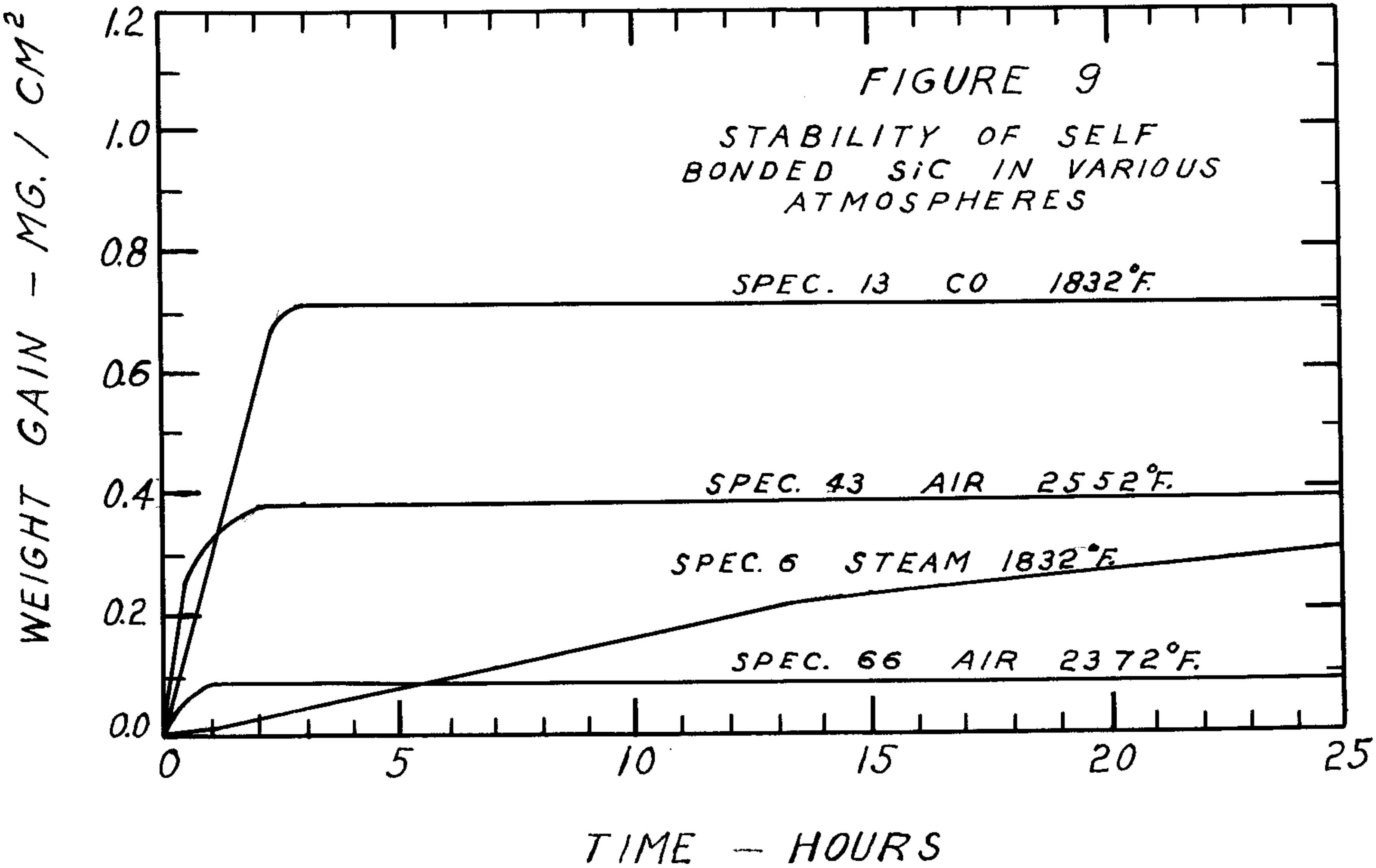


FIGURE 9

STABILITY OF SELF BONDED SiC IN VARIOUS ATMOSPHERES

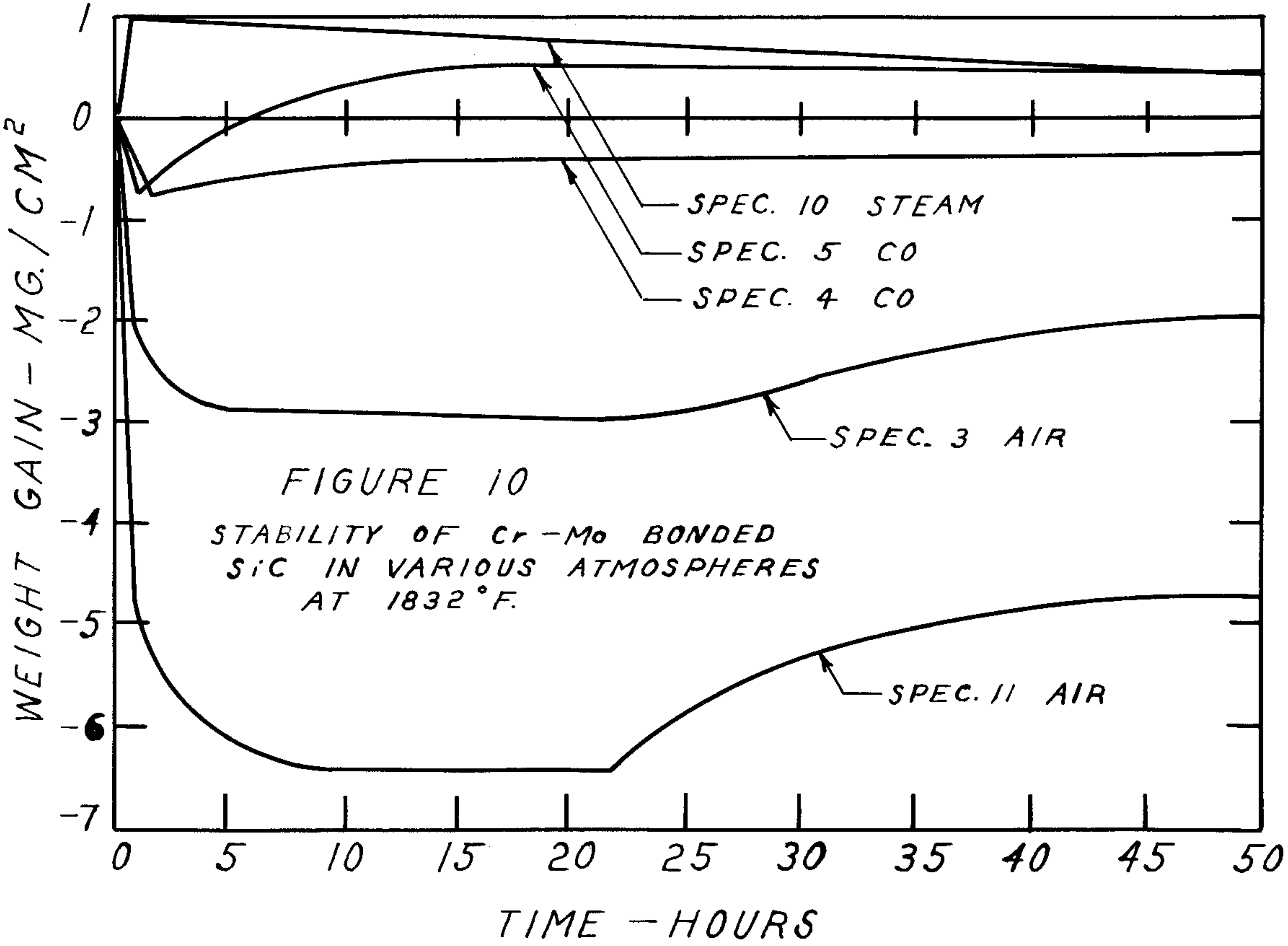


FIGURE 10

STABILITY OF Cr-Mo BONDED SiC IN VARIOUS ATMOSPHERES AT 1832 °F.

difficulty was still encountered. The horizontal tube furnace using periodic weighings was found to be more satisfactory for atmospheres of water vapor and carbon monoxide.

Self bonded silicon carbide curves are characterized by a slight weight increase and then stability. Carbon monoxide at 1832°F was more corrosive than air at a considerably higher temperature (2552°F). The slow weight increase of silicon carbide in water vapor may be due to the low degree of dissociation of water at this temperature.

Metal bonded silicon carbide was characterized by an initial weight loss and then a slight increase. The initial loss is undoubtedly due to oxidation of the molybdenum to the volatile trioxide. Air caused the greatest weight loss and protective layers again formed most slowly in water vapor.

V CONCLUSIONS

1. Silicon carbide develops protective layers when heated in atmospheres of CO, air or steam.

2. The protective layer develops least rapidly in steam.

3. Chromium-molybdenum bonded silicon carbide specimens develop protective layers slowly and are characterized by an initial loss in weight when heated to 1832°F in air, steam or CO.

PART IV

X-RAY AND METALLOGRAPHIC STUDIES OF HOT PRESSED SELF BONDED SILICON CARBIDE

I DISCUSSION

This study was undertaken to determine changes of structure and orientation resulting from hot pressing alpha silicon carbide. This discussion does not apply to the hot pressing of silicon carbide from beta silicon carbide. Hardness measurements of some of the grains of the hot pressed material were much higher than the hardness reported in the literature and other grains were much softer. Polished sections of the hot pressed silicon carbide showed two phases;

a gray phase and a light reflective phase which was the softer of the two. It was, therefore, of interest to determine whether hot pressing promoted the formation of certain types of alpha silicon carbide.

Hot pressing might also result in a preferred orientation of the grains and it was of interest to determine the direction of orientation. In general, it was hoped that a better understanding of the hot pressing mechanism would result from this study.

II EXPERIMENTAL PROCEDURE AND RESULTS

A. Density and Orientation as a Function of Hot Pressing Temperature

A series of silicon carbide specimens 3/4 inches in diameter and 3/4 inches long were hot pressed in graphite molds in the induction furnace at 10,000 psi to temperatures from 4305 to 4640°F. Each specimen was prepressed at 5,000 psi and the soaking time was held constant at 10 minutes. The following composition designated "Mix 0" was used throughout the series.

60.0%	SiC	100 mesh
15.0%	SiC	240 mesh
25.0%	SiC	1200 mesh

Each specimen was cleaned of adhering graphite and the density determined using the kerosene immersion method. The specimens were then cut lengthwise and polished with diamond paste. A region of very high density was noted at the top end of each specimen. The thickness of the dense region was measured using a microscope and a Filar eyepiece. This dense region was cut off and its density determined. Table XVII lists the thickness of the dense region and the density achieved at various temperatures.

Laue patterns were made of the dense end section in directions parallel to and perpendicular to the direction in which pressure was applied during hot pressing. Patterns were made after cutting the specimen but before polishing and no preferred orientation was observed, Fig. 11a. Patterns made after polishing, Fig. 11b, show a preferred orientation but this is due to polishing rather than hot pressing.

B. Effect of Soaking Time on Density and Types of Silicon Carbide Obtained

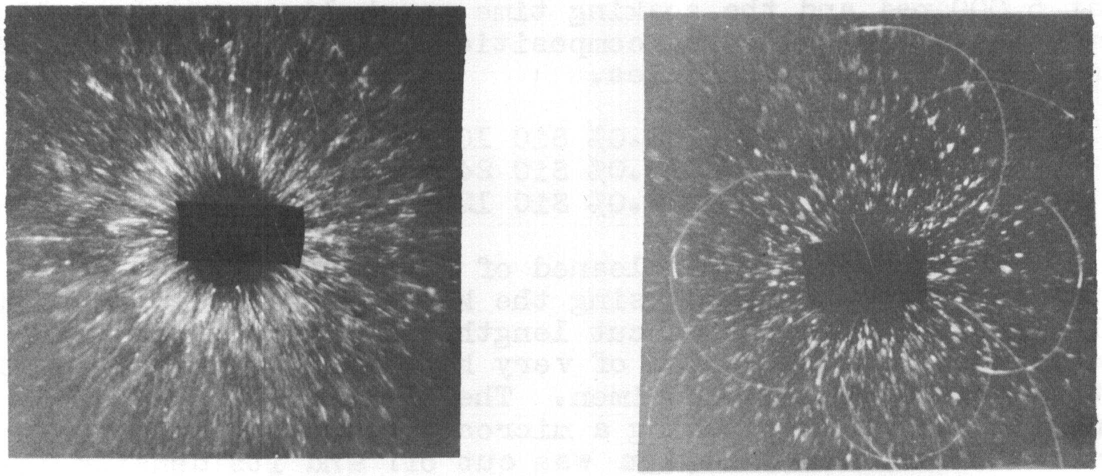
In this work, a composition designated "Mix 33" was used and consisted of the following grain sizes of alpha

TABLE XVII

Effect of Hot Pressing Temperature on Density Distribution Using "Mix O"

Maximum Temperature °F	Total Spec. Density (g/cc.)	Thickness Dense Region (mm.)	Density Dense Region (g/cc.)
4305	2.67	0.33	----- (1)
4415	2.66	--- (2)	2.80
4500	2.70	1.2	2.94
4590	2.72	1.7	3.03
4640	2.75	1.8	3.08

1. Dense region too thin for measurement.
2. Dense region slanted because of uneven application of pressure.



(a) (b)

Fig. 11

Laue Patterns of Dense Regions of SiC
(a) before polishing
(b) after polishing

silicon carbide.

35% SiC	-	100 mesh
40% SiC	-	240 mesh
25% SiC	-	1200 mesh

A series of cylindrical specimens 3/4 inches in diameter and 3/4 inches long were hot pressed using graphite dies in the induction furnace. Each specimen was prepressed at 25,000 psi in its graphite mold. A steel ring was used to reinforce the mold and steel push rods were employed. The steel ring was removed and the steel push rods replaced by graphite and each specimen was hot pressed at 10,000 psi to temperatures ranging from 4600 to 4655°F while the soaking time was varied from 0 to 20 minutes.

The density of each specimen was measured and then they were cut lengthwise and polished. A microscope and Filar eyepiece were used to measure the thickness of the dense region of the upper end of the specimen. This dense region was then cut off and its density measured. Table XVIII lists these results.

TABLE XVIII

Effect of Soaking Time on Specimen Density Distribution Using "Mix 33"

Soaking Time Min.	Maximum Temp. (°F)	Total Specimen Density (g/cc.)	Thickness Dense Upper Region (mm.)	Density of Dense Upper Region (g/cc.)
0	4650	2.70	1.2	3.06
5	4655	2.79	3.0	3.07
10	4645	2.96	3.5	3.08
15	4600	2.95	3.1	3.04
20	4645	-----*	---*	-----*

*Sample Decomposed

(1) X-Ray Investigation - The dense end pieces were crushed in a diamond steel mortar and ground in a boron carbide mortar and pestle in preparation for making powder patterns. To determine the types of alpha silicon carbide present after the various soaking times, a General Electric XRD3 Spectrogoneometer unit was employed. Nickel filtered copper radiation was used for diffraction and the counts

per second obtained on a Gieger-Muller tube were registered by a recorder. The areas under the peaks were measured and compared to the area under the 2.53 A^{o} line for each specimen. From three to ten runs were made on the powder from each specimen and the results averaged to obtain the curves shown in Fig. 12. In Table XIX are listed the "d" values obtained for "Mix 33" before hot pressing and after hot pressing with a soaking time of 15 minutes. Also the literature values for silicon are given.

(2) Metallographic Examination - The dense ends of the specimens were polished using diamond paste, and as shown in Fig. 13 two phases were observed. Gray grains predominated surrounding a lighter phase. The amount of light phase was observed to increase with temperature and soaking time and was identified as silicon. Hardness measurements of the silicon indicated a Vickers hardness of 1200-1800 kgm/mm^2 and the darker phase was found to be between 2500 and 3500 kgm/mm^2 using a load of 25 grams.

C. Discussion of Results

In Table XVII it can be seen that the bulk density of the whole specimen increased slowly due to the formation of a very dense region in the specimen near the top of the mold and the remainder of the specimen did not become appreciably denser. A great number of large voids oriented parallel to the pressing force were observed in the region of lower density. This observation and the fact that densification occurred at only the top and not the bottom (although pressure was applied from both ends) led to the belief that silicon from the interior of the specimen migrated as a vapor to the top and there it solidified.

Fig. 11b is evident of cold working of the material during polishing since no preferred orientation is found before polishing. This would indicate the presence of a less brittle material than silicon carbide such as uncombined silicon.

The results of the etching tests and the hardness measurements along with the x-ray patterns shown in Table XIX definitely establish the light phase (Fig. 13) to be silicon.

This increase of type 6 H silicon carbide as indicated by the increase intensity of the 1.67 A^{o} line in Fig. 12 for soak times greater than five minutes may be due to a loss of critical impurities through volatilization. Type 4 H decreased in quantity with soaking time evidently reverting to Type 6 H.

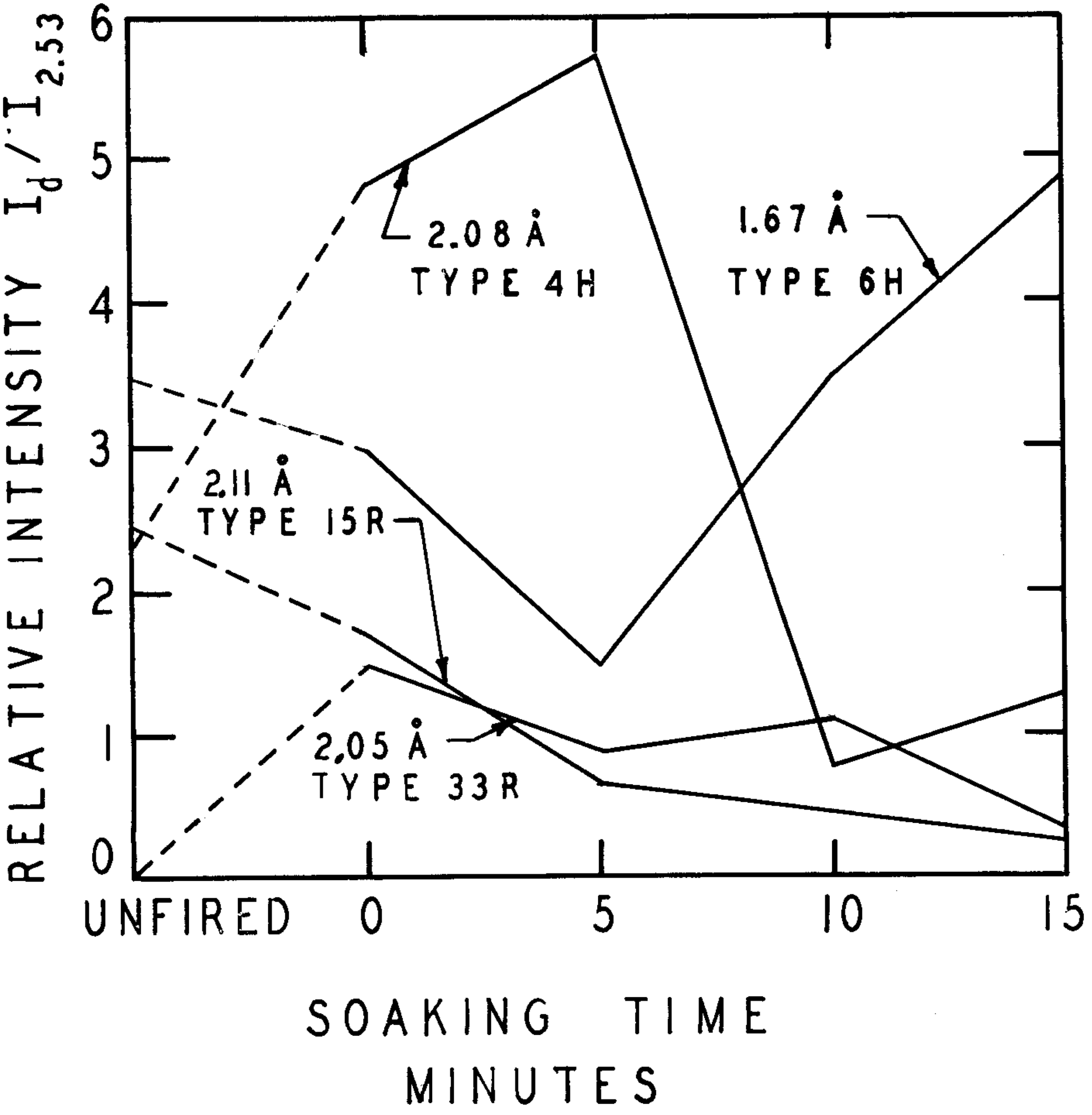
TABLE XIX

Evidence of Formation of Silicon During Hot Pressing

"Mix 33" Before Hot Pressing		"Mix 33" Soaked 15 min.		Catalog Values Silicon		Representative Lines of Pure Types of SiC
"d"	I	"d"	I	"d"	I	
		3.15	4	3.15	8	silicon
2.67	5					
2.64	7	2.64	6			
2.59	6	2.59	3			
2.53	9	2.53	8	2.52	4	
2.37	7	2.37	8			
2.19	6	2.19	6			
2.08	4	2.08	3			4H
2.01	5	2.01	5			
		1.90	5	1.90	10	silicon
1.84	3					4H
1.68	5	1.68	6			6H
		1.64	4	1.63	10	silicon
1.61	4	1.61	3			
1.54	10	1.54	10	1.52	10	
1.450	4					
1.426	8	1.426	8			
1.405	3					15R
		1.365	2	1.36	4	silicon
1.335	4	1.335	4			
1.320	10	1.320	10			
1.294	6	1.294	6			
1.273	3					
1.264	3	1.264	6			
		1.252	3	1.25		silicon
1.244	2					
1.225	4	1.225	5			

FIGURE 12

EFFECT OF SOAKING TIME ON TYPES OF ALPHA SiC PRODUCED



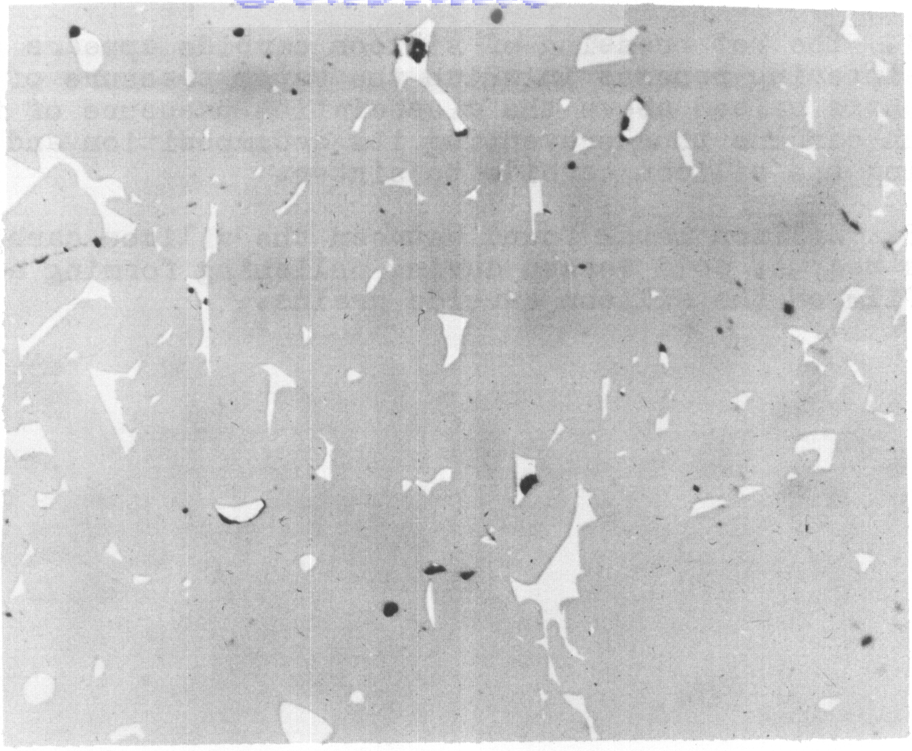


Fig. 13

Micrograph Dense Silicon Carbide Showing Light (Silicon) and dark (SiC) Phases 405x Unetched

The recrystallization of asymetrical grains under a directional pressure would be expected to cause a preferred orientation. Since no preferred orientation occurs it may be assumed that the pressure is in effect non-directional and the application of pressure confines the silicon vapors in contact with the silicon carbide allowing it to sinter rather than decompose. The presence of silicon in the most dense regions of the specimen is further evidence supporting this conclusion.

D. Conclusions (X-Ray and Metallographic Examination of Hot Pressed Alpha Silicon Carbide)

1. Hot pressed alpha silicon carbide consists of two phases; silicon carbide, a dark gray phase and silicon, a light metallic phase.

2. The original alpha grain, consisting of types 4 H, 6 H, and 15 R, is converted to type 6 H at the expense of the other types upon hot pressing for long soaking periods (15 minutes).

3. No preferred orientation occurs in the hot pressed silicon carbide grain.

4. The hot pressing of silicon carbide appears to be a sintering process in which the vapor pressure of the silicon is raised above the dissociation pressure of the silicon carbide thus preventing its decomposition and allowing the silicon carbide to sinter.

5. Silicon metal found between the silicon carbide grains becomes cold worked during polishing forming a thin film on the silicon carbide grains.