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METAL AND SELF-BONDED SILICON CARBIDE

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FOREWORD

This report concerns the work of R. E. Wilson, M. T. Curran, J. F. Grant, Research Associates, and J. R. Tinklepaugh, Project Director, at the New York State College of Ceramics, Alfred University, Alfred, New York. The work was accomplished under the direction of Dr. W. G. Lawrence, Chairman, Department of Research, and Dr. M. Tuttle was a Consultant.

The report summarizes research during the period 1 January 1955 to 31 December 1955 in which studies were continued on the metal bonding of silicon carbide and the factors effecting densification of self-bonded hot pressed silicon carbide. Prior studies were reported in WADC Technical Reports 53-5 and 54-38, Parts 1 and 2. The investigation of silicon carbide is terminated with this report.

The work was accomplished under Contract No. AF33(038)16190; administered under the direction of the Aeronautical Research Laboratory with Mr. Murray A. Schwartz as project engineer and is identified under Task No. 70634, "High Temperature and High Stress Characteristics of Ceramics and Cermets", Project 7350, "Ceramic and Cermet Materials."

ABSTRACT

Aluminum and iron, added in amounts of one to three percent, had a marked effect on the density achieved in hot pressing silicon carbide. Several other elements had minor effects. The Al_2O_3-SiC, Cr_3C_2-SiC and ZrB_2-SiC systems were studied briefly and the ZrB_2-SiC compositions showed some promise for use in uncooled rocket nozzles.

Molybdenum-SiC compositions were investigated in detail and it was found that Mo_4CSi_3 was the reaction product bond resulting from this combination. Mo_4CSi_3 was synthesized and used as the aggregate in a nickel bonded cermet.

Three compositions were selected from those studied for evaluation as rocket nozzle materials by the Bell Aircraft Corporation.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

Aldro Lingard

ALDRO LINGARD
Colonel, USAF
Chief, Aeronautical Laboratory
Directorate of Research

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I. INTRODUCTION

Silicon carbide is available commercially in any quantity desired at a very low price compared to all other carbides. It is used in high temperature applications by the industry in various forms, bonded by many different materials including: clay, silicon, silicon nitride, carbon and various ceramic binders.

When bonded by any of these binders the product is an excellent refractory material for many applications but the strength of the material is too low for some high stress - high temperature requirements in aircraft power plants.

The work described in this report is a continuation of research described in three previous publications.[1/2/3/] The work over the four year period involved two general approaches to the development of a strong, high temperature, silicon carbide material:

(1) The formation of dense, self-bonded silicon carbide.

(2) The bonding of silicon carbide by various metals, silicides, carbides and oxides.

1/ Alliegro, R. A., Tinklepaugh, J. R., "Investigation of the Bonding of Silicon Carbide by Metals," WADC Technical Report 53-5, January 1953, N.Y. State College of Ceramics, Alfred University.

2/ Alliegro, R. A., Coffin, L. B., Tinklepaugh, J. R., "Metal and Self-Bonded Silicon Carbide," WADC Technical Report 54-38, Part 1, January 1954, N.Y. State College of Ceramics, Alfred University.

3/ Wilson, R. E., Coffin, L. B., Tinklepaugh, J. R., "Metal and Self-Bonded Silicon Carbide" WADC Technical Report 54-38, Part 2, January 1955, N.Y. State College of Ceramics, Alfred University.

In the first publication[1], thermodynamic calculations were made to predict the reactions that would occur between various metals and silicon carbide. This work was supplemented and confirmed by wettability studies and x-ray diffraction-metallographic examinations of reaction zones. The first experiments in the hot pressing of relatively pure silicon carbide to high densities were reported.

In the second report[2], techniques were disclosed for the hot pressing of silicon carbide to densities in the 97 to 98% of theoretical density range using both alpha (commercial grain) and beta (synthesized in the laboratory) silicon carbide. A more uniform density was obtained using the beta grain. Densities of this order had not previously been reported.

Silicon carbide bonded by Cr:Mo (1:1) was described having a room temperature modulus of rupture strength of 31,000 psi. The bonding of silicon carbide by infiltrating a porous carbide structure with Hastalloy C under pressure was reported.

In the third publication[3], the influence of small additions or contamination (in the silicon) of aluminum on the hot pressing of dense silicon carbide was disclosed. It was found that the strength of dense self-bonded silicon carbide increased with temperature to 69,000 psi, modulus of rupture, at 2500°F. Initial tests of dense silicon carbide in the laboratory rocket test stand disclosed that the material had much higher resistance to flame erosion than any material previously tested (including Alfred 410 and Niafrax) but was sensitive to failure by thermal shock.

A molybdenum-silicon carbide cermet was studied which had a modulus of rupture of 70,000 psi at 1800°F. The partial substitution of titanium carbide for silicon carbide in such cermets was unsuccessful.

The present report brings this study of silicon carbide to a close. The sensitivity of dense silicon carbide to thermal shock failure in rocket nozzles was relieved partially by adding alumina and zirconium diboride to the carbide.

None of the metal bonded silicon carbide cermets developed were sufficiently thermal shock and impact resistant to warrant testing of blade shapes for eventual application in turbojet power plants.

The study was completed by the preparation of three compositions in the form of hot pressed nozzle inserts which were inserted in the throats of Alfred 410 nozzles for testing by the Bell Aircraft Corporation.

II DENSE SILICON CARBIDE AND TWO COMPONENT SYSTEMS

A. Properties of Hot Pressed Beta Silicon Carbide With Various Metallic Additions

The effect of aluminum in amounts varying from 1 to 5% by weight on the production of uniformly dense silicon carbide had been noted previously. It was conceivable that other elements might also markedly effect the formation of dense silicon carbide. In these experiments the beta silicon carbide process was used. This involved the synthesis of beta silicon carbide from silicon and carbon by heating mixed powder to approximately 2900°F, followed by hot pressing the grain thus formed at a temperature of 3900°F, converting the beta to alpha silicon carbide in the process.

(1) Procedure: To study the effect of several elements on the hot pressing of silicon carbide, three mole percent each of eighteen metals were substituted for a corresponding percent of silicon in the silicon-carbon batch from which the beta silicon carbide was synthesized. Similar mixtures were prepared in which, in addition to the three mole substitutions, a one mole percent substitution of aluminum was included.

The elements substituted are listed in Table I with weight percent indicated as well as mole percent.

These batches, consisting of carbon, silicon and the added elements, were thoroughly mixed, packed in a graphite container in an induction heated furnace, and heated to approximately 2900°F. At this temperature the beta, or cubic, form of silicon carbide is formed. The resulting grain was very fine. The beta silicon carbide was treated to remove excess carbon by floatation and with nitric and hydroflouric acids to remove the excess silicon.

TABLE I

SUBSTITUTIONS FOR SILICON IN THE SILICON-CARBON BETA SILICON CARBIDE BATCH

Element	Element Substituted Alone		Element Substituted With Aluminum			
			Element		Aluminum	
	Mole %	Wt. %	Mole %	Wt. %	Wt. %	Mole %
Aluminum	3.0	2.02	---	----	----	1.0
Iron	3.0	4.07	3.0	4.07	0.65	1.0
Lithium	3.0	0.53	3.0	0.53	0.68	1.0
Boron	3.0	0.82	3.0	0.81	0.64	1.0
Barium	3.0	9.48	3.0	8.51	0.62	1.0
Magnesium	3.0	1.82	3.0	1.82	0.67	1.0
Manganese	3.0	4.02	3.0	4.02	0.66	1.0
Molybdenum	3.0	4.77	3.0	4.75	0.65	1.0
Zirconium	3.0	6.50	3.0	6.50	0.64	1.0
Strontium	3.0	6.23	3.0	6.27	0.64	1.0
Cobalt	3.0	4.28	3.0	4.28	0.66	1.0
Chromium	3.0	3.81	3.0	3.82	0.66	1.0
Titanium	3.0	3.52	3.0	3.53	0.66	1.0
Calcium	3.0	2.97	3.0	2.97	0.67	1.0
Tantalum	3.0	12.12	3.0	12.13	0.60	1.0
Tungsten	3.0	12.30	3.0	12.30	0.60	1.0
Nickel	3.0	4.28	3.0	4.29	0.64	1.0
Copper	3.0	3.81	3.0	3.82	0.66	1.0

Hot pressing was accomplished in graphite dies using 8000 psi and heating to a maximum temperature of 3900°F.

(2) Results: The densities, porosities and in come cases, the resistivities of the carbides containing the various substitutions are listed in Table II. A graphic plot of the densities is shown in Fig. 1. The density obtained by pressing pure beta silicon alone was used for comparison purposes in the graphs.

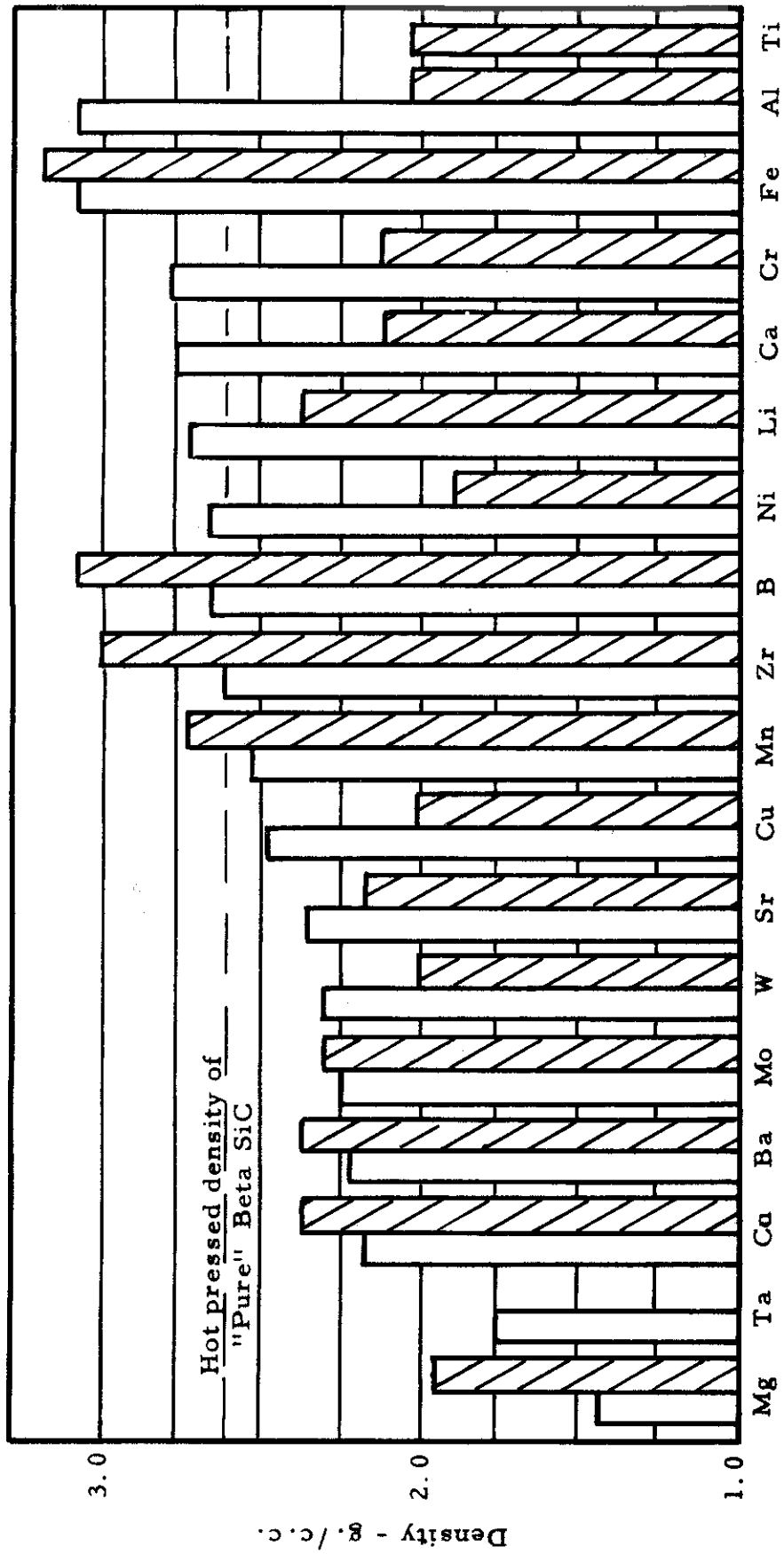
(3) Discussion of Results: It is evident from Fig. 1 and Table II that some elements substituted for silicon in amounts of three mole percent in the beta silicon carbide batch had a beneficial effect on the density obtained in the subsequent hot pressing. These elements were boron, nickel, lithium, calcium, chromium, iron and aluminum. When one mole percent of aluminum was also present, zirconium, boron, and iron had a marked effect. The most uniform, high density was obtained with the iron-aluminum combination.

The specific resistance data, included in Table II, showed a fairly wide change in resistance with the various substitutions. The increase in resistance of the carbide containing iron and boron at low temperatures was very marked and the effect of aluminum on the electrical resistance was evident.

The manner in which the aluminum entered the carbide structure was not clear. Usually aluminum was added to the silicon-carbon mixture in the form of alumina. The oxide was reduced in the process of synthesizing the beta silicon carbide, was not removed by the acid and floatation treatment (aluminum carbide is water soluable) and by chemical analysis, was present in the finished hot pressed products. X-ray diffraction did not reveal the presence of aluminum carbide but did show a slight shift in the silicon carbide lattice.

B. The Silicon Carbide-Alumina Systems

It has been stated previously in this report that silicon carbide, in dense form, had excellent resistance to erosion, but was deficient in resistance to thermal shock failure. Excellent thermal shock resistance was obtained previously using a composition 70% SiC, 25% Al_2O_3, 5% Sagger clay, in a porous sintered body. The SiC-Al_2O_3 system appeared worthy of investigation.



Cross hatched bars represent specimens containing 1 mole % aluminum in addition to the 3 mole % substitutions

Figure 1

Histogram showing effect of elements substituted for silicon on density achieved by hot pressing to 3900°F

TABLE II

DENSITIES, POROSITIES AND RESISTIVITIES OF SILICON CARBIDE CONTAINING VARIOUS ADDITIONS

Added Element	Density g/cc. Without Aluminum	Density g/cc. With Aluminum	Porosity % Without Aluminum	Porosity % With Aluminum	Spec. Resistance Ohm. Cm. 300°K	77°K	2°K
Aluminum	----	3.08	---	1.0	--	---	--
Iron	3.08	3.17	4.9	1.0	*21.0	550.0	4×10^5
Lithium	2.72	2.31	8.1	22.0	0.8	1.0	1.4
Boron	2.65	3.03	12.2	0.4	* 5.0	85.0	7 x 10
Barium	2.18	2.37	26.0	20.9			
Magnesium	1.60	2.01	40.0	30.1			
Manganese	2.55	2.71	15.7	9.5		0.6	0.7
Molybdenum	2.26	2.22	23.8	24.6			
Zirconium	2.62	3.00	13.4	1.4	* 4.0	6.0	7.0
Strontium	2.39	2.27	20.1	23.0			
Cobalt	2.18	2.40	25.0	19.1			
Chromium	2.62	2.08	15.0	29.1	0.13	0.16	0.2
Titanium	----	2.03	----	29.5			
Calcium	2.75	2.11	8.5	26.5	0.15	0.21	0.25
Tantalum	1.80	----	---	35.5			
Tungsten	2.30	2.25	22.9	29.9			
Nickel	2.67	12.8	1.73	46.7			
Copper	2.48	2.03	17.5	29.6			

*Those resistance values marked with the asterisk were for SiC containing Al as well as the element noted, those without the asterisk did not contain Al.

(1) Procedure: The materials used were 1200 mesh SiC (Carborundum Company), beta silicon carbide prepared in the laboratory, and 500 mesh alumina (Norton Company). The compositions studied are shown in Table III. In the compositions designated by the B preceding the number, the alumina was added to the Si-C mixture from which the beta silicon carbide was synthesized before hot pressing. In all other compositions the alumina was added to the alpha SiC before mixing. The SiC and Al_2O_3 were mixed in a dry blender for four hours. The mixtures were hot pressed at temperatures ranging from 3375°F to 3700°F, depending on the composition, at a pressure of 8600 psi. Discs, 3/4 inch diameter by 1/4 inch thick were prepared for metallographic examination of the microstructure and laboratory rocket test nozzles were pressed from the compositions.

Polished samples for microstructure examination were prepared by diamond polishing. Rocket test nozzles were hot pressed of Compositions B31, B36, 684, and 688. The hot pressing temperatures, densities and test data are included in Table III. Two of the nozzles tested were plated with nickel, 1/16 inch thick, on their outside surfaces to hold them together so that area enlargement data could be obtained even if the material cracked in testing.

(2) Results and Discussion: The sintering range (hot pressed) for compositions in the SiC-Al_2O_3 system is shown graphically in Fig. 2. The upper boundary of the cross hatched area indicates that temperatures at which alumina was lost from the composition in excessive amounts. The lower boundary indicates the minimum temperatures at which the compositions hot pressed to a low porosity. It was not possible to hot press specimens of low porosity in the high silicon carbide range without the loss of some alumina.

Two photomicrographs are shown in Fig. 3 that represent the type of microstructure obtained in the SiC-Al_2O_3 series.

In B, the 70% SiC - 30% Al_2O_3 Composition 688, the silicon carbide forms a continuous structure, while in A, the 30% SiC - 70% Al_2O_3 Composition 684, the alumina forms the continuous structure. It is evident that when silicon carbide constitutes the continuous structure, higher hot pressing temperatures must be used and this results in the loss of alumina from the structure.

TABLE III

Al_2O_3-SiC Compositions

Comp. No.	SiC Weight Percent	Al_2O_3 Percent	Fe	Hot pressing Temp. °F	Bulk Density	Time To Failure	Nozzle Enlargement	Cracks
B31	98	1	1	3900	3.0	25 sec.	-	Shattered
B31	98	1	1	3900	3.1	150 sec.	*0.8%	Fine Cracks
B36	94	5	1	3900	3.1	-	-	Three Fine Cracks
B36	94	5	1	3900	3.0	150 sec.	*1.8%	One Fine Crack
682	10	90	-	3275	3.9	-	-	-
683	20	80	-	3275	3.7	-	-	-
684	30	70	-	3275	3.7	5 sec.	-	Complete
684	30	70	-	3275	3.7	11 sec.	-	Failure
685	40	60	-	3425	3.6	-	-	-
686	50	50	-	3425	3.5	-	-	-
687	60	40	-	3465	3.4	-	-	-
688	70	30	-	3320	3.3	20 sec.	-	-
689	80	20	-	3525	3.2	-	-	-
690	90	10	-	3525	3.1	-	-	-

*These nozzles were plated on their outside surface with 1/16th inches of nickel.

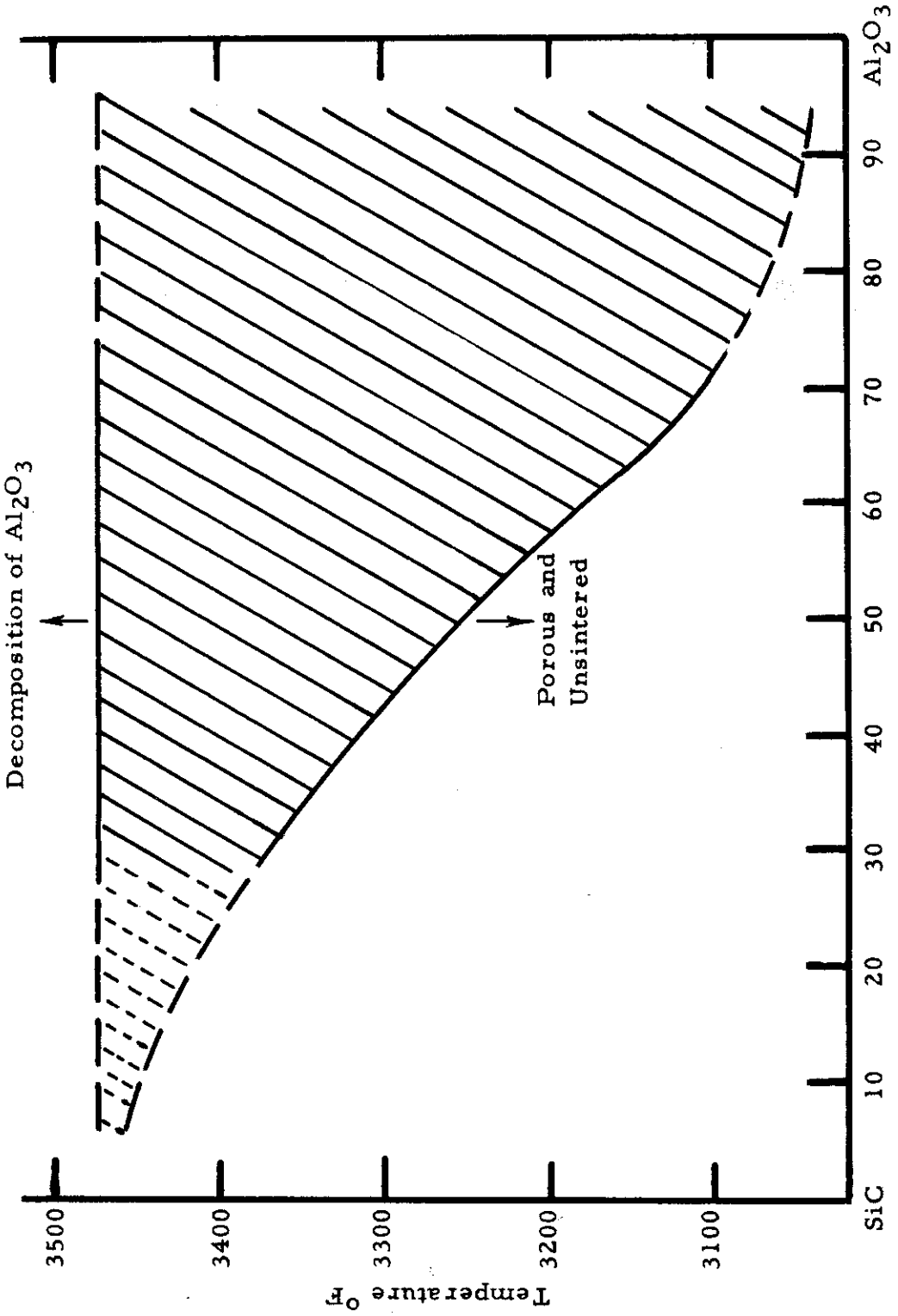
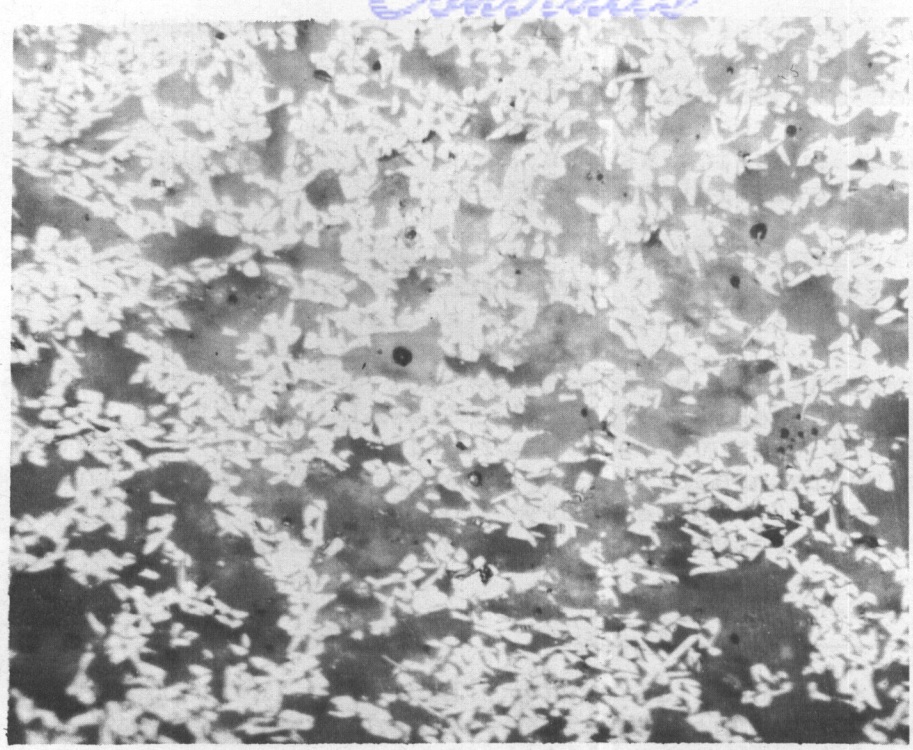


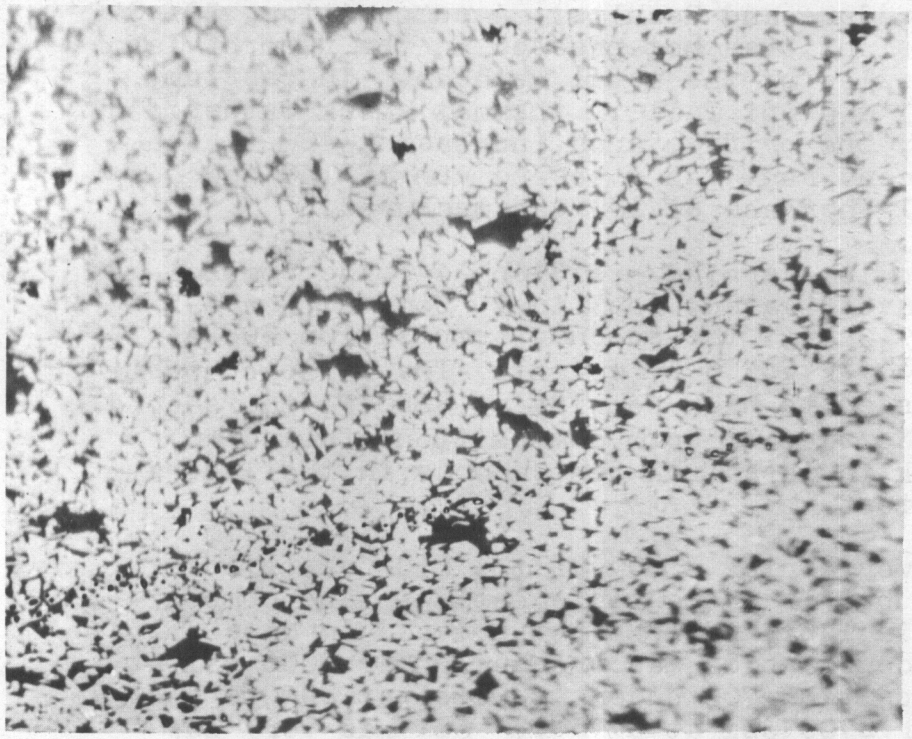
Figure 2

Sintering Range of SiC-Al_2O_3 Compositions



(A)

Composition 684



(B)

Composition 688

Photomicrographs - Al_2O_3-SiC Structure

Fig. 3

During the process of this work it was discovered that small additions to commercial alpha silicon carbide of the order of one percent of aluminum or two percent of alumina had much the same effect in producing high densities in hot pressing as was previously found in hot pressing of beta silicon carbide.

(3) Conclusions: It is evident that silicon carbide-alumina compositions do not have sufficient resistance to failure in thermal shock for use as rocket nozzles.

Dense compacts can be formed by hot pressing using a wide range of compositions in the SiC-Al_2O_3 system. It is very likely that there are materials in the system that might prove interesting for other applications. The present work was, of course, very empirical and with only one objective, the rocket application, in mind.

C. SiC-TiC, SiC-Cr_3C_2, SiC-ZrB_2

Several binary carbide systems had been investigated in previous work and selected compositions were picked from these for laboratory rocket tests.

(1) Procedure and Results: A composition, 80% SiC-20% TiC by weight, was hot pressed in the form of laboratory test nozzles by the usual methods. In testing, this material did not fail in thermal shock but eroded very rapidly, the orifice area increasing 42% in the first 150 second run. In a second run of 150 seconds an additional increase of 18% was measured.

Two chromium carbide - silicon carbide compositions were investigated; the first, Composition 697 - 47% SiC - 53% Cr_3C_2; the second, Composition 698 - 66.7% SiC - 33.3% Cr_3C_2 by weight. The first composition hot pressed to high density at 2850°F; the second at 3700°F. Nozzles of both compositions failed in thermal shock in less than ten seconds in the laboratory rocket test.

Only a very brief study of the SiC-ZrB_2 system was possible but it proved interesting. The compositions shown in Table IV were hot pressed in disc shape. The B31 silicon carbide was pressed under 8000 psi at 3900°F; Composition 703 under 4800 psi at 3900°F and the 705 under 2700 psi at 3775°F. All had very low porosities.

TABLE IV

Electrical Resistivities of SiC-ZrB_2 and SiC

Comp. No.	SiC	Al_2O_3	ZrB_2	Resistivity Ohm.*
	Weight Percent			
B31	99.0	1.0	-	60.0
704	81.8	1.0	17.2	1.5×10^{-6}
703	67.0	1.0	32.0	0.1
705	--	-	100.0	0.1

*Resistivity values are not specific resistance but rather total resistance of specimens 1-1/2 in. diameter and 1/4 in. thick, measured between parallel faces.

The high resistivity of Composition 704 as compared to the other compositions of the series is very interesting and would have been investigated more thoroughly had there been time available.

Composition 703 was selected for laboratory rocket tests. Two nozzles were tested. The first ran the entire 150 seconds developing only one fine crack and very little erosion. The second failed by thermal fracture in ten seconds. The SiC used in making these nozzles was 1000 mesh. Four additional nozzles were tested in which two contained coarser 400 mesh silicon carbide. The two nozzles containing coarse SiC failed in 10 and 20 seconds. One of the nozzles, containing the fine SiC failed in seven seconds, the other survived the 150 second run without failure and showed a 4.1% nozzle enlargement. This is considered very good.

(2) Discussion of Results: It was quite obvious that neither the SiC-TiC nor SiC-Cr_3C_2 compositions were of immediate interest for the rocket application.

The SiC-ZrB_2 compositions showed sufficient promise to warrant further rocket testing and Composition 703 is mentioned in a later section of this report describing the preparation of nozzles for testing by the Bell Aircraft Corporation.

III METAL BONDED SILICON CARBIDE

The term "metal bonded silicon carbide" is used very loosely here to designate all compositions in which metal in excess of 10% was introduced in the powder batch. In many cases this metal was converted to silicides or complex carbides in the sintering process and the final product was not necessarily metal bonded.

The exceptional cross-bending strength at room temperature and at 1800°F of molybdenum-SiC was reported previously.[3] It was quite evident, however, from examination of the microstructure that the molybdenum and SiC were reacting during sintering to form a new phase which constituted the binder in the finished product. Examination of the Mo-Si-C phase diagram [4] indicated such a reaction was likely with the release of free carbon. L. Brewer and O. Krickorian[5] had identified a compound, Mo_4CSi_3, which was stable in the presence of carbon and it was hypothesized that this was the end product of the reaction under discussion.

A. Molybdenum-Silicon Carbide

(1) Procedure and Results: Brewer and Krickorian reported that Mo_4CSi_3 had a $D8_8$ structure; was isomorphous with Mn_5Si_3, with a c-axis of 5.242 A and an a-axis of 7.285A, resulting in a c/a ratio of 0.7196. This data was used to determine the calculated "d" values in Table V using the Hull-Davy chart for the hexagonal system.

To study the reactions involved in the original Mo-SiC cermet, the mixtures shown in Table VI were prepared.

4/ Kieffer, R., and Benesovsky, F., "Silicides of the Transition Metal of the 4th, 5th and 6th Groups of the Periodic Table," Iron and Steel Institute, Preprints of Symposium Paper, December 1954.

5/ Letter from L. Krickorian, Dept. of Chemistry and Chemical Engineering, University of California, Berkely, California.

Powder diffraction patterns were made using the XRD-3 spectrogoniometer unit. The data obtained are compared to the calculated in Table V.

TABLE V

Powder Diffraction Patterns

Theoretical Mo_4CSi_3		Comp. 678 Synthesized Mo_4CSi_3		Comp. 680	Comp. 676
"d"	hk•l	"d"	I	"d"	"d"
3.17	20.0	3.16	17	3.16	3.15
2.97	11.1	2.97	37	2.96	2.95
2.68	20.1	2.68	8	2.67	2.64
2.58	00.2	2.52	8	2.53	2.59
2.39	10.2	2.40	41	2.38	2.38
2.38	12.0	2.34	39	2.35	2.37
2.16	12.1	2.16	100	2.16	2.15
2.10	30.0	2.11	27	2.10	2.10
2.02	20.2	2.08	67	2.07	2.06
1.95	30.1				
1.82	22.0				
1.76	12.2				
1.71	00.3				
1.67	10.3				
1.63	30.2	1.61	8	1.60	1.59
1.53	11.3	1.52	6		1.51
1.51	20.3	1.47	10	1.48	1.47
1.39	12.3	1.37	17	1.39	1.37
1.33	30.3	1.34	12	1.34	1.33
1.28	00.4				
1.25	10.4	1.26	8		
1.20	11.4	1.19	6		

TABLE VI

Compositions Used in Mo-SiC Experiments

Comp. No.	Composition by Weight Percent					*To Produce by Reaction These Compounds in Volume Percent	
	SiC	Mo	Si	C	Cr	SiC	Mo_4CSi_3
678	--	80.0	17.5	2.5	--	--	100
679	3.5	77.3	16.9	2.4	--	7.9	92.1
680	11.5	70.8	15.5	2.2	--	20.0	80.0
676	32.2	65.1	--	--	2.7	20.0	80.0

Materials - SiC - 1200 mesh, Carborundum Co.
99.9% Mo - North American Phillips Co.
99.9% Si - Electro-Metallurgical Co.
Carbon, low ash - Will Corporation

*Disregarding free carbon formed

These components were well mixed and hot pressed into cylinder shapes using a maximum temperature of 3050°F and 2000 psi. Modulus of rupture bars, metallographic samples and powders for x-ray diffraction were obtained from these cylinders.

Comparison of the X-ray patterns for synthesized Mo_4CSi_3 with the theoretical pattern indicated that the compound had been formed. Composition 680 produced a pattern very close to that of the synthesized material plus some of the stronger silicon carbide lines. The slight shift to lower "d" values in the Composition 676 was probably the result of the chromium going into solid solution in the Mo_4CSi_3 structure. Other patterns of compositions having higher chromium contents were made and an increased amount of displacement in the same direction was noted. The bond resulting from the Mo-SiC reaction was definitely identified as Mo_4CSi_3.

The strengths obtained from the various compositions in Table VI are shown in Table VII.

TABLE VII

Cross Bending Strength - Mo-SiC

Comp. No.	Porosity %	Modulus of Rupture Psi Room Temp.	1800°F
676	2.8	40,200	71,900
678	0.1	24,500	46,100
679	1.1	28,000	53,000
680	1.1	38,400	46,600

The cross bending strengths of Composition 676 and 679 at 1800°F places them among the stronger cermets in this temperature range.

Continuing the development of this type of material, a series of compositions were selected for laboratory rocket testing. These compositions are included in Table VIII along with the test data.

TABLE VIII

Compositions Evaluated as Rocket Nozzle Materials

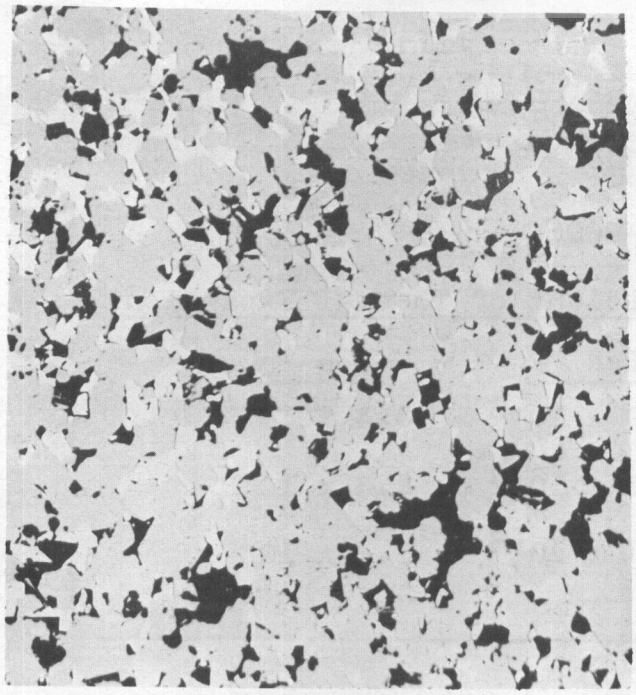
Comp. No.	Weight Percent Mo	Cr	SiC	Test Time	Enlargement Percent	Test Time	Enlargement Percent
676	65.1	2.7	32.2	Av. 19 sec. to failure* (2 nozzles)			
675	54.9	2.3	42.8	Av. 12 sec. to failure (3 nozzles)			
694	32.5	1.4	66.1	6 sec.	--	--	--
694	32.5	1.4	66.1	150 sec.	11.7	150	5.9
694	32.5	1.4	66.1	150 sec.	4.3	150	5.1
681	27.3	1.1	71.7	150 sec.	0.7	150	5.1
681	27.3	1.1	71.7	150 sec.	10.8	150	5.1
681	27.3	1.1	71.7	150 sec.	1.7	--	--
681	27.3	1.1	71.7	Av. 12 sec. to failure (4 nozzles)			
693	21.7	0.9	77.3	150 sec.	6.6	150	2.8
693	21.7	0.9	77.3	Av. 12 sec. to failure (3 nozzles)			

*All failures were by thermal cracking

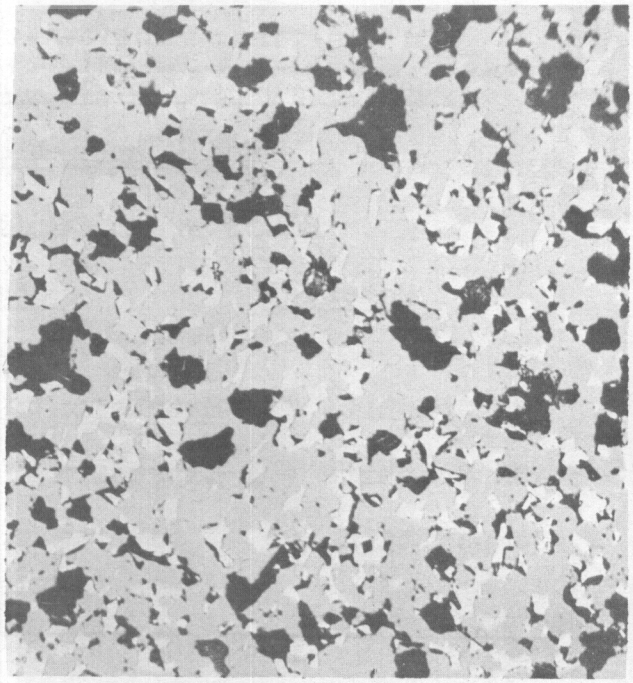
Representative microstructures of these compositions are shown in Fig. 4. The gray phase is silicon carbide, Mo_4CSi_3 is the light phase, and the black areas are largely pores with some graphite.

It was quite evident from the nozzle test data reported in Table VIII that performance of the nozzles was erratic, i.e. nozzles of the same composition, density and porosity exhibited a wide range in resistance to thermal shock. There was evidence that some nozzles had micro-cracks present prior to testing and that these cracks contributed to early failure. One possible source of these micro-cracks was the known difference in thermal expansion of the graphite used in the mandrel of the hot press mold in which the parts were produced and the nozzle material.

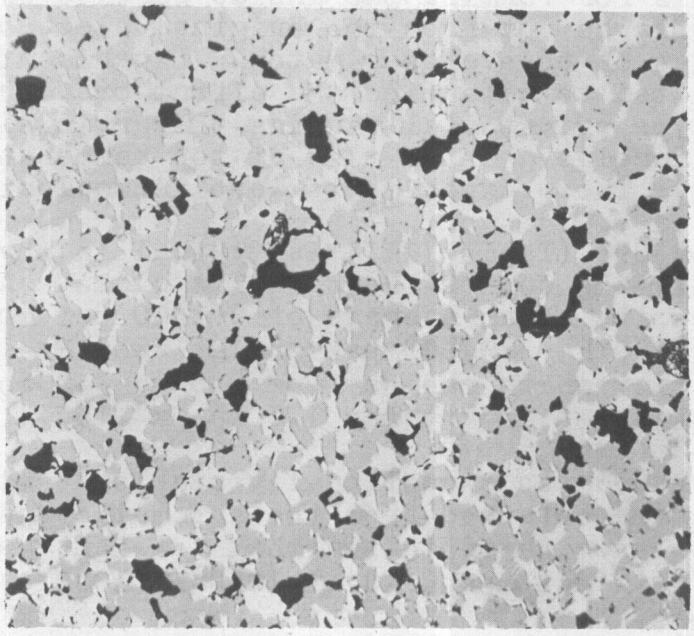
To verify this, thermal expansion data were obtained for AGX graphite in two directions: (1) normal to the extrusion direction; (2) parallel to the extrusion direction and also for Composition 693. These data are shown in Table IX.



Composition
681



Composition
693



Composition
694

Representative Microstructures of Compositions

681, 693, 694

Fig. 4

TABLE IX

Coefficient of Thermal Expansion, Graphite and Composition 693

212°F - 1475°F (100-800°C)

Material	Coefficient of Thermal Expansion	
	Per °F	Per °C
AGX Graphite (// Extrusion)	1.9×10^{-6}	3.4×10^{-6}
AGX Graphite (⊥ Extrusion)	1.3×10^{-6}	2.3×10^{-6}
Composition 693	2.1×10^{-6}	3.8×10^{-6}

Since the expansion parallel to the direction of extrusion in the graphite stock more closely matches that of the materials being hot pressed, it follows that the mandrels for forming the inside surface of the nozzles should be cut from the original electrode to take advantage of this closer match. Experiments were also conducted to determine the effect on thermal shock in this type of material varying the grain size of the silicon carbide and the time at top temperature in hot pressing. These experiments were inconclusive.

Composition 693 (Table VIII) is typical in physical properties of all the compositions in its class. At room temperature it had an average of 26,500 psi modulus of rupture, at 1800°F - 29,300 psi and at 2500°F - 37,800 psi. Its impact strength ranges from 0.5 to 1.0 in-lbs. on the standard cermet impact bar 1.5 in. x .187 x .187.

Composition 693 was exceptionally stable at high temperatures. Data obtained from the automatic recording oxidation balance demonstrated that a weight gain of only 0.5 mg/cm.2 was measured at 1832°F (1000°C) in twenty-five hours.

In an earlier report[2]/Alliegro described the development of a metal bonded silicon carbide utilizing equal quantities, by weight, of chromium and molybdenum as the binder metal. Two of these compositions, Composition 699

17.5% Mo, 17.5% Cr, 65% SiC and Composition 700 - 5.0% Mo, 5.0% Cr, 90% SiC (by weight), were prepared in the form of laboratory test nozzles by hot pressing to 3000°F and 4000°F, respectively. These nozzles failed by thermal cracking in test after ten seconds running time.

(2) Conclusions: When molybdenum and silicon carbide were sintered at high temperatures, Mo_4CSi_3 was the reaction product and constituted the bond in such materials. Some carbon was precipitated in this process.

Materials of the Mo_4CSi_3 - SiC type (Composition 693) were excellent in resistance to thermal erosion as indicated by testing in the laboratory rocket nozzle test but were susceptable to failure by thermal shock.

The cross bending strength of these compositions was high at 1800°F, placing them among the stronger class of materials at this temperature.

The Cr-Mo-SiC compositions described by Alliegro[2/] were not sufficiently resistant to thermal shock to be considered for the uncooled rocket nozzle application.

B. Nickel-Mo_4CSi_3 Cermets

The Mo_4CSi_3 compound formed in the Mo-SiC compositions was in itself of interest as an aggregate in a nickel bonded cermet. For this purpose Mo_4CSi_3 was synthesized from a stoichiometric mixture of Mo, Si, and C by heating in a graphite crucible to 3700°F. A jaw crusher was used to pulverize the fused material formed and the free carbon was removed by floatation in water using pine oil as a floatation medium. The material was ball milled for twenty-four hours to reduce the grain size to the micron range.

This powder was hot pressed in the form of discs, 1/8 inch thick, 3/4 inches in diameter, using a temperature of 2800°F and 5000 psi. These discs were intentionally porous; about 20%. Pellets of nickel were set on these discs in a vacuum furnace and heated to 2700°F at a pressure of less than one micron. Upon removing the discs from the furnace, it was found that the nickel had infiltrated the Mo_4CSi_3.

Following this, a composition, designated 701, and consisting of 24% Ni, 76% Mo_4CSi_3 by weight, was ball milled for twenty-four hours, cold pressed into cylinders, and heated to 2300°F in the vacuum furnace. Dense, well sintered parts were obtained. Twelve bars, of a size to produce standard impact bars, were cold pressed and sintered in the same way. While these were being ground to final size they were broken, apparently by the thermal shock encountered in dry diamond grinding. It was quite evident that, while the material might have some good properties otherwise, it would be eliminated from consideration for power plant applications by poor resistance to thermal shock. Attempts to etch polished sections with nickel etchants such as Carapella's Reagent failed to reveal nickel. It was concluded that brittle nickel silicides were probably formed in sintering.

IV FABRICATION OF BELL AIRCRAFT CORPORATION

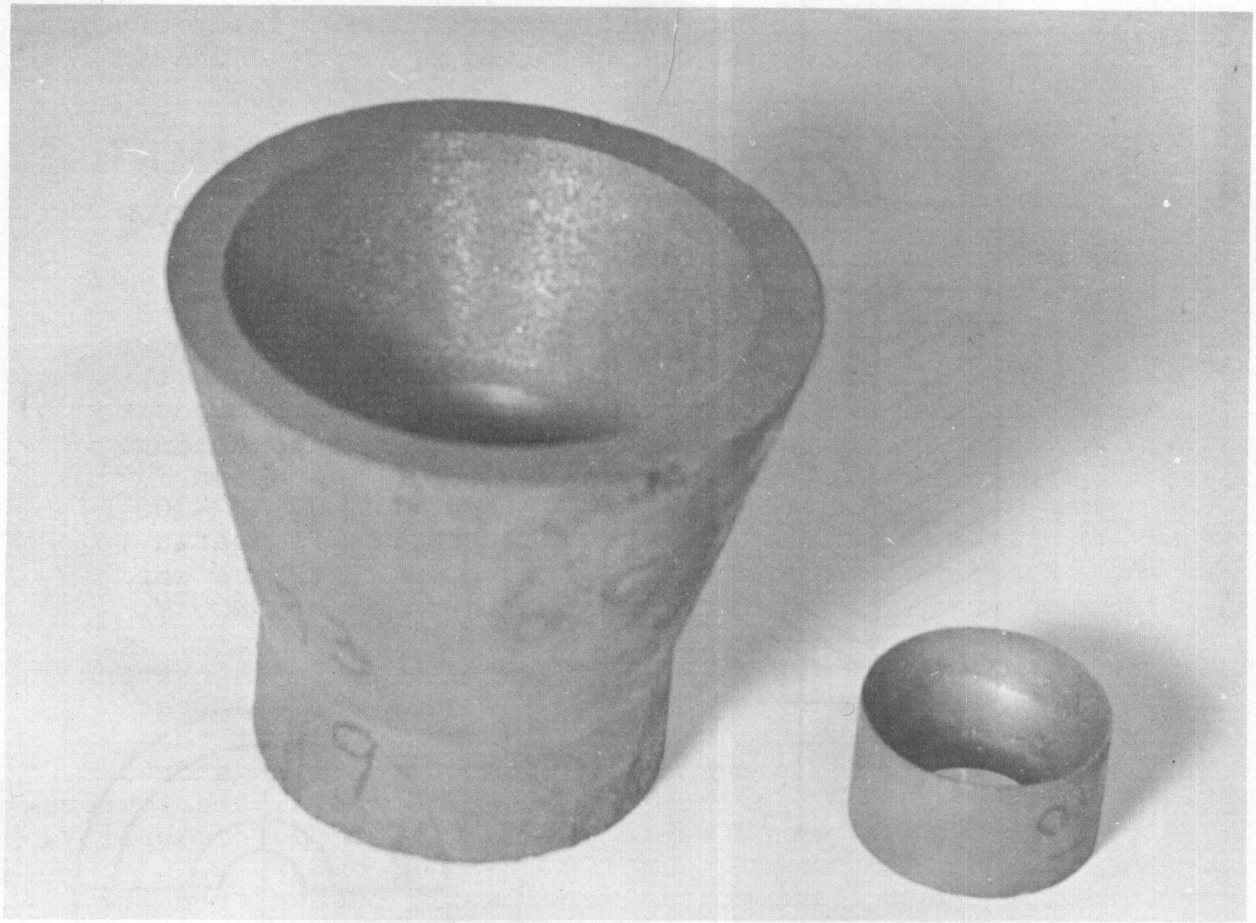
NOZZLE INSERTS

During the process of the work described in this report several compositions had been discovered that showed exceptional resistance to flame erosion when tested in the laboratory rocket nozzle test. Composition B36 (Table III), 693, (Table VIII) and 703 (Table IV) were selected for this purpose.

All of these compositions had to be hot pressed to achieve the desired density. The size of the hot presses in the laboratory was such that parts requiring hot pressing in the range from 3500 to 4500°F were limited to an outside diameter of two inches.

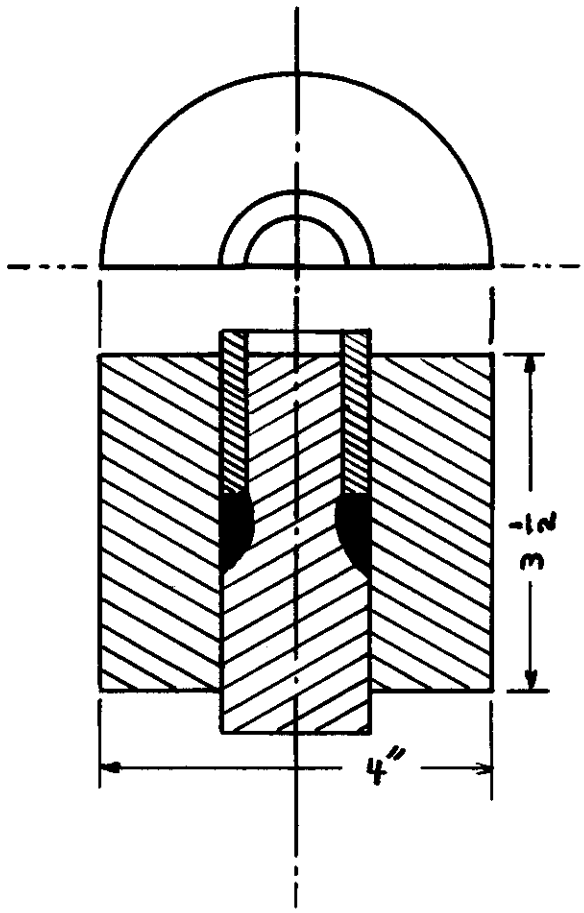
The Bell Aircraft ceramic test nozzle (Drawing No. 56-470-212) is one of the smallest nozzles available for realistic material evaluation. An insert could be made for this nozzle within the limitations mentioned above. A sketch of this nozzle and insert, along with the hot press die used to produce the insert is shown in Fig. 5. The completed nozzle and an insert are shown in Fig. 6.

While the insert appears simple in shape, calculations show nearly a 30° under-cut in filling to the narrowest part of the mandrel. Composition 693 did not become plastic or fluid at hot pressing temperatures up to 4300°F. For this reason force applied to the material by the push rods was transmitted only at very small angles to the direction in which it is applied and filling of under-cut sections was difficult.



Nozzle and Insert

Fig. 6



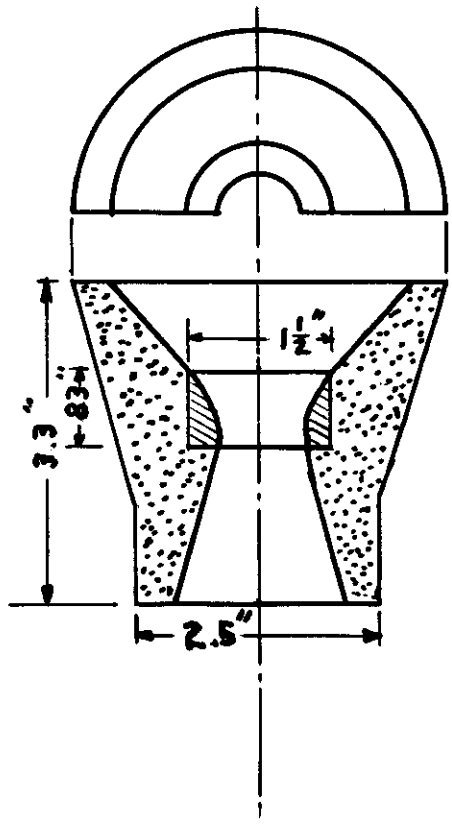


FIG. 5

The chief difficulties encountered were in forming the thin edge dense enough and in forming the material to fit the mandrel. Also, it was found necessary to make the graphite mandrel 0.005 in. oversize because of thermal contraction of the material on cooling.

Hot pressing techniques were developed which formed inserts having high density in all regions and had the correct contours except for a small grove near the throat.

Sufficient material to form the piece was loaded into the die and pressed lightly. The top push rod was then pushed flush with the top of the mold leaving the mandrel protruding from the bottom. This permitted the thin feather edge to become dense during hot pressing. The die was then heated to 4100°F in the induction furnace without the application of pressure. At 4100°F, 8000 psi was applied while the temperature increased to 4200°F, where the power was turned off. Pressure was applied until the furnace had cooled to about 3800°F.

If pressure was applied at the start of the heating period, some sintering occurred at lower temperatures forming rigid material which would not deform at the peak temperatures to assume the contour of the mandrel. For this reason, no pressure was applied until the temperature was reached which would assure maximum deformability.

The mandrel and nozzle were easily pushed from the die, but the mandrel had to be cut off at the insert and removed from the center of the nozzle by drilling.

This same procedure was followed for all three of the compositions with the exception of the necessary difference in pressing temperatures. The completed inserts were placed in their proper position in a steel mold and Composition Alfred 410 was tamped around the insert to form the balance of the nozzle. Alfred 410 is a carbon bonded silicon carbide-graphite composition that has demonstrated good performance in several rocket applications. After the nozzles were formed, they were heated to 1800°F in a reducing atmosphere to carbonize the carbon bond in the Alfred 410.

The results of the tests by the Bell Aircraft Corporation will not be available in time to be included in this report.

V. SUMMARY OF REPORT CONCLUSIONS

1. Boron, nickel, lithium, calcium, chromium, iron and aluminum aid in the densification of Beta SiC in hot pressing. When one mole percent of aluminum is already present zirconium, boron, and iron have a marked effect.

2. Compositions in the Al_2O_3 system can be hot pressed to high densities, have interesting properties, but are too sensitive to thermal shock to be of use in rocket nozzles.

3. Compositions in the TiC-SiC and Cr_3C_2-SiC system are also of no immediate interest because of excessive flame erosion in the first case and low thermal shock resistance in the second.

4. Compositions in the SiC-ZrB_2 system did show some promise with respect to thermal shock and flame erosion and further testing was indicated.

5. Mo_4CSi_3 was found to be the bond resulting when Mo-SiC mixtures were hot pressed. The Mo_4CSi_3-SiC compositions thus formed show excellent promise for use in the critical nozzle areas. These materials were also very strong at high temperature.

6. Three compositions, Composition B36 - 94% SiC, 5% Al_2O_3, 1% iron by weight; Composition 693 - 21.7% Mo, 0.9% Cr, 77.3% SiC; and Composition 703 - 67.0% SiC, 1.0% Al_2O_3, 32.0% ZrB_2; were selected for full scale rocket tests by the Bell Aircraft Corporation and were incorporated in suitable nozzles for evaluation.