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(71) Applicant: CERAMATEC, INC. [US/US]; 2425 South 900 West, Salt Lake City, UT 84119 (US).

(72) Inventors: VIRKAR, Anil, V. ; 1875 Suzette Circle, Salt Lake City, UT 84106 (US). CUTLER, Raymond, A. ; 1433 Harrison Avenue, Salt Lake City, UT 84105 (US). LESSING, Paul, A. ; 5608 Walden Meadows Drive, Murray, UT 84123 (US). HUANG, Jow-Lay ; 119 Q Street, Salt Lake City, UT 84103 (US).

(74) Agents: BRITT, William, S. et al.; Trask, Britt & Rossa, P.O. Box 1978, Salt Lake City, UT 84110 (US).

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(54) Title: DENSE CERAMICS CONTAINING A SOLID SOLUTION AND METHOD FOR MAKING THE SAME

(57) Abstract

Dense ceramic composites comprising a mixture of a solid solution containing the elements Si, C, Al, O and N (referred to by the acronym SiCAlON) and a high temperature refractory phase have desirable physical properties and can be formed by pressureless sintering techniques. The refractory phase can be SiC, AlN, Al_2O_3,or AlON and constitutes between 1 and 99% of the volume of the ceramic. The method for pressureless sintering may also be used for densification of SiCAlON ceramics, or composites containing SiCAlON, allowing fabrication of the same into complex shapes economically.

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DENSE CERAMICS CONTAINING A SOLID SOLUTION AND METHOD FOR MAKING THE SAME

Background of the Invention

Field: This invention relates to the field of ceramics and particularly to ceramics containing solid solutions containing the elements Si, C, Al, O, and N (referred to by the acronym SiCAlON), and a method for densifying such ceramics.

Description of the Prior Art: Silicon based ceramics are leading candidates for applications in high temperature environments including energy conversion devices due to their high strength to temperatures on the order of 1500°C. SiC and Si_3N_4 ceramics also find use in applications, over a wide temperature range, where wear and/or chemical resistance is required.

Pressureless sintering of SiC has been accomplished using either B and C (or B_4C) or Al (or Al_2O_3) as sintering aids to obtain nearly single phase SiC with densities greater than 97% of theoretical. Very active powders having high surface area (mean particle size is less than 0.5 micrometers) are required to provide the driving force for sintering. Very little densification occurs by pressureless sintering with SiC particle sizes greater than 1 micrometer. Since pressureless sintering allows fabrication of complex shapes economically, it would therefore be an improvement in the art if SiC particles in the 1-10 micrometer range could be densified without pressure.

Similarly, several methods have recently been developed for the pressureless sintering of Si_3N_4. One of the most successful methods for pressureless sintering involves the formation of a solid solution of aluminum

oxynitride in silicon nitride to form SiAlON (a coined term consisting of the chemical abbreviations for the elements present in the solid solution). This family of materials sinter via a transient liquid phase and has proven successful in making cutting tools.

In analogy with the SiAlONs, Cutler et al. (U.S. Patent 4,141,740 issued FEB. 27, 1979 for SOLID SOLUTION AND PROCESS FOR PRODUCING A SOLID SOLUTION) discovered that a complete solid solution exists between alpha phase SiC (2H polytype), AlN, and Al_2OC. This family of new materials was named using the acronym SiCAlON, analogous to the SiAlON system. These compounds exhibit the same hexagonal wurtzite structure and have similar lattice parameters.

Subsequent studies on the SiC-AlN system indicated that the system had mechanical properties similar to silicon carbide. The main advantage of the solid solutions was that by changing composition, one could control properties (i.e., density, hardness, fracture toughness, Young's modulus and thermal expansion co-efficient) of the dense ceramic. This family of materials thus appears to have the potential to broaden the applications of SiC. It would also appear that the solid solubility range in the SiC-AlN-Al_2OC system is much greater than that found in the SiAlON system, thus broadening the physical property range where engineering of properties is possible.

The major limitation of the prior SiCAlON work was that attempts to pressureless sinter the composites were unsuccessful and processing was expensive, requiring hot pressing. While hot pressing resulted in dense polycrystalline ceramics, in order to make complicated shapes economically in large volumes, one must preform the material to a shape similar to that desired for the

final component and sinter without pressure. As an example of the utility of such a technique, one is referred to the work of Cutler (U.S. Patent 3,960,581, issued June 1, 1976, for PROCESS OF PRODUCING A SOLID SOLUTION OF ALUMINUM OXIDE IN SILICON NITRIDE) where SiAlON materials were pressureless sintered. No techniques heretofore have been reported that allow sintering (without hot-pressing) of compounds in the SiC-AlN-Al_2OC phase field into a substantially dense polycrystalline ceramic.

In recognition of the interest in high-strength ceramic materials having specific physical properties, it would be an advantage in the art to provide an inexpensive method for fabricating complex shapes of a solid solution consisting of silicon carbide, aluminum oxycarbide and aluminum nitride.

Summary of the Invention

A process for pressureless sintering (i.e., sintering in the absence of applied pressure) SiCAlON ceramics has been invented. In addition, this process allows mixtures of the solid solution with other materials to be formed. Specifically, mixtures of the solid solution with SiC and AlN allow improved thermal conductivity as compared to the complete solid solutions, while retaining the desirable aspects of pressureless sintering and engineering of properties.

A method is disclosed for densifying solid solutions of at least aluminum oxycarbide and silicon carbide and/or aluminum nitride (i.e., SiCAlON ceramics).

Materials can be made which consist of an intimate mixture of SiCAlON solid solution with a distinct second phase of either SiC or AlN.

A technique for pressureless sintering of oxides, carbides and nitrides of silicon and aluminum in the presence of aluminum and carbon or aluminum carbide or aluminum oxycarbide to form a substantially dense polycrystalline body of virtually any shape has been discovered.

These ceramic bodies can comprise about 1 to 99% by volume of a solid solution consisting of aluminum oxycarbide and silicon carbide and/or aluminum nitride and at least one refractory phase of SiC and/or AlN.

Description of the Drawings

FIG. 1 is an x-ray diffraction pattern of a pressureless sintered SiCAlON ceramic described in Example 2.

FIG. 2 is an optical micrograph of the SiCAlON ceramic in FIG. 1, taken at 1500 magnifications, showing the existence of two distinct phases. The solid solution is therefore inhomogeneous.

FIG. 3 is an x-ray diffraction pattern illustrating peaks due to the solid solution and SiC.

FIG. 4 is a graphical representation of the strength data from pressureless sintered bars of SiCAlON (containing a refractory phase of SiC) in comparison to pressureless sintered SiC (without the solid solution).

FIG. 5 is a graphical representation of the fracture toughness data from SiCAlON (containing a refractory phase of SiC) in comparison to SiC without the solid solution.

FIG. 6 is a graphical representation of the sintering behavior of $SiC \cdot Al_2OC$ without containment when sintered at 2000°C in N_2 for 5 minutes.

FIG. 7 is a graphical representation of the sintering behavior of SiC and SiCAlON (containing a

refractory phase of SiC) as a function of the starting SiC particle size.

Description of the Invention

In contrast to previous work which required intimate mixtures of reactants to form a solid solution and hot pressing to densify SiCAlON materials, the present invention relies upon conventional ceramic processing. Dense polycrystalline SiCAlON ceramic bodies (or mixtures of SiCAlON with SiC and/or AlN) can be made according to the instant invention by mixing certain compounds containing the elements Si, C, Al, O, and N in the proper proportions and manner, forming shaped bodies (including complex shapes) by conventional pressing techniques, slip casting, injection molding, and the like, and sintering without applied pressure in a furnace. There are a number of compounds which can be used, some of which are illustrated by the following reactions:

$$x(SiC) + z(4Al + Al_2O_3 + 3C) \rightarrow [xSiC \cdot 3z(Al_2OC)]$$

$$x(SiC) + z(Al_2O_3 + Al_4C_3) \rightarrow [xSiC \cdot 3z(Al_2OC]$$

$$x[a\ SiC.\ bAlN] + z(Al_2O_3 + Al_4C_3) \rightarrow [xaSiC \cdot 3z(Al_2OC) \cdot xbAlN]$$

$$(n-1)SiC + SiO_2 + Al_4C_3 \rightarrow [nSiC \cdot 2Al_2OC]$$

$$Si + SiO_2 + 4Al + 4C \rightarrow 2[SiC \cdot Al_2OC]$$

The bracket [ ] is meant to imply that a solid solution of the indicated chemical composition can be formed. However, a complete solid solution is not necessarily formed in the densified ceramic. Several types of solid

solutions may exist as discrete particles within the ceramic body that might be rich or deficient in certain elements. However, the overall or averaged composition of the resulting body would be essentially that of the bracketed compound.

Cutler and Miller (U.S. Patent 4,141,740) claimed that a complete solid solution exists between Al_2OC, SiC and AlN indicating that the variables a, b, n, x, and z vary over the entire stoichiometry range. Rafaniello and Virkar found that the solid solution between SiC and AlN varied between 5 and 100 weight percent aluminum nitride at 2100°C. Since the formation of the solid solution is diffusion limited, the wide range for the solid solution is dependent on particle size, sintering temperature and time. Since the present invention does not rely on the formation of a complete solid solution, the only limitation on x and z is that there be enough liquid phase to allow sintering. Since minor liquid amounts allow activated sintering to occur, the ratio of x to z can be as great as 99:1. SiC, AlN or other compounds (i.e., $BeSiN_2$, $MgSiN_2$, beta Al_4SiC_4, beta Al_5C_3N, $Si_3Al_4N_4C_3$, and the like) having the wurtzite structure are needed to stabilize Al_2OC so ratios of x to z are preferably not less than 2:98.

The unique technique of the present invention comprises performing the sintering in such a manner as to substantially limit decomposition or volatilization of the powder compact prior to densification. Densification occurs rapidly over a narrow temperature range (between 1800 and 2000°C). It is therefore believed that densification takes place primarily via a liquid phase or transient liquid phase mechanism. A liquid phase is known to be present at temperatures in excess of 1840°C in the Al_2O_3-Al_4C_3 system due to a eutectic reaction between

Al_2O_3 and Al_4O_4C. Microstructural evidence of solution-precipitation confirms that a liquid phase is present during the reaction. Liquid phase sintering therefore competes with decomposition of some of the reaction constituents due to their high vapor pressure.

Decomposition may be limited by a number of different techniques including 1) using a closed crucible containing the green body (i.e., a graphite or boron nitride crucible); 2) by embedment of the green body in a loosely packed mass of ceramic particles of a substantially similar chemical composition; 3) by controlling the heating rate and sintering time to limit decomposition and promote sintering; and 4) by controlling the sintering atmosphere so as to suppress the decomposition and subsequent volatization of reaction components. By suppressing decomposition, sintering to high densities is possible. There is a minimum temperature at which the above reactions take place. At temperature extremes in excess of the minimum temperature required for densification, there is evidence of decomposition of the reaction products. The range of acceptable sintering temperatures is obviously dependent on the volume of the liquid phase, but temperatures between 1750 and 2200°C have been found to be acceptable.

The technique is not limited to speciality chemicals but rather can utilize commercially available raw materials with starting purities preferably greater than 98.5%. Starting particle size determines the extent of the solid solution formed. Substantial densification has been obtained from starting materials with powders in the 1-10 micron particle size range. The finer the starting particle size, the greater the amount of solid solution formed.

In each of the examples cited below, a method for controlling decomposition and volatilization is disclosed. In the absence of controlling the vapor pressure of the reaction, little or no densification takes place.

As cited above, previous work was limited to making powders which were complete solid solutions (U.S. Patent 4,141,740). The present invention in contrast permits mixtures of the solid solution and other high temperature refractory phases which have good physical properties to be made. The pressureless sintering technique herein disclosed can be applied to either homogeneous solid solutions, inhomogeneous solid solutions, or mixtures of SiCAlON and other phases.

EXAMPLE 1

METHOD FOR DENSIFYING A HOMOGENEOUS SOLID SOLUTION

SiC (0.615 grams) made by the carbothermal reduction of SiO_2, 0.255 grams Al_2O_3 (Meller 0.3 micrometers) and 0.360 grams Al_4C_3 made by the carbothermic reduction of Al_2O_3, were mixed in an agate mortar and pestle for 15 minutes. Approximately 3 wt. % polyvinyl pyrrolidone (PVP) was added as a binder during the mixing operation and the powder was uniaxially pressed at 70 MPa to form a 18 mm diameter disk. The binder was pyrolyzed by slowly heating to 900°C under N_2. The compacted powder was then placed in a 20 mm diameter by 20 mm deep cavity within a dense graphite (Poco graphite) crucible 9 cm in diameter and 10 cm high. The crucible was closed using a graphite foil seal which mated the crucible to a threaded graphite lid. The crucible was then placed in a graphite resistance heated furnace and heated at a rate of approximately 75°C/minute to 2015°C under flowing N_2 and held for 15 minutes. The disk sintered (16% linear shrinkage

in diameter) to closed porosity and a density of 3.1 g/cc (greater than 99% of theoretical density). The microstructure indicated the presence of a single phase when viewed optically at 1500X magnification. X-ray diffraction also indicated that a homogeneous solid solution had formed (see Table 1) and confirmed that the samples had reacted to form a solid solution consisting of 70 mole percent SiC and 30 mole percent Al_2OC. Since sintering was done in a nitrogen environment there is no doubt that the solid solution contains some AlN.

Table 1

XRD PEAK POSITIONS FOR Cu Kα RADIATION

COMPOUND	2θ AT PLANE							
	(100)	(002)	(101)	(102)	(110)	(103)	(200)	(112)
SiC (2H)	33.5	35.6	38.1	49.8	60.0	65.2	70.8	72.0
AlN (4H)	33.1	36.0	37.9	49.8	59.3	66.0	69.7	71.4
Al_2OC (4H)	32.5	35.3	37.1	48.6	58.4	64.2	67.9	70.8
SiC-Al_2OC*	33.0	35.3	37.6	49.2	59.2	65.2	69.6	71.0

*Experimentally measured values for solid solution composed of 70 mole percent SiC and 30 mole percent Al_2OC.

EXAMPLE 2

METHOD FOR DENSIFYING AN INHOMOGENEOUS SOLID SOLUTION

SiC (150 grams of Starck BD-10 beta SiC, 17 m^2/g containing B and C additions), Al_2O_3 (58.19 grams of Biakowski CR-30), and Al_4C_3 (87.81 grams, Cerac) were milled for 10 hours in a polyethylene ball mill with 425 ml of 2-propanol and 1 kg. of high purity alumina milling media to make a uniform mixture of the powders. After air drying the 5 gram disks of the powders was formed by uniaxial pressing at 34.5 MPa, followed by isostatic

pressing at 207 MPa. The pressed disk was loaded into the graphite cylinder described in example 1 and heated in N_2 at a rate of approximately 60°C per minute to 2000°C and held there for 1 hour. Upon cooling, it was determined that the linear shrinkage was 13.6% and the density was 2.93 g/cc or 95% of theoretical. X-ray diffraction showed that the SiC·30 mole % Al_2OC material was a complete solid solution (FIG. 1). Optical microscopy showed two distinct phases (FIG. 2), which were apparently Si and Al rich SiCAlON solid solutions.

EXAMPLES 3-7

FORMATION OF A MIXTURE OF SiCAlON AND SiC AND METHOD FOR DENSIFICATION

Commercial grades of SiC (Ibiden beta SiC, 17 m^2/g and contains no boron), Al_2O_3 (Biakowski CR-30), and Al_4C_3 (Cerac), with weights as given in Table 2, were vibratory milled for 15 hours in 1050 cc of cyclohexane and 6 kg Al_2O_3. The powders were air dried and screened through a 40 mesh screen before uniaxial pressing at 35 MPa, followed by isostatic pressing at 207 MPa. The parts were contained in a graphite crucible as described in Example 1 and sintered at the conditions listed in Table 3. The powders sintered to closed porosity with shrinkages and densities as indicated in Table 3. X-ray diffraction (FIG. 3) showed that invariably the sintered samples consisted of SiC and the solid solution (SiCAlON). Optical microscopy revealed three phases, indicating that the solid solution was hot homogeneous. Bar samples were tested in four point bending (FIG. 4) and the strengths were comparable with SiC. Fracture toughness of the new materials as determined by the indentation method was superior to SiC (FIG. 5). Similar results were obtained with a a wide variety of SiC materials including Starck

BD-10 (beta SiC with B and C additions), Starck B-10 (beta SiC without B and C additions), Starck AD-10 (alpha SiC with B and C additions), and Starck A-10 (alpha SiC without B and C additions).

Table 2

Composition of Examples 3-7

Example	Composition (grams)			% SiC in SiC.Al_2OC (mole percent)
	SiC	Al_2O_3	Al_4C_3	
3	280.0	26.4	37.3	90.0
4	240.0	51.0	72.0	80.0
5	150.0	58.2	87.8	70.0
6	120.0	68.0	96.0	60.0
7	80.0	68.0	96.0	50.0

Table 3

Sintering Conditions and Densification of Examples 3-7

Example	Sintering Conditions		Shrinkage (%)	Density (g/cc)
	Temp(°C)	Time at Temp(min)		
3	1925	60	14.8	3.12
4	2050	5	14.2	3.15
5	2050	5	14.2	3.15
6	2050	5	16.3	3.14
7	1925	60	13.0	3.07

EXAMPLE 8

METHOD FOR SINTERING SiC·AlN TO FORM SiCAlON

SiC (made by carbothermal reduction of silica, 3.0 grams), AlN·15SiC (made by Cutler process (U.S. Pat. 4,141,740), 3.0 grams), Al_2O_3 (Meller, 0.8293 grams), C (carbon black, 0.2928 grams), and Al (-325 mesh, 0.8778 grams) were mixed in a mortar and pestal for 30 minutes and processed and sintered as in Example 1. The sample sintered to a density near 80% of theoretical.

EXAMPLE 9

METHOD FOR PRESSURELESS SINTERING SiCAlON VIA EMBEDMENT

SiC (Stark AD-10, 90 grams), Al_2O_3 (Reynolds HP-DBM, 51 grams), Al (Cerac, 54 grams), and C (Cabot Mogul L, 18 grams) were ball milled with 1500 grams of high purity alumina media in a plastic mill with 500 ml isopropanol for 12 hours. The powder was pressed into a pellet as in Example 2 and subsequently embedded in its own powder. The embedded sample was heated to 2000°C in 10 minutes and held for 5 minutes. The embedded disk sintered to greater than 95% of theoretical density and had an x-ray diffraction pattern of a mixture of SiCAlON and SiC.

EXAMPLE 10

METHOD FOR PRESSURELESS SINTERING WITHOUT CONTAINMENT

The pressed pellets prepared as in Example 2 were sintered uncontained in N_2 by heating from 1000°C in less than 5 minutes (FIG. 6). The SiC· 30 mole % Al_2OC disks sintered to closed porosity, being greater than 95% of theoretical density. The densification occurs quicker than decomposition and containment is not necessary. Since CO is the major product of the decomposition process, control of CO partial pressure will allow the pressureless sintering of SiCAlON ceramics at low heating rates without containment.

EXAMPLE 11

SINTERING 1-5 MICRON SiC USING SiCAlON

SiC (Carborundum 1500 grit alpha SiC without B or C additions, 152.04 grams), Al_2O_3 (Reynold's HP-DBM, 58.98 grams), and Al_4C_3 (Cerac, 89.00 grams) were mixed for 2 hours in hexane. The powder was compacted and

sintered as described in Example 2. Considerable shrinkage and densification occurred (FIG. 7) whereas little or no densification occurred when the powder was sintered in the absence of SiCAlON. Sintering of larger particle size powders is possible due to the presence of the liquid phase.

EXAMPLE 12

SINTERING SiCAlON USING SiO_2 AS THE OXYGEN SOURCE

SiO_2 (M5 Cab-O-Sil, 30 grams), Al (Alcoa 123, 54 grams), Si (Atlantic Equipment, 13.5 grams), and C (Gulf Acetylene Black, 24 grams) were ball milled in 600 ml 2-propanol for 10 hours with 1 kg high purity alumina media. The parts compacted as in Example 2 and sintered at 1925°C in N_2. The disk sintered (13.3% linear shrinkage) and X-ray diffraction showed SiCAlON and SiC phases.

The present invention is unique in the following respects:

1. Starting materials may be conventional ceramic powders in terms of composition (e.g., SiC, Al_2O_3, and the like), which are of a conventional particle size (i.e., less than 10 microns in diameter). The starting particle sizes are preferably 1-5 microns if inhomogeneous solid solutions or mixtures of the solid solution and a refractory phase are desired, or preferably less than 0.5 microns if a complete solid solution is desired.

2. Complex shapes may be formed in the green state (using conventional binders) and sintered without the application of external pressure to form a dense, strong ceramic body having properties equivalent to those of

SiCAlON ceramics heretofore only attainable using applied pressure while hot pressing.

3. By selecting the appropriate particle size, the compositions of the ceramic body can be controlled while still allowing densification to occur. The processing technique allows for the densification of complete solid solutions or mixtures of the solid solution with another refractory phase. The solid solution can therefore be used as a sintering aid to promote the densification of ceramics which are otherwise difficult to sinter.

Numerous variations and modifications can be made without departing from the invention. For example, AlN could be the primary secondary phase instead of SiC. Accordingly, it should be clearly understood that the form of the invention described above is illustrative only and is not intended to limit its scope.

Claims

1. A ceramic comprising: 1 to 99 volume % of a solid solution (SiCAlON) comprised of at least aluminum oxycarbide and silicon carbide and/or aluminum nitride, with at least one secondary phase comprised of SiC, AlN, Al_2O_3, or AlON.

2. The ceramic described in Claim 1 where the secondary phase is either alpha or beta phase SiC.

3. The ceramic described in Claim 1 where the secondary phase is AlN.

4. The ceramic described in Claim 1 where the secondary phase is Al_2O_3.

5. The ceramic described in Claim 1 where the secondary phase is AlON.

6. The ceramic described in Claim 1 where the secondary phases are any combination of SiC, AlN, Al_2O_3, and AlON.

7. The ceramic described in Claim 1 where the secondary phase is SiC and the starting SiC particle size is greater than 1 micron prior to pressureless sintering.

8. A process for reactive sintering SiCAlON or SiCAlON - refractory phase ceramics in the absence of applied pressure comprising:
mixing elements or compounds containing the elements Al, O, C, Si, and optionally N;
forming a shape of said reaction mixture using ceramic processing techniques; and

sintering the reactant mixture while limiting the volatilization of species from the reaction mixture.

9. The process defined in Claim 8 where a highly impervious container is used to control the vapor pressure.

10. The process defined in Claim 8 where embedment is used to control the vapor pressure.

11. The process defined in Claim 8 where heating rates greater than 200°C/minute above 1000°C are used to limit volatilization.

12. The process defined in Claim 8 where atmospheric control is used to establish an equilibrium partial pressure of carbon monoxide.

13. The process defined in Claim 8 where the pressureless sintered ceramic is a homogeneous solid solution.

14. The process defined in Claim 8 where the pressureless sintered ceramic is an inhomogeneous solid solution.

15. The process defined in Claim 8 where the pressureless sintered ceramic is a mixture of the solid solution, either homogeneous or inhomogeneous, and a refractory phase.

16. The process defined in Claim 8 where the starting materials are SiC, Al_2O_3, and Al_4C_3.

17. The process defined in Claim 8 where the starting materials are SiC, Al_2O_3, Al, and C.

18. The process defined in Claim 8 where the starting materials are AlN·SiC, Al_2O_3, and Al_4C_3 (or Al and C).

19. The process defined in Claim 8 where the starting materials are AlN, Al_2O_3, and Al_4C_3 (or Al and C).

20. The process defined in Claim 8 where the starting materials are SiO_2, Si, and Al_4C_3 (or Al and C).

21. The process defined in Claim 8 where the starting materials are SiO_2, SiC, and Al_4C_3 (or Al and C).

22. The process defined in Claim 8 where the SiC contains no B and/or C additions.

23. The process defined in Claim 8 where the SiC is greater than 1 micrometer in particle size prior to pressureless sintering.

24. The process defined in Claim 8 where the SiC (or SiC·AlN) powders have been prepared by carbothermal reduction, resulting in starting powders with surface area greater than 20 m^2/g, so that the pressureless sintered material is single phase when viewed optically at 1500 magnifications.

AMENDED CLAIMS

[received by the International Bureau on 16 February 1987 (16.02.87);
original claims.1-24 replaced by amended claims 1-24 (4 pages)]

1. A sintered ceramic body consisting essentially of:
1 to 99 percent by volume of a solid solution consisting of at least aluminum oxycarbide and at least one member selected from the class consisting of silicon carbide and aluminum intride; and
at least one secondary phase selected from the group consisting of SiC, AlN, Al_2O_3 or AlON constituting the remainder of the body.

2. The sintered ceramic body described in Claim 1 where the secondary phase is either alpha or beta phase SiC.

3. The sintered ceramic body described in Claim 1 where the secondary phase is AlN.

4. The sintered ceramic body described in Claim 1 where the secondary phase is Al_2O_3.

5. The sintered ceramic body described in Claim 1 where the secondary phase is AlON.

6. The sintered ceramic body described in Claim 1 where the secondary phases are any combination of SiC, AlN, Al_2O_3, and AlON.

7. The sintered ceramic body described in Claim 1 where the secondary phase is SiC and the starting SiC particle size is greater than 1 micron prior to pressureless sintering.

8. A process for forming dense, sintered ceramic bodies of solid solutions (a) of Si, O, C and Al and (b) solid solutions thereof with an additional refractory phase by reactive sintering in the absence of applied pressure consisting essentially of:
mixing starting particles containing the elements Al, O, C and Si, to form a reactive mixture;
forming a shaped body of said reaction mixture using ceramic processing body shaping techniques; and
reactively sintering the reactant mixture while limiting the volatilization of volatile reaction products from the reaction mixture.

9. The process defined in Claim 8 wherein a highly impervious container is used to control the vapor pressure.

10. The process defined in Claim 8 wherein embedment is used to control the vapor pressure.

11. The process defined in Claim 8 wherein heating rates greater than 200°C/minute above 1000°C are used to limit volatilization.

12. The process defined in Claim 8 wherein atmospheric control is used to establish an equilibrium partial pressure of carbon monoxide.

13. The process defined in Claim 8 wherein the pressureless sintered ceramic is a homogeneous solid solution.

14. The process defined in Claim 8 wherein the pressureless sintered ceramic is an inhomogeneous solid solution.

15. The process defined in Claim 8 wherein the pressureless sintered ceramic is a mixture of the solid solution, either homogeneous or inhomogeneous, and a refractory phase.

16. The process defined in Claim 8 wherein the starting particles are SiC, Al_2O_3, and Al_4C_3.

17. The process defined in Claim 8 wherein the starting particles are SiC, Al_2O_3, Al, and C.

18. The process defined in Claim 8 wherein the starting particles are AlN·SiC, Al_2O_3, and Al_4C_3 (or Al and C).

19. The process defined in Claim 8 wherein the starting particles are AlN, Al_2O_3, and Al_4C_3 (or Al and C).

20. The process defined in Claim 8 wherein the starting particles are SiO_2, Si, and Al_4C_3 (or Al and C).

21. The process defined in Claim 8 wherein the starting particles are SiO_2, SiC, and Al_4C_3 (or Al and C).

22. The process defined in Claim 8 wherein the SiC contains no B and/or C additions.

23. The process defined in Claim 8 wherein the SiC is greater than 1 micrometer in particle size prior to pressureless sintering.

24. The process defined in Claim 8 where the SiC (or SiC·AlN) powders have been prepared by carbothermal reduction, resulting in starting powders with surface area greater than 20 m^2/g, so that the pressureless sintered material is single phase when viewed optically at 1500 magnifications.

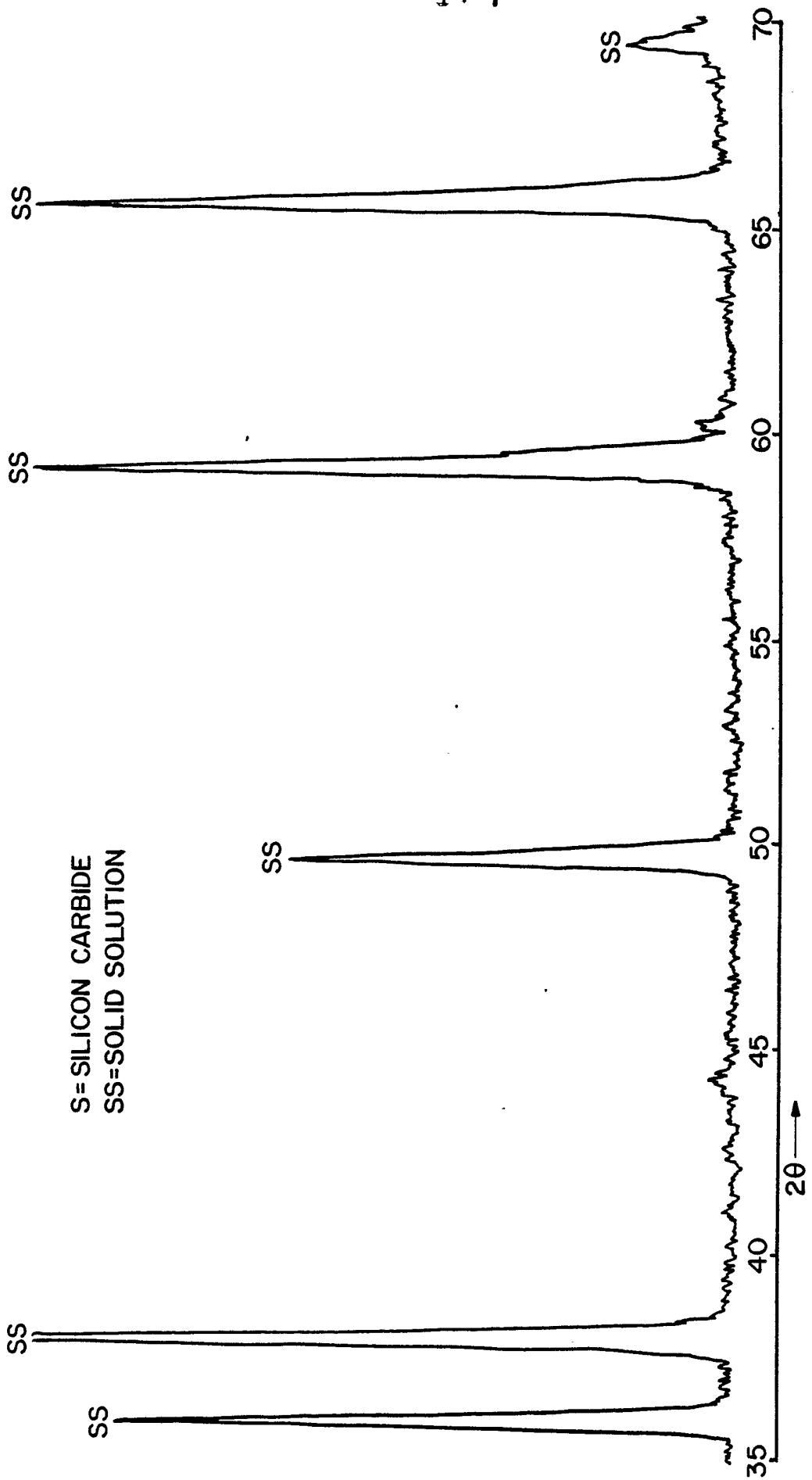

S=SILICON CARBIDE
SS=SOLID SOLUTION
SS
SS
SS
SS
SS
SS
35
40
45
50
55
60
65
70
2θ

FIG.I

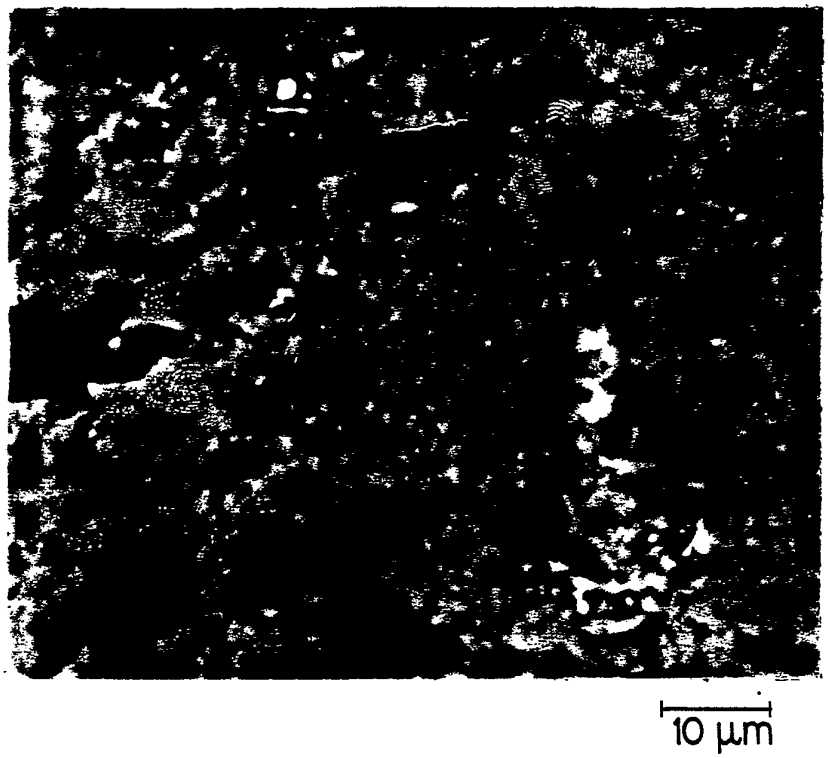


FIG. 2

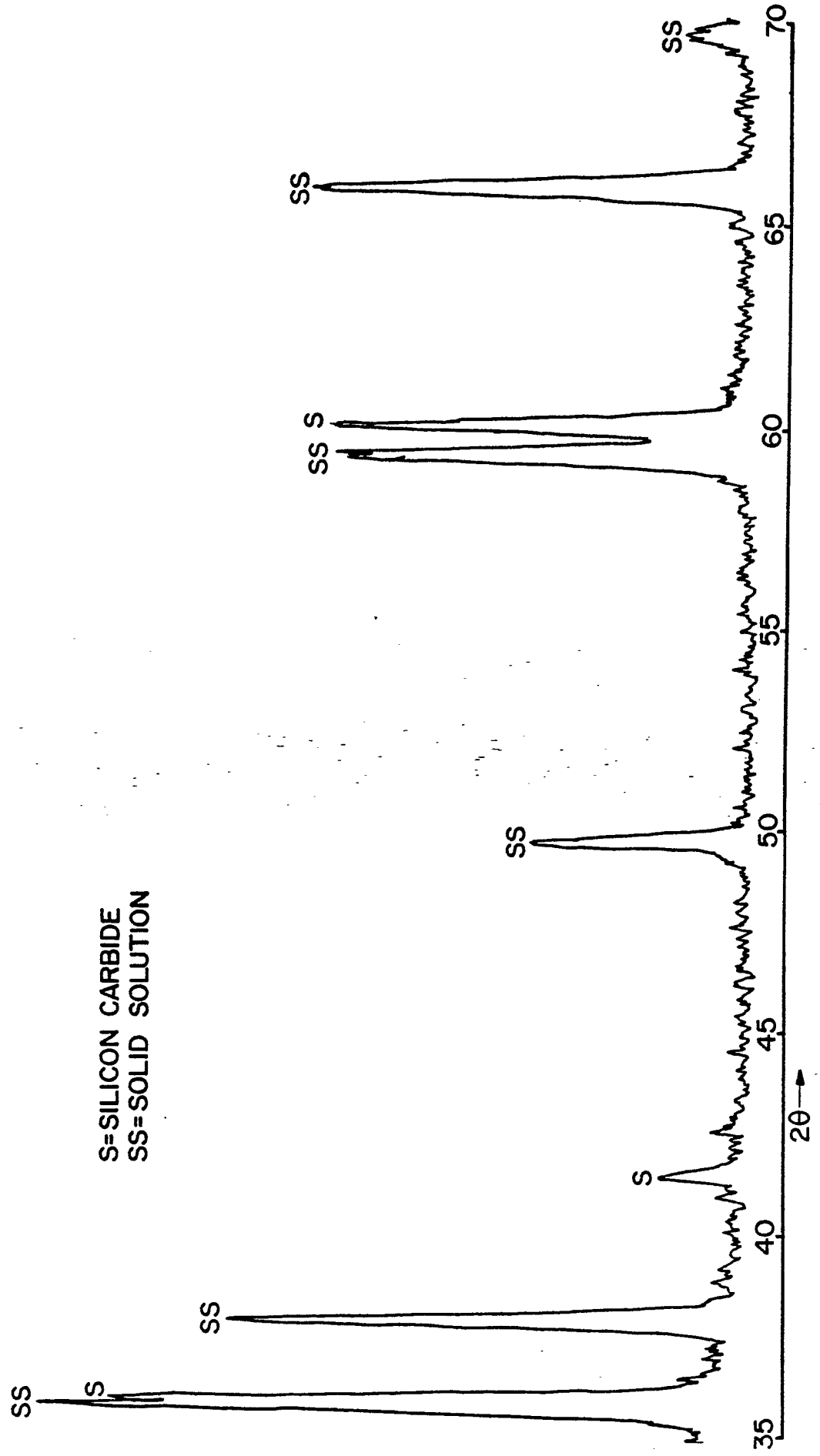

S=SILICON CARBIDE
SS=SOLID SOLUTION
SS
S
SS
SS
S
SS
SS
S
SS
35
40
45
50
55
60
65
70
2θ

FIG.3

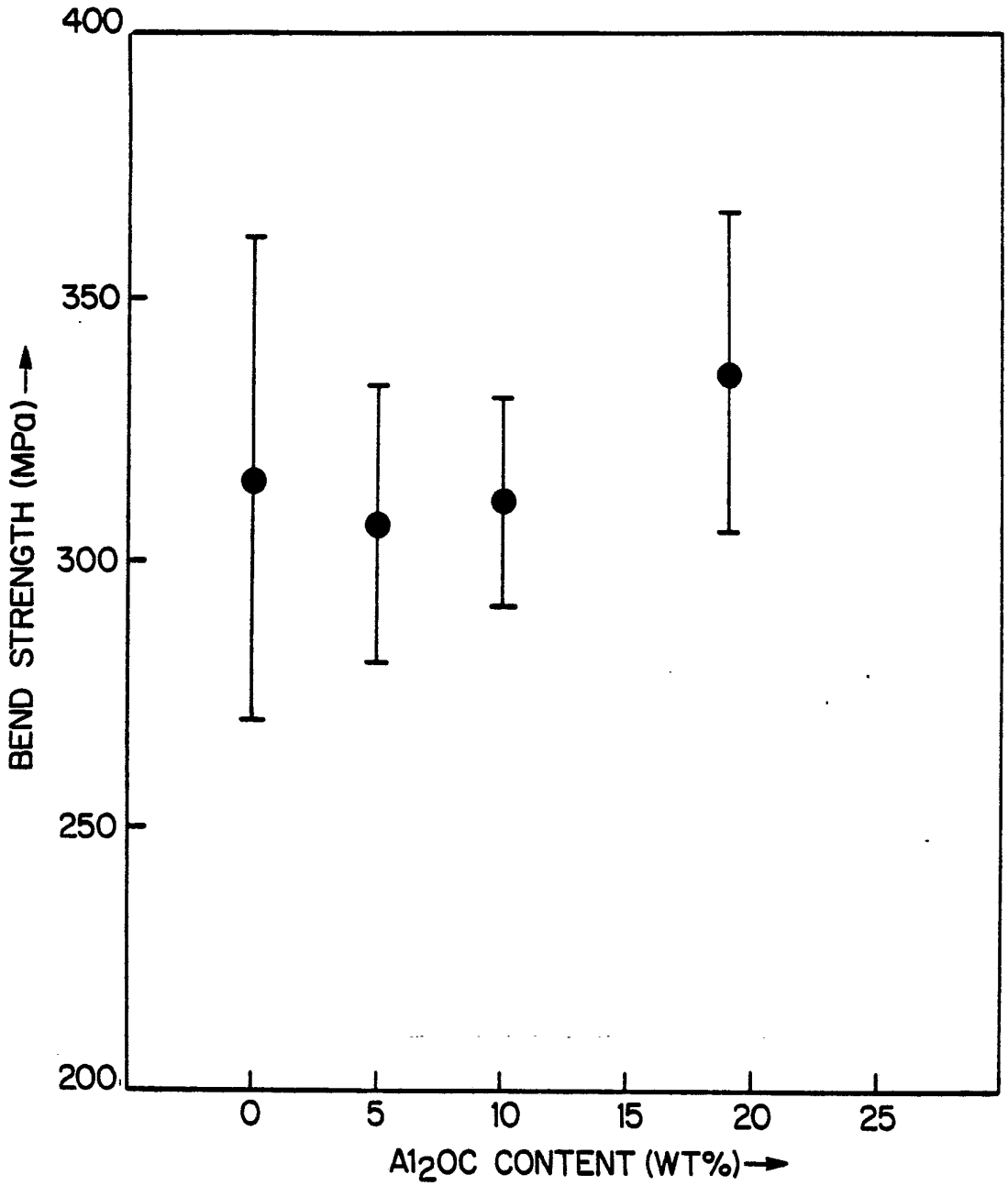

400
350
300
250
200
BEND STRENGTH (MPa)
0
5
10
15
20
25
Al2OC CONTENT (WT%)

FIG.4

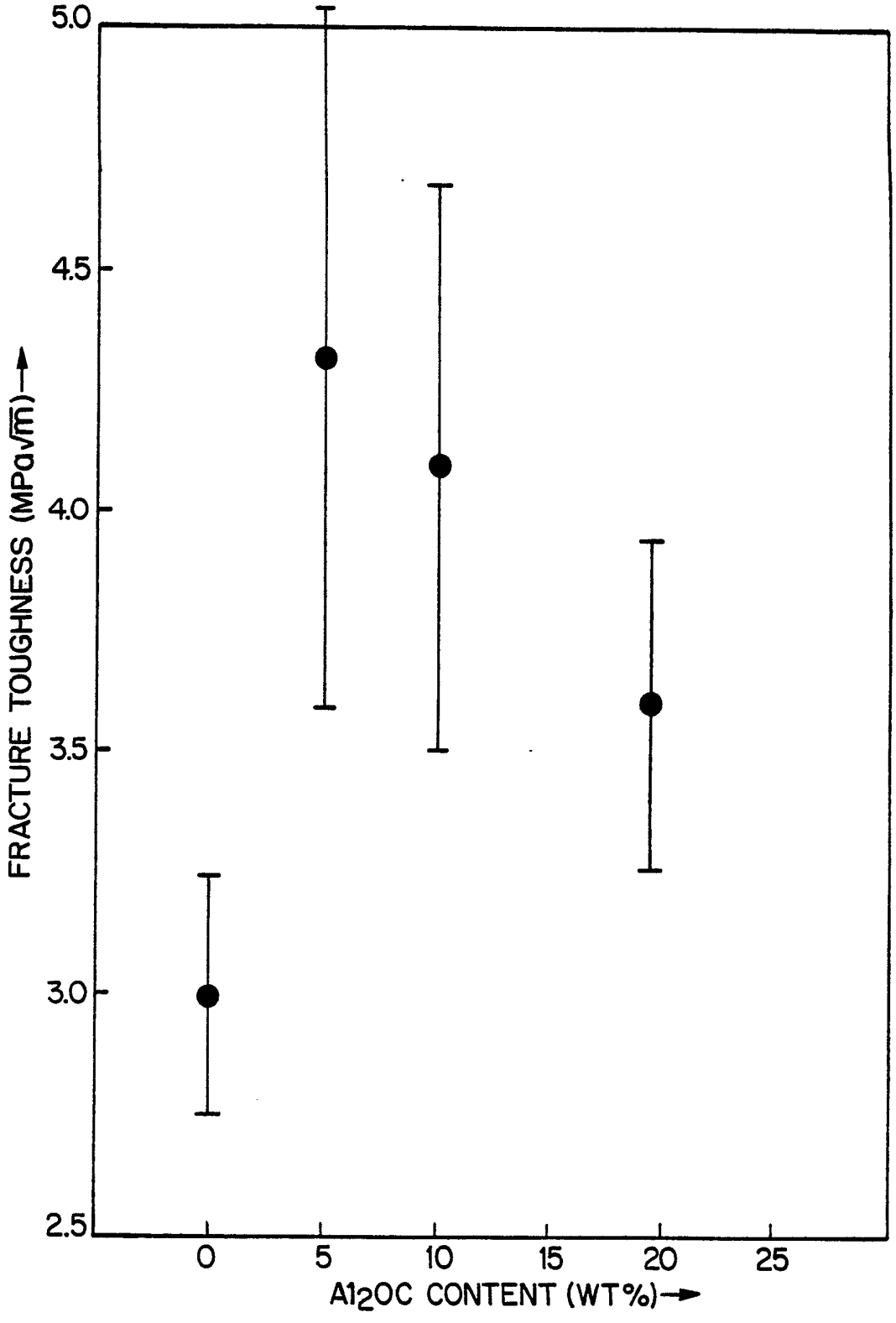

5.0
4.5
4.0
3.5
3.0
2.5
FRACTURE TOUGHNESS (MPa√m)→
0
5
10
15
20
25
Al2OC CONTENT (WT%)→

FIG.5

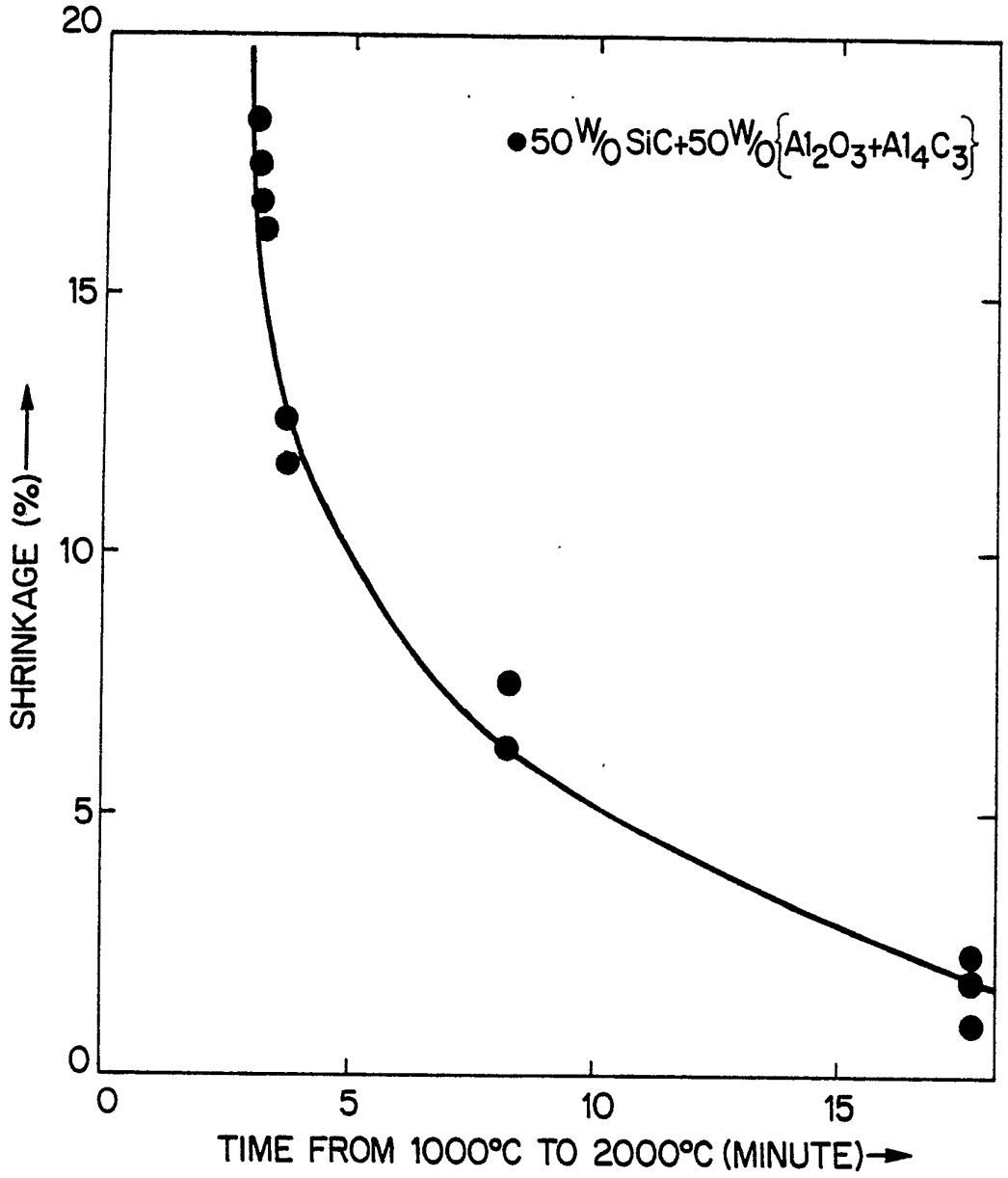

20
15
10
5
0
0
5
10
15
SHRINKAGE (%)
TIME FROM 1000°C TO 2000°C (MINUTE)
●50W/0 SiC+50W/0{Al2O3+Al4C3}

FIG.6

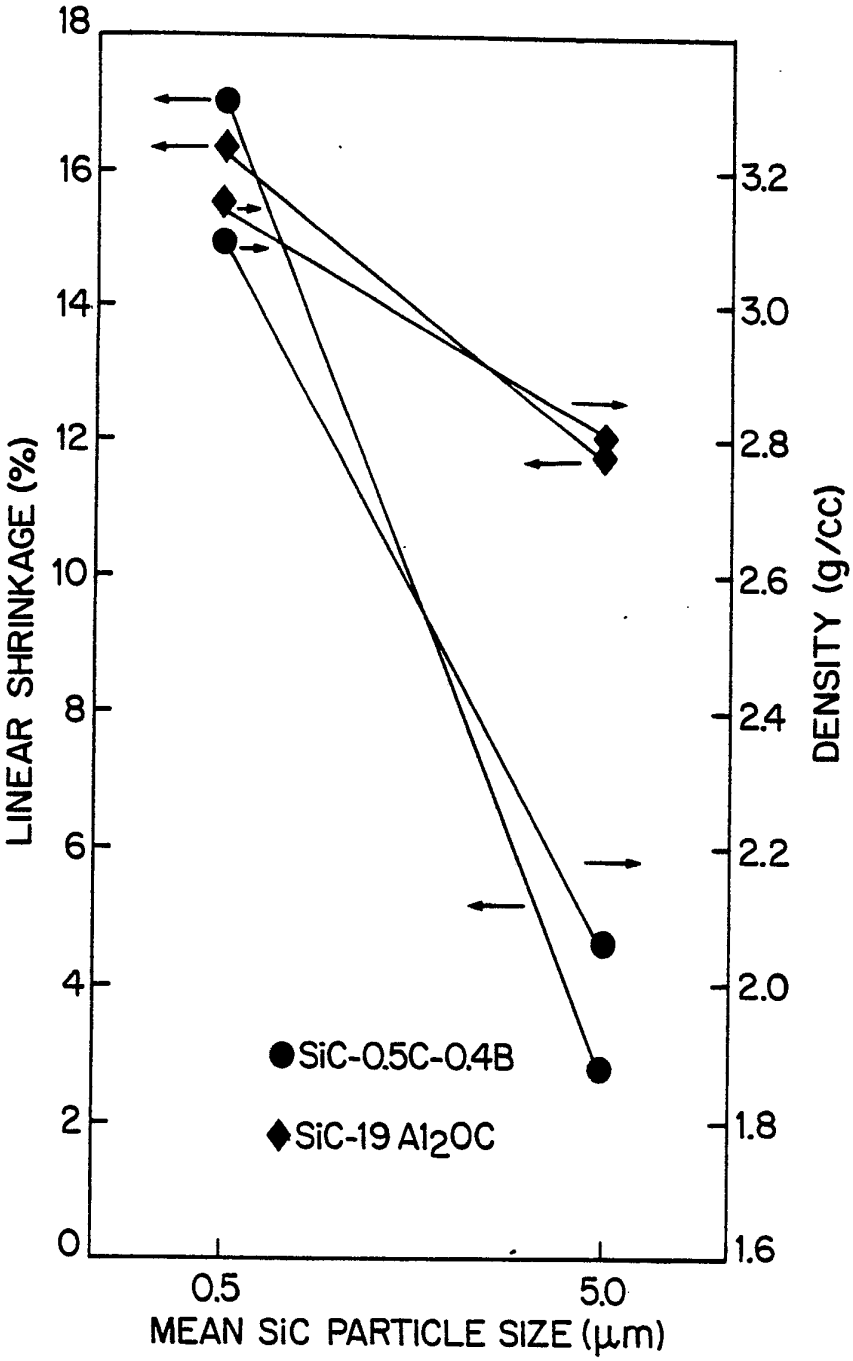

18
16
14
12
10
8
6
4
2
0
LINEAR SHRINKAGE (%)
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
DENSITY (g/cc)
SiC-0.5C-0.4B
SiC-19 Al2OC
0.5
5.0
MEAN SiC PARTICLE SIZE (μm)

FIG. 7

INTERNATIONAL SEARCH REPORT

International Application No PCT/US86/01957

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL.[4] C04B 35/56, 58

U.S. CL. 501/89, 98

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S.	501/89, 91, 92, 98

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
Y X	US, A, 4,141,740 (CUTLER ET AL) 27 February 1985, See column 5, line 63 - column 6, line 10 and claims.	1-7 8-24
X	US, A, 4,053,303, (COCHRAN ET AL), 11 October 1977, See entire document.	8-24
Y, P	US, A, 4,569,922 (SUZUKI) 11 February 1986, See entire document.	1-24
A	US, A, 4,141,740 (CUTLER ET AL) 27 February 1979.	1-24
A	US, A, 3,974,106 (RICHERSON) 10 August 1976.	1-24
A	US, A, 3,960,581 (CULTER) 01 June 1976.	1-24
A	US, A, 3,895,219 (RICHERSON ET AL) 15 July 1975.	1-24
A	US, A, 3,890,250 (RICHERSON) 17 June 1975.	1-24

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
07 December 1986	15 DEC 1986
International Searching Authority [1]	**Signature of Authorized Officer [20]**
ISA/US	Karl Group

Form PCT/ISA/210 (second sheet) (May 1986)