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Fabrication, thermal treatment and microstructure development in SiC–AlN–Al_2OC ceramics

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Samples containing equimolar amounts of SiC, AlN and Al_2OC were fabricated by hot pressing a mixture of SiC, AlN, Al_2O_3 and Al_4C_3. The predominant constituent in the hot pressed material was of 2H crystal type. The samples were subsequently annealed at a temperature up to 2050° C for up to 153 h in an atmosphere of nitrogen. Samples made with Ibigawa β-SiC exhibited formation of needle-type precipitates. Carbon deficient specimens contained substantial amounts of Al_3O_3N. Principal characterization techniques employed consisted of optical microscopy, electron microscopy, X-ray diffraction and chemical analysis.

1. Introduction

Alloying of ceramics for either ease of processing or improvements in properties or both has often been done in many cases. Sialon, which is a solid solution between Si_3N_4 and Al_3O_3N, is much easier to densify in comparison with Si_3N_4 while still retaining excellent properties to elevated temperatures. Superior mechanical properties in zirconia ceramics are possible through additions of other oxides in controlled amounts. In the case of the 2H form of SiC, which is isostructural with several other ceramics such as AlN, Al_2OC, $BeSiN_2$, etc. a potential for alloying and probably ease of fabrication and/or property engineering exists. Work of Cutler *et al.* [1], in fact shows that a solid solution between SiC, AlN and Al_2OC can be formed. The pseudobinary SiC–AlN has been investigated by Rafaniello *et al.* [2, 3] and by Ruh and Zangvil [4]. In both of the studies, samples were fabricated by hot pressing. Rafaniello *et al.*[2] demonstrated that SiC and AlN form a solid solution at elevated temperatures (> 2000° C) which decomposes into two solid solutions, one SiC-rich and the other AlN-rich at lower temperatures. Further, physical and mechanical poroperties were shown to depend upon the composition [3]. Recent work [5] in the SiC–Al_2OC system has shown that dense specimens can be fabricated by pressureless sintering and that densification occurs due to the presence of a transient liquid phase in the Al_4C_3–Al_2O_3 pseudobinary system. Thus, property engineering as well as relative ease of fabrication has been demonstrated in the SiC–AlN–Al_2OC system.

The objective of the present work was to fabricate dense specimens in the SiC–AlN–Al_2OC system by hot pressing and examine microstructural development that occurs when the samples are subjected to thermal treatment at elevated temperatures. Samples containing equimolar amounts of SiC, AlN and Al_2OC were fabricated by hot pressing a mixture of SiC, AlN, Al_2O_3 and Al_4C_3 in graphite dies in an atrmosphere of nitrogen. Samples were subsequently heat treated at temperatures up to 2050° C for times up to 153 h in sealed graphite crucibles in nitrogen. X-ray diffraction, optical microscopy, and electron microscopy were the principal characterization tools employed.

2. Experimental procedure

2.1. Choice of raw materials

SiC, AlN, Al_2O_3 and Al_4C_3 powders from commercial sources were used for the present study. Three different types of SiC powders were used; two of them were β-SiC while the third one was α-SiC. None of the powders were doped with boron. Pertinent information about the powders is given in Table I.

2.2. Power preparation and sample fabrication

SiC, AlN, Al_2O_3 and Al_4C_3 were weighed in appropriate amounts so as to finally yield a ceramic with equimolar amounts of SiC, AlN, and Al_2OC. Since Al_4C_3 oxidizes upon prolonged exposure to air, weighing and premixing was done in an atomosphere of argon. Subsequently, the powder mixtures were thoroughly milled in cyclohexane for periods of times up to 24 h using alumina milling media. Cyclohexane was subsequently evaporated by applying suction using a mechanical vacuum pump. The powder was subsequently sieved and loaded in graphite dies in air for subsequent hot pressing in nitrogen. The powder

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TABLE I

Material	Surface area ($m^2 g^{-1}$)	Impurities
Ibigawa β-SiC	19.3	SiO_2–0.36%, free C–0.51% Al–0.03%, Fe–0.03%
Starck β-SiC	13–17	O–0.40%, free C–1.0% Al–0.1%, Fe–0.02% Ca–0.04%
Starck α-SiC	13–17	O–0.4%, free C–0.2% Al–0.02%, Fe–0.01%, Ca–0.005%
Starck AlN	2–4	O–1 to 1.5%, C–0.05% Fe–0.1%
Cerac Al_4C_3	– 325 mesh	B–0.001% Fe–0.1% Si–0.5%, Cr–0.01%

was exposed to air for a very short time. Some samples were fabricated with Al_4C_3 that had been exposed to air for prolonged periods of time.

Hot pressing was conducted in atmosphere of nitrogen at a temperature of 2000 ± 15° C for 0.5 h under a pressure of 30 MPa. The hot pressed specimens had a small amount of closed porosity and the density was typically 3.08 ± 0.01 $g\,cm^{-3}$. Theoretical density of the solid solution is estimated to be 3.11 $g\,cm^{-3}$ assuming Vegards' law. Samples were sliced from the hot pressed billets for thermal treatment, X-ray diffraction analysis, microstructural characterization and chemical analysis.

2.3. Thermal treatment

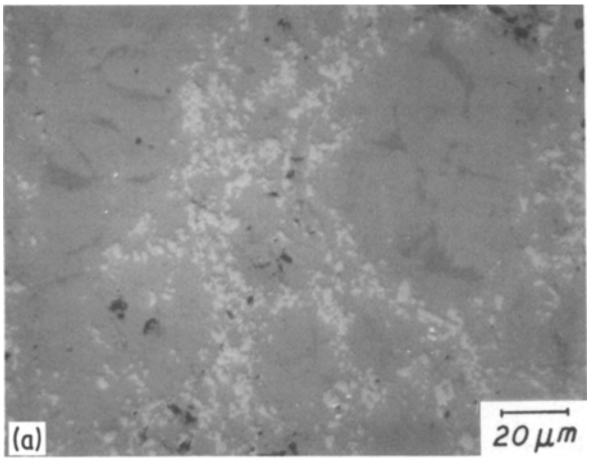
Samples were annealed at a temperature ranging from 1800 to 2050° C for periods of time up to 153 h. In order to minimize the loss of volatiles, principally oxygen, nitrogen and aluminium, samples were placed inside a high density graphite crucible with a screw-on lid. The crucible containing the specimens was heated in a graphite element furnace in an atmosphere of nitrogen. Although the crucible was porous, the partial containment allowed near equilibrium (with regards to volatile species) conditions to be established and thereby reducing the rate of volatilization. After annealing, the surface layers of the samples were ground off and the bulk portions were used in further characterization which included the determination of density, X-ray diffraction analysis, chemical analysis for the determination of oxygen and nitrogen content and microscopic observations.

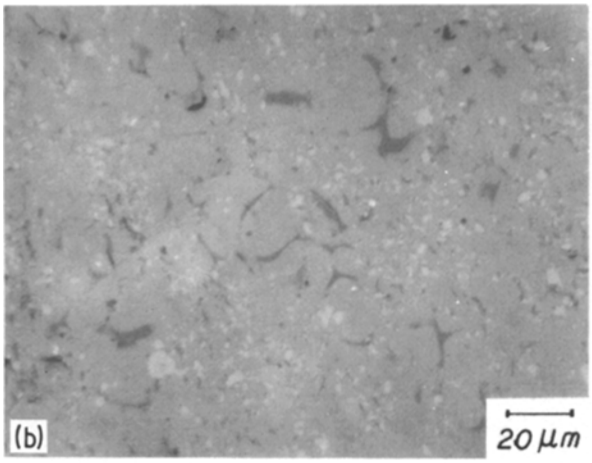
3. Results

3.1. Optical microscopy

Fig. 1a shows an optical micrograph of a hot pressed sample with β-SiC from Ibigawa as the source of SiC. The microstructure exhibits some dark and light regions in a homogeneous grey matrix. The light regions are believed to be the ones rich in SiC while the dark regions are believed to be rich in AlN and/or Al_2OC. (These expectations are based on prior studies on SiC–AlN system [2].) The sample was hot pressed at 1990° C for 0.5 h. Figs 1b and c show optical micrographs of samples with Starck β-SiC and Starck α-SiC as the sources of SiC respectively. Both of these micrographs, although exhibiting similar features in that dark and light regions are distributed in a nearly homogeneous matrix, indicate that these microstructures are more heterogeneous compared to Fig. 1a.

Fig. 2a depicts an optical micrograph of a sample, made with Ibigawa β-SiC, that had been annealed at 2050° C for 50 h in a closed graphite crucible in an atmosphere of nitrogen. The microstructrure is clearly two phase with sharp needles of the light phase distributed in a grey homogeneous matrix. The specimen has also become porous with large voids evident in the micrograph. The needles are believed to be SiC-rich, which are harder leading to relief polishing evident in





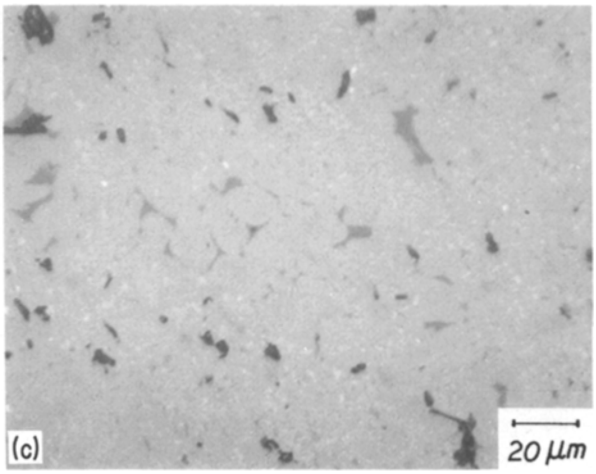
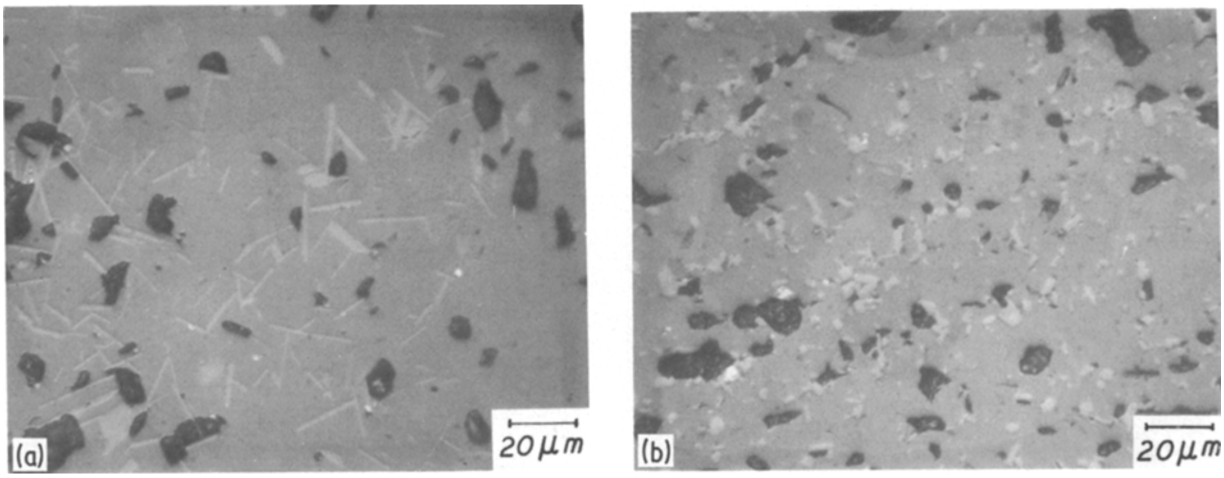


Figure 1 Optical micrographs of as-hot pressed specimens of SiC–AlN–Al_2OC ceramics in equimolar amounts. Magnification: 640 ×. (a) Ibigawa β-SiC, (b) Starck β-SiC, (c) Starck α-SiC.



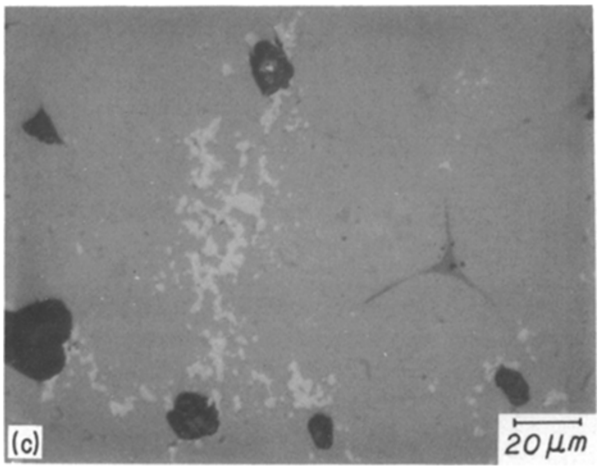


Figure 2 Optical micrographs of SiC–AlN–Al_2OC ceramics subjected to various thermal treatments. Magnification: 640 ×. (a) Ibigawa β-SiC: annealed at 2050° C/50 h, (b) Starck β-SiC: annealed at 1960° C/50 h, (c) Starck α-SiC: annealed at 1960° C/52 h.

the microstructure. The dark phase has all but disappeared in the annealed sample. Fig. 2b shows an optical micrograph of a sample made with Stark β-SiC that was annealed at 1960° C for 50 h. In this microstructure, the light phase is seen to have become coarser, the dark phase has decreased in amount and voids have been formed. Although a few needle-shape particles are seen in the micrograph, the precipitate morphology is predominantly nodular. Microstructure of a sample made with Starck α-SiC after annealing at 1960° C for 52 h is shown in Fig. 2c. This specimen also exhibits coarsening of the light phase which is not in the needle shape.

The dark phase is still present in the sample at the grain boundaries as evidenced in Fig. 2c. Comparison of Figs 1c and 2c indicates a substantial amount of grain growth of the matrix. During the annealing treatment, the grain size has increased from about 20 μm to about 100 μm. The morphology of the dark phase also shows that the dihedral angle is very small, suggesting excellent wetting between the dark phase and the matrix. Some samples were fabricated using Al_4C_3 that had been exposed to the atmosphere for long periods of time. Prolonged exposure to air is known to oxidize Al_4C_3. Samples made with α-SiC and Al_4C_3 exposed to air exhibited quite a different microstructure (Fig. 3a). Light and dark precipitates, nearly equiaxed, were essentially uniform in size and upon annealing at 1875° C/153 h, showed little change in the microstructure other than coarsening of the precipitates (Fig. 3b). Fig. 3c shows a micrograph of a sample made with β-SiC and Al_4C_3 exposed to air for a long time. This sample had a considerably greater amount of Al_3O_3N. Fig. 3d shows a micrograph of the same sample that was annealed at 1875° C/72 h. Other than some coarsening, little microstructural change is seen.

3.2. Xray diffraction

X-ray diffraction patterns were obtained using Cu*K*α radiation. Hot pressed specimens with Ibigawa β-SiC as the source of SiC exhibited an essentially single phase 2H diffraction pattern shown in Fig. 4a with a trace of β-SiC. The lattice parameters of the 2H solid solution are determined to be $a = 0.312/75$ and $c = 0.500/98$ nm. X-ray diffraction pattern of the hot pressed specimen made with Starck β-SiC shows predominantly 2H solid solution along with some β-SiC, 6H and some very low intensity peaks that could not be identified (Fig. 4b). Finally, sample made with Starck α-SiC exhibited 2H along with some 6H and some low intensity peaks not identified as shown in Fig. 4c.

Sample made with Ibigawa β-SiC, upon annealing for 50 h at 2050° C, shows splitting of the 2H peaks (Fig. 4d). The new set of peaks, which occur at slightly higher angles are probably due to the lighter SiC-rich phase. This is consistent with the fact that the 2H form of α-SiC has somewhat smaller lattice parameters in comparison with the solid solution. By contrast, samples made with Starck β-SiC and Starck α-SiC respectively exhibited no noticeable change in the X-ray diffraction patterns except the latter showed some reduction in the amount of 6H.

X-ray diffraction pattern of the sample made with Al_4C_3 exposed to air for a long time showed predominantly 2H pattern along with substantial amounts of Al_3O_3N.

3.3. Electron microscopy

A hot pressed sample made with Ibigawa-β-SiC was examined using a scanning transmission electron

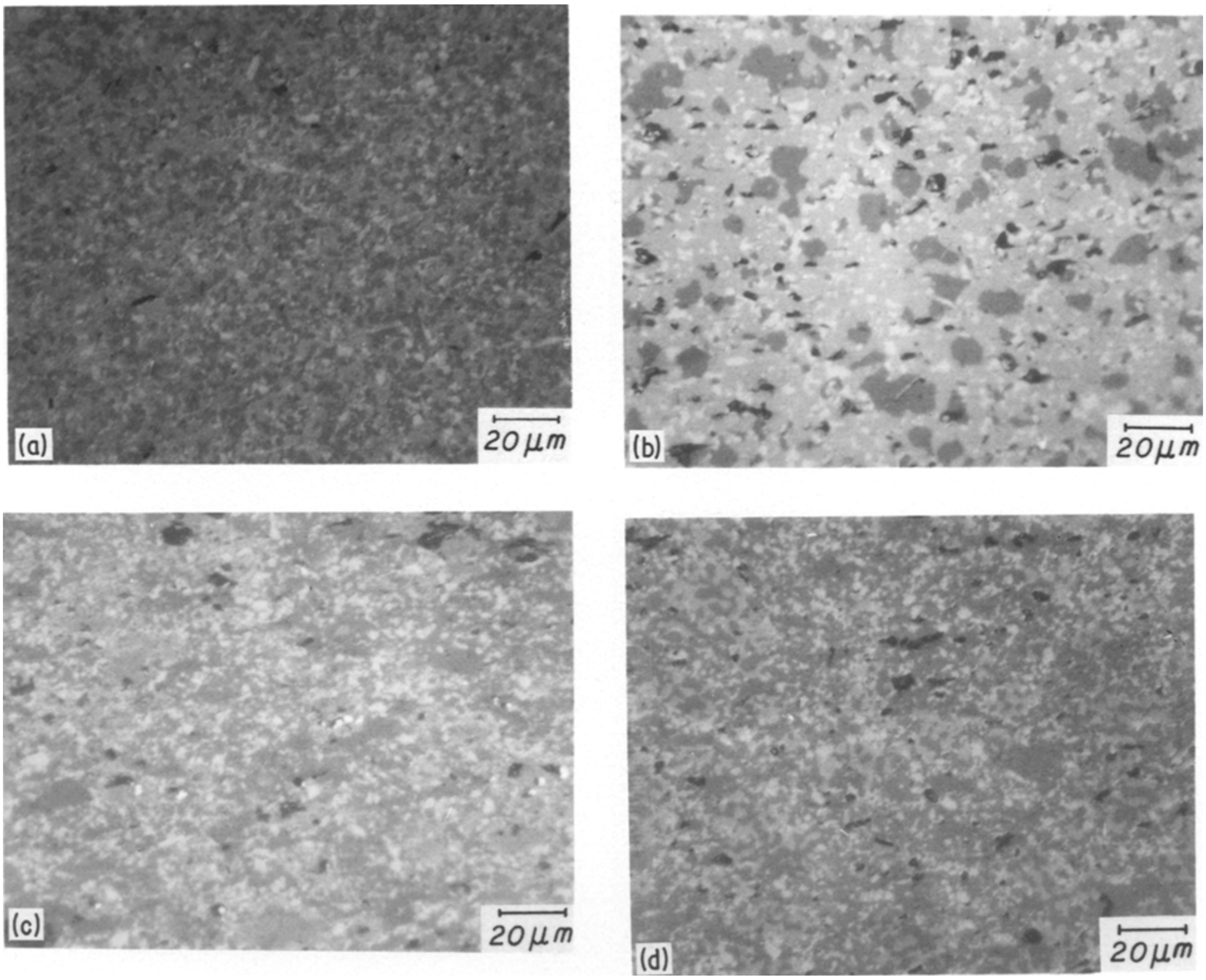


Figure 3 Optical micrographs of specimens made with partially oxidized Al_4C_3. The samples contain varying amounts of Al_3O_3N Magnification: 640 ×. (a) Starck α-SiC + Al_3O_3N: as-hot pressed, (b) Starck α-SiC + Al_3O_3N: annealed at 1875° C for 153 h, (c) Starck β-SiC + Al_3O_3N: as-hot pressed, (d) Starck β-SiC + Al_3O_3N: annealed at 1875° C/72 h.

microscope* (STEM). A TEM micrograph of the sample is shown in Fig. 5. The micrograph shows an equiaxed solid solution (of crystal type 2H) of grain size of the order of 15 μm with submicrometre SiC polytype particles at the grain boundaries.

3.4. Density and chemical analysis

Samples made with either Ibigawa β-SiC, Starck β-SiC or Starck α-SiC all had a density of 3.07 to 3.09 g cm^{-3}. The samples were essentially free of any porosity. Density of the samples made with Al_4C_3 exposed to atmosphere was generally quite high – greater than 3.3 g cm^{-3} and as high as 3.47 g cm^{-3}. This is consistent with the fact that Al_3O_3N, which has a cubic spinel type structure has a higher density (ϱ = 3.9 g cm^{-3}).

Samples made with Ibigawa β-SiC upon annealing at 2050° C for 50 h showed a decrease in density to 2.92 g cm^{-3} (corresponding to 4.9% wt loss) Densities of samples made with Starck β-SiC and Starck α-SiC upon annealing (at 1960° C) were 3.01 g cm^{-3} (2.5% wt loss) and 2.90 g cm^{-3} (5.8% wt loss, respectively). All of these specimens exhibited considerable amounts of porosity (even when very thick (1.2 cm) specimens were used in the annealing experiments) as evidenced in the micrographs. By contrast, the samples containing Al_3O_3N showed essentially identical density even after annealing at 1875° C/73 h (ϱ = 3.48 g cm^{-3}). The microstructure, of the bulk region, exhibited little porosity.

Some of the samples were analysed for the oxygen and the nitrogen contents using a Leco Analyzer before and after annealing. In the hot pressed condition, the sample made with Ibigawa β-SiC had oxygen and nitrogen contents of 10.7 and 8.4 wt %, respectively. These compare reasonably with the calculated values for an equimolar composition of SiC–AlN–Al_2OC of 9.81 wt % for oxygen and 8.58% for nitrogen. A slightly greater amount of oxygen in the actual sample is probably due to SiO_2 layer over SiC, oxygen in AlN that was not accounted for in the calculations and contamination from alumina milling media. Chemical analysis of a sample that was annealed for 72 h at 1990° C indicated oxygen content of 8.7 wt % and nitrogen content of 10.2 wt %. Loss of oxygen is due to volatilization of oxygen along with some aluminium and carbon (as carbon monoxide) while gain in nitrogen is probably due to gain in AlN. Chemical analysis of a sample containing Al_3O_3N indicated oxygen content of 24.8 wt % and nitrogen

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*Model 200 CX, Japan Electron Optics Laboratory, Tokyo, Japan.

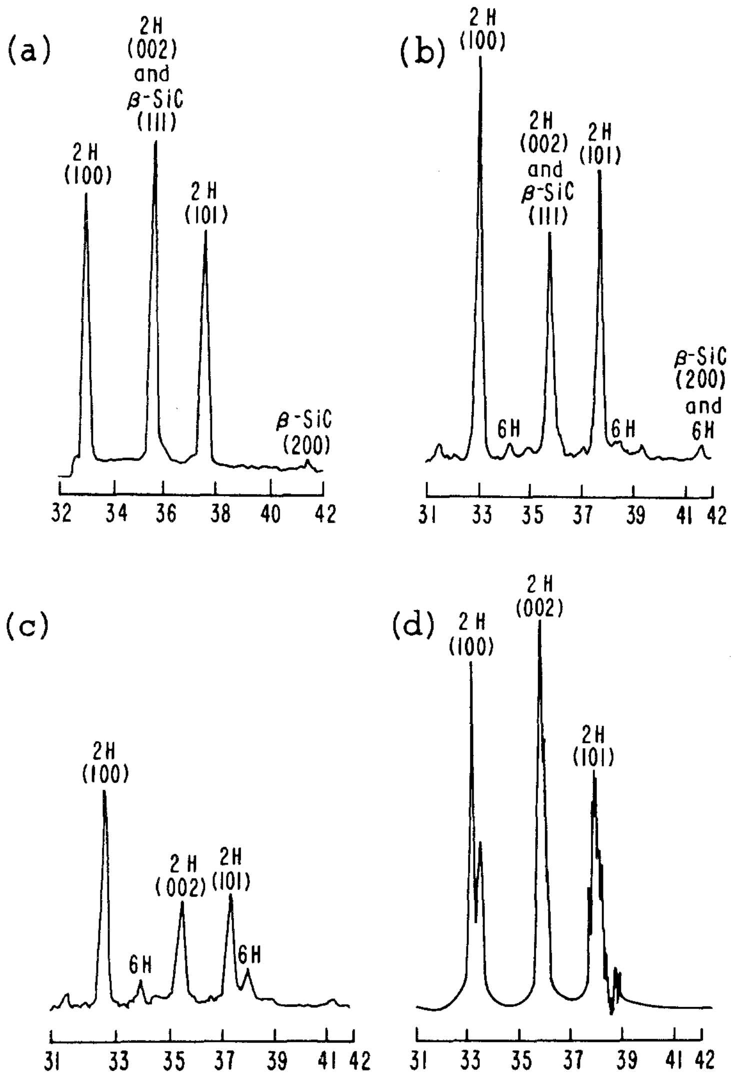

Figure 4 X-ray diffraction patterns of SiC–AlN–Al_2OC ceramics taken with Cu*Kα* radiation. (a) Ibigawa β-SiC: as-hot pressed, (b) Starck β-SiC: as-hot pressed, (c) Starck α-SiC: as-hot pressed, (d) Ibigawa β-SiC: annealed at 2050° C/50 h.

content of 6.7 wt %. If all of the Al_4C_3 had oxidized to Al_2O_3 upon exposure to atmosphere, the sample is expected to have an oxygen content of 26.2 wt % and a nitrogen content of 7.65 wt %. The measured value of the oxygen content of 24.8 wt % suggests that not all of the Al_4C_3 was oxidized although a large amount of it was. X-ray diffraction annalysis of the powder showed that some Al_4C_3 was indeed still present. Experimentally determined nitrogen content, however, is lower than expected.

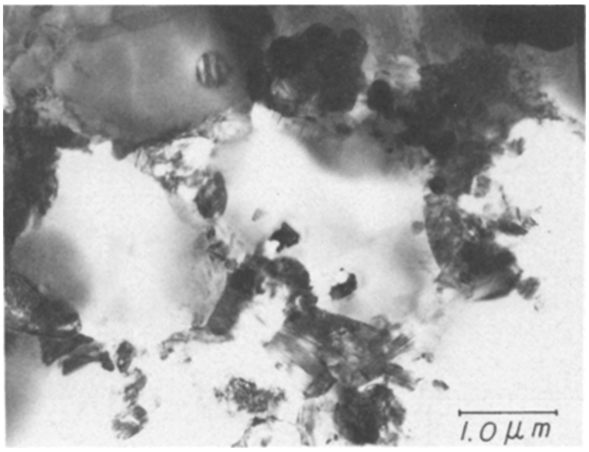

Figure 5 A transmission electron micrograph of a SiC–AlN–Al_2OC specimen (as-hot pressed) made with Ibigawa β-SiC. The micrograph shows nearly homogeneous solid solution along with SiC polytypes.

4. Discussion

The present work on the SiC–AlN–Al_2OC system has shown that essentially a 2H form solid solution can be formed by hot pressing a mixture of SiC, AlN, Al_2O_3 and Al_4C_3. However, optical micrographs clearly indicated that a complete solid solution was not obtained when hot pressing was conducted at 2000° C. Microscopically heterogeneous samples still gave the appearance of a nearly complete solid solution (based on X-ray analysis) due to the fact that the variation in lattice parameters with composition is very small in the SiC–AlN–Al_2OC system. Similar considerations in the prior work [2] indicated a lack of solid solution in some SiC–AlN ceramics. Nearly homogeneous microstructures were obtained when Ibigawa β-SiC powder was used. Samples made with α-SiC always had a small amount of 6H despite prolonged annealing at temperature in the range from 1950 to 2000° C. The relative ease with which a 2H solid solution forms when the starting SiC is β-SiC seems to suggest that the kinetics of dissolution of β-SiC in AlN and Al_2OC to form a 2H solid solution are faster than if the starting SiC is α-SiC. Apparently, the conversion of other polytypes of SiC into the 2H structure to form a solid solution is difficult.

Annealing at a temperature in the range from 1950 to 2050° C for times up to 52 h did not lead to the formation of a single phase solid solution. In the case of the samples made using Ibigawa β-SiC, needle shaped precipitates rich in SiC were formed. In samples made with Starck β-SiC and Starck α-SiC also, homogeneous solid solution did not form. The light SiC rich phase exhibited nearly spherical morphology. The formation of needle shaped precipitates in the Ibigawa sample and the occurrence of precipitate coarsening in the other samples indicates that diffusion was not a limiting factor. Thus, phase equilibrium may be assumed to have occurred. Although there was some weight loss with concurrent appearance of porosity upon annealing, the fact that the major constituent was of the 2H structure and that no other peaks occurred in the X-ray diffraction patterns suggests that volatilization occurred in such a way that the stoichiometry may still be defined on the basis of SiC–AlN–Al_2OC pseudoternary. As such the formation of SiC-rich precipitates in the three sets of samples studied indicates that at 2050° C a complete solid solution does not exist in the SiC–AlN–Al_2OC system. Rather, two solid solutions, both of 2H structure coexist in equilibrium. Further work is, however, needed to confirm this.

Chemical analysis on the hot pressed specimens indicated an oxygen content of 10.7 wt % and nitrogen content of 8.4 wt %. Theoretical values for equimolar composition are 8.7 wt % for oxygen and 8.58 wt % for nitrogen. Excess oxygen is probably due to SiO_2 layer on SiC and oxygen in AlN. According to the analysis supplied by the vendor, the oxygen content in AlN is 1 to 15 wt %. If the oxygen content in AlN is assumed to be 1 wt %, the calculated value of the nitrogen content in the sample (containing SiC, AlN, Al_2OC) is 8.41% which is in excellent agreement with the experimental value. Upon annealing at 2050° C for 50 h, the nitrogen content was found to increase to 10.2 wt % while the oxygen content dropped to 8.7 wt %. If it is assumed that the loss of oxygen occurs via volatilization of SiO_2 and Al_2OC while the gain in nitrogen occurs by the reaction of free aluminium with nitrogen as well as the conversion of Al_2O_3 into AlN, a total weight loss of 8.61% is calculated. Experimentally, it is difficult to determine the weight loss on account of surface depleted region. However, bulk portions, upon which chemical analyses were performed, exhibited formation of porosity. Density determination indicated a drop by about 4.9%. Presumably, the pores formed upon weight loss by volatilization must have partially shrunk by sintering thereby not causing as much loss in density as one would calculate based on the weight loss alone. Also, a thorough chemical analysis of the as-hot pressed and the annealed samples with respect to all the constituent elements would be required to ensure that the assumptions made in the calculations are justified.

Sample made with Al_4C_3 that was exposed to the atmosphere for a prolonged period of time had a substantial amount of Al_3O_3N. These samples exhibited a considerable stability at elevated temperatures for a prolonged period of time, except in the near surface regions on account of the decomposition of Al_3O_3N in one atmosphere of nitrogen. The bulk of the sample was essentially unchanged in composition and only a slight coarsening of the microstructure occurred. This indicates that SiC and Al_3O_3N are compatible phases. The microstructural stability exhibited at elevated temperatures by these specimens suggests that SiC–Al_3O_3N may be a potentially important class of structural ceramics.

Acknowledgements

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