Covalently-Bonded Solid Solution Formed by Combustion Synthesis

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The feasibility of synthesizing SiC-AlN solid solution by field-activated combustion synthesis was demonstrated. At lower fields of 8-16.5 V/cm, composites of AlN-rich and SiC-rich phases were synthesized, but at fields of 25-30 V/cm, the product was a 2H structure solid solution. Combustion synthesis of the solid solution by nitridation of aluminum with silicon carbide under a nitrogen gas pressure of 4-8 MPa was also investigated. The maximum combustion temperature and wave propagation velocity were found to be influenced by the electric field in the field-activated combustion synthesis, and by the green density and nitrogen pressure in the combustion nitridation. In both cases the formation of solid solutions is complete within seconds, considerably faster than in conventional methods which require hours.

Key words : Combustion synthesis, Field-activation, AlN-SiC solid solutions

I. Introduction

The formation of solid solutions of covalently-bonded materials requires, generally, high temperatures and relatively long reaction time. For example, formation of AlN-SiC solid solutions is typically made by hot-pressing a mixture of the two components at temperatures in the range 2100-2300 °C for several hours under an atmosphere of nitrogen or argon at a pressure of several tens of MPa.[1-7] In this paper, we describe the rapid formation of AlN-SiC solid solutions by two approaches of the method of combustion synthesis. One of these approaches is the field-activated combustion synthesis and the other is combustion nitridation. The difference between the formation mechanisms of the conventional and combustion synthesis methods is discussed.

Over the past decade SiC-AlN ceramics have generated considerable interest as promising materials, primarily because of the improvement of the fracture toughness of silicon carbide resulting from the addition of aluminum nitride.[2] Fig. 1 shows the tentative phase diagram of AlN-SiC system.[1] The presence of aluminum and nitrogen stabilizes the 2H-structure of SiC which has nearly the same lattice parameters as the 2H structure of AlN. An extensive solid solubility exists between these phases in the compositional range of 25 to 100 mol% at temperatures above about 1960 °C.[1] Upon cooling, these solid solutions undergo spinodal decomposition leading to the formation of modulated structures[2,10] with improved fracture toughness.[2]

The synthesis of the solid solutions has been attempted by different techniques. In the first report by Ervin[11] AlN-

SiC solid solutions were obtained by the vapor deposition of aluminum nitride onto silicon carbide porous bodies. Subsequently, solid solutions were prepared by hot-pressing of mixtures of AlN-SiC[3,4] or Al_4C_3-Si_3N_4.[12] Details of these processes were described by Zangvil and Ruh.[13] The typical parameters of the hot-pressing method[1-7] include, as indicated above, high temperatures and long annealing times. The formation of the solid solution is governed by interdiffusion between AlN and SiC, a process recognized to be very slow.[14]

A new effective approach to produce AlN-SiC solid solutions by combustion synthesis was recently employed.[15-17] In this new approach, the formation of solid solutions is complete within seconds, making it an attractive alternative, energy-saving process. There are several possible
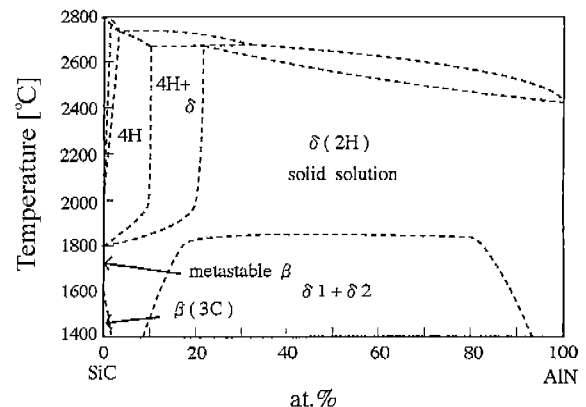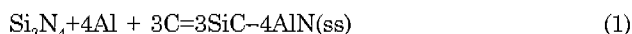
Fig. 1. Phase diagram of AlN-SiC system.

routes to synthesize AlN-SiC solid solutions through a combustion reaction. In one route, solid solutions are prepared by the following reaction:

$$Si_3N_4 + 4Al + 3C = 3SiC - 4AlN(ss) \qquad (1)$$

where (ss) refers to the solid solution. However, despite the high adiabatic temperature for the reaction in Eq. (1), it is difficult to initiate it without a form of activation. In this work, an electrical field was applied to initiate and sustain the reaction. This concept of field activated combustion synthesis has recently been developed[18] and its utility was demonstrated in the synthesis of a variety of materials.[19-25] The use of this method has made it possible to prepare materials which heretofore could not be formed by combustion synthesis (without preheating). Ceramics such as (β-SiC, B_4C, TaC) and composites such as $MoSi_2$-SiC and B_4C-TiB_2 (with extensive compositional ranges) could only be synthesized through field-activation. In the second approach, the combustion synthesis of solid solutions was achieved by a reaction between SiC and Al powders under high- pressure nitrogen gas[17] according to

$$x(Al+0.5N_2)+(1-x)SiC=xAlN-(1-x)SiC(ss) \qquad (2)$$
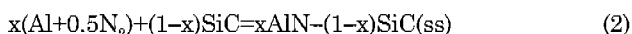
The reaction of Eq. (2) can be easily ignited because the main reaction, that of the combustion nitridation of Al, is sufficiently exothermic to sustain a self-propagating combustion wave through the sample, leading to the formation of the solid solution within a time frame of seconds.

Thus it is interesting to understand the mechanism of these combustion reactions and how it provides such high rates of transformation compared to conventional processing methods.

II. Experimental Procedure

1. Field-Activated Combustion Synthesis

Powders of Si_3N_4, Al, and C, mixed according to the stoichiometric ratios of Eq (1), were uniaxially pressed into orthorhombic pellets with dimensions of $21 \times 12 \times 8$ mm. The silicon nitride (Ube Industrial, Ube City, Japan) was 98% pure and had an. average particle size of 0.5 μm. The aluminum powders, (Valimet, Stockton, CA, USA) were 99.7% pure and had a particle size in the range of 3-4.5 μm. The 99.9% pure carbon was obtained from the Ultra Carbon Corp. (Bay City, MI, USA) as a submicron powder. The green density of all pressed pellets was kept constant at about 60%.

Field-activated combustion was carried out inside a stainless steel chamber under a 0.1 MPa atmosphere of argon. Each sample was placed between two graphite electrodes and a tungsten ignition coil was placed near a free surface as shown schematically in Fig. 2. In the presence of a field (above a minimum, threshold, value), the activation of the ignition coil causes the initiation and propagation of a combustion wave. A time-coded video recorder measured the wave velocity and its temperature
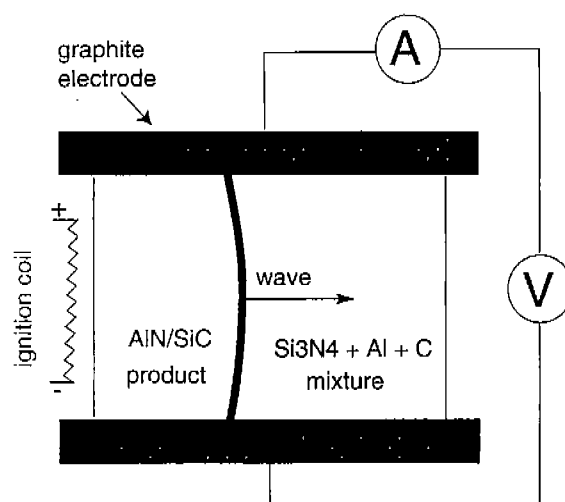

Fig. 2. Schematic representation of the field-activated combustion apparatus.

was measured by a two-color optical pyrometer with a response time of 0.01s. Experimental details of the process of field-activated synthesis have been provided in previous publications.[21,22]

2. Combustion nitridation

Powders of aluminum and silicon carbide were dry-mixed for one hour in proportions that gave a product with a molar ratio of AlN/SiC=6/4. The 3C-SiC powder (Kojundo Chemical Lab. Co. Ltd, Japan) was 99% pure with a particle size in the range of 2-3 μm. The Al powder (Kojundo Chemical Lab. Co. Ltd, Japan) was 99.9% pure and had an average particle size of 20 μm. The green mixture was poured into a porous graphite crucible (diameter: 15 mm, height: 30 mm). In order to understand the morphology of the transformation during combustion, whiskers of 3C-SiC were used in some experiments. The whiskers were 98% pure and were about 0.3-1.4 μm in diameter and 5-30 μm in length. When whiskers were used, the mixture was prepared by wet-milling in ethanol in a Si_3N_4 jar with Si_3N_4 balls for 12 hours. After milling the suspension was dried and the mixture was sifted through a 10 mesh sieve. To understand the effect of the relative density of the reactants on the combustion process, samples with relative densities ranging from 23 to 64% were prepared and investigated. To obtain samples with densities higher than about 40%, powders were pressed into pellet form.

The combustion experiments were performed in a reaction chamber (Ueno Metal Inc., Japan) under a nitrogen atmosphere. The nitrogen gas pressure was varied from 0.1 to 8.0 MPa. To initiate the reaction between Al, gaseous nitrogen, and SiC, an ignition pellet of Ti-C mixture (diameter: 16 mm, height: 6-8 mm; molar ratio: 1/1) was placed on top of the crucible. A current of ca. 70 A (at 40 V) was passed through a carbon ribbon in contact with the ignition pellet, causing it to ignite. This in turn

ignited the green mixture of Al-SiC under the set nitrogen gas pressure. Combustion reactions, thus initiated, are typically completed within a few seconds. The temperature of the combustion reaction was measured by means of two-color optical pyrometer (Model IR-AQ, Chino Co. Ltd.) focused on a hole in the middle part of the crucible (diameter of the hole was about 5 mm). To measure the wave propagation velocities, two holes drilled in the side of the crucible at 10 mm from center to center were used as markers for wave displacement. The combustion process was video-recorded (Sony CCD-V800 with a Kenko ND400 filter) and the velocity was determined from the optical images.

The products were analyzed by X-ray powder diffraction, using CuK_α radiation (RINT-2500, Rigaku Co. Ltd.). For phase identification, the scanning rate was set at 2θ of 2 °/min., and for peak curve comparison, the (110) peak pattern near $2\theta=60$ ° was run in a mode of step-scanning under conditions of $2\theta=0.02$ ° and a collecting time of 2 seconds. The lattice constant was also measured by the same scanning method using five peaks each of internal standard Si and the sample. The morphology of the products was determined by SEM analysis (JSM-5410, JEOL).

III. Results and Discussion

1. Field-activated combustion synthesis of AlN-SiC solid solution

In order to initiate a self-sustaining reaction for Eq. (1), the imposition of a field equal to or greater than a threshold of 8 V/cm was found necessary. As the field strength is increased, the velocity of the combustion wave also increased (Fig. 3), in agreement with previous observations on other systems.[21-23] A more significant aspect of the effect of field strength, is the nature of the product
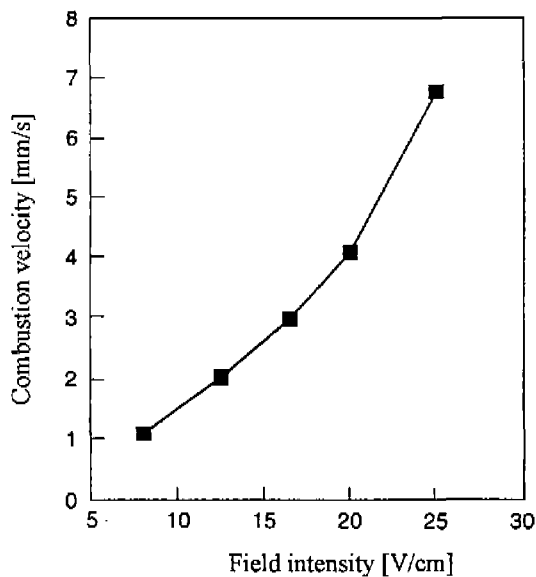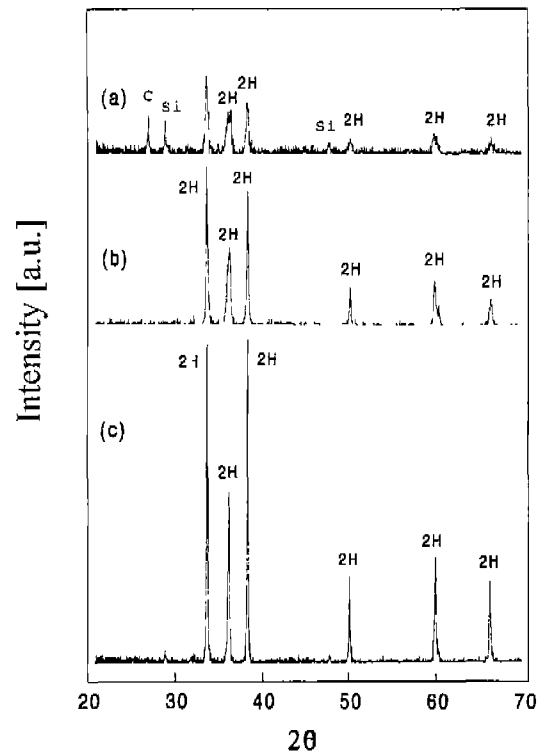
Fig. 3. Effect of field on the wave velocity.

Fig. 4. X-ray diffraction patterns of products obtained with E=8.0 (a), 16.5 (b), 25.0 (c) V/cm^{-1}.

obtained at the end of the process. Fig. 4 shows the x-ray diffraction patterns of products obtained with fields of 8, 16.5 and 25 V/cm. The product obtained at the threshold field (part a in Fig. 4) is a mixture of unreacted Si, C, and a 2H phase. The latter can be either AlN, 2H SiC, or both since the two structures are very similar and have only small differences in their lattice parameters (for the 2H-SiC, a=3.0763 and c=5.0480 Å and for the 2H-AlN, a= 3.114 and c=4.979 Å). When the applied field is increased to 16.5 or 25 V/cm, the product contained peaks corresponding to the 2H-structure only, i.e. the reaction is complete, as shown in Fig. 4.

In order to determine the exact nature of the 2H-phases observed in the XRD analysis, the diffraction lines of the (110) planes were carefully examined. These lines provide the largest 2θ difference (0.64 °) for the two sets of the 2H structures of AlN and 2H-SiC. The diffraction line of the (110) planes of 2H-SiC is at $2\theta=59.996$ ° and the corresponding line for AlN is at $2\theta=59.350$ °. Diffractions of the (110) lines of products of Eq(1) are shown in Fig. 5. Fig. 5 also shows the (110) diffraction lines of a random mixture of commercial α-SiC and AlN. The patterns for the products obtained with fields of 8 and 16.5 V/cm (parts b and c in the figure) are relatively broad but can be deconvoluted to provide two peaks representing AlN and 2H-SiC. As the field increases from 8 to 16.5 V/cm, the resultant peaks move closer to each other. This indicates that each represent a solid solution of one phase into the other, as will be discussed subsequently. When the field is
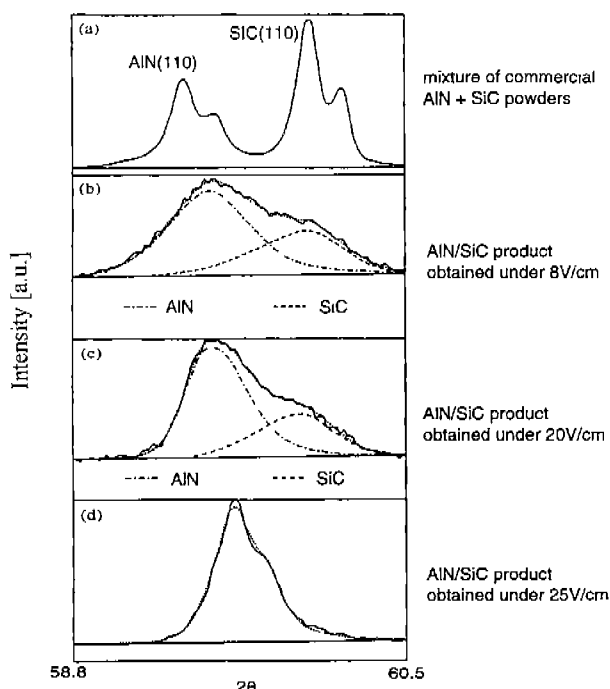
Fig. 5. X-ray diffraction peaks of the (110) planes of a random mixture of AlN and SiC and products of synthesis under different fields.
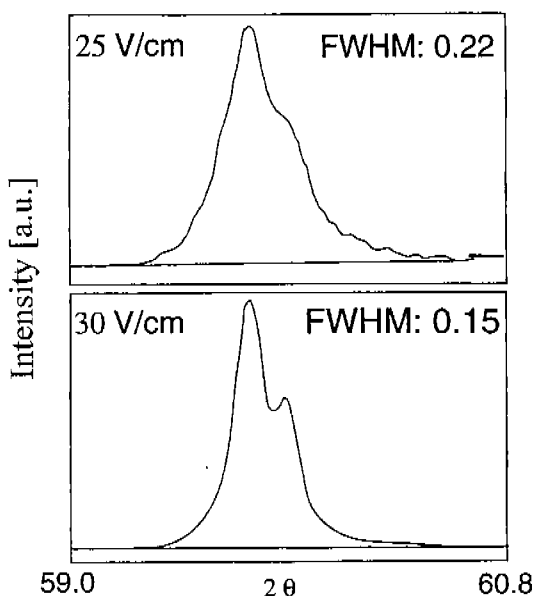

Fig. 6. X-ray diffraction peaks of AlN-SiC solid solutions synthesized under 25.0 and 30.0 V/cm^{-1}.

increased to 25 V/cm, the peak becomes relatively narrow (part d in Fig. 5) and cannot be deconvoluted to give two peaks as in the above cases. In this case, it represents a solid solution of AlN and SiC. When the field is further increased to 30 V/cm, the (110) diffraction peak is similar to that obtained at 25 V/cm, except that it is significantly narrower, as seen in Fig. 6. The full widths at half maxi-
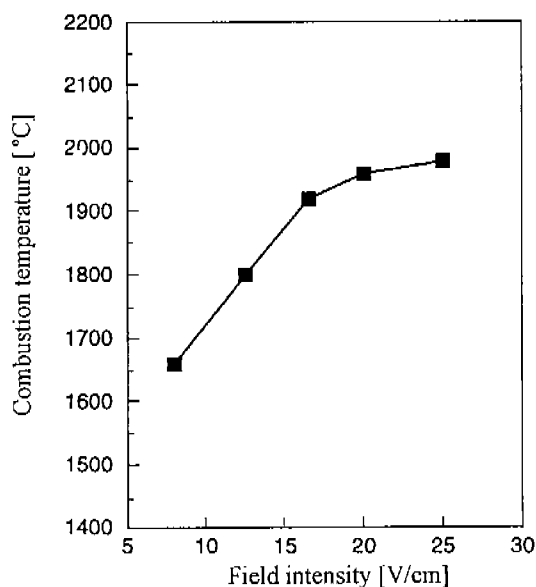

Fig. 7. Effect of field on the combustion temperature.

mum (FWHM) for these peaks are 0.22 and 0.15 for the products obtained at 25 and 30 V/cm, respectively. This observation is taken as an indication of the increase in randomness of the solid solution when the field is increased. Since the product particle size is relatively large (>1 µm), we have discounted the possibility that changes in line width are related to the formation of very small particles. We have also assumed that the change in the peak width is not caused by differences in microstrain. This is based on the trend in the combustion temperature with applied field (to be presented later). The combustion temperatures of the 25 and 30 V/cm systems are approximately the same and thus the thermal history for both cases should provide no significant difference in microstrain.

Fig. 7 shows the effect of the applied field on the combustion temperature of reaction (1). The temperature increases from 1660 °C at the lowest applied (8 V/cm) to 1980 °C at a field of 25 V/cm. According to Fig. 1, at 1660 °C the composition of the SiC-rich phase is about 10 mol% AlN which is in reasonable agreement with the calculated composition from the experimental results.[16] At a field of 16.5 V/cm, the SiC-rich product contained about 11 mol% AlN. At this field, the combustion temperature is 1920 °C which corresponds to an SiC-rich phase with an approximate composition of 23 mol% AlN. With a higher field, 25 V/cm, the combustion temperature is 1980 °C, a temperature corresponding to a complete solid solution on the phase diagram and consistent with the experimental observations.

2. Combustion nitridation of AlN-SiC solid solution

When the pressure of N_2 was 6.0 MPa, steady-state regime of wave propagation was observed for the samples with green densities of <45%. The mode changed to the

spin-combustion regime for densities above 45%. When the pressure was 0.1 MPa, combustion took place only in mixtures with densities less than 40%. The temperature profiles contained a sharp peak which is followed by a second, wide peaks indicating that the process is a multistage SHS reaction.[17]

Fig. 8 and 9 demonstrate the dependencies of combustion temperature (T_c) and wave propagation velocities on the green density. The values of T_c for N_2 pressure of 6.0 MPa exceed 2500 °C and decrease slightly with increasing density. It is worth noting that the values of T_c are above the melting points of Al, Si, and AlN[11], but are below the melting point of SiC. They are also higher than T_c values for the case of 0.1 MPa. The latter are scattered
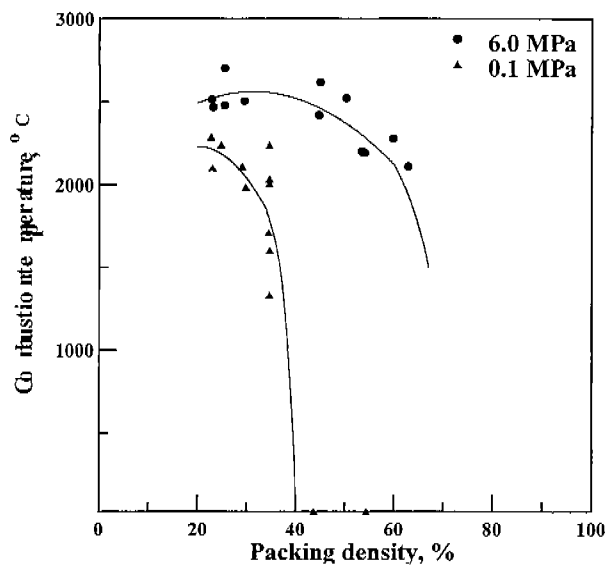
around 2200 °C and decrease drastically at densities above 35%. The T_c data for densities of about 30-40% have a large scatter. The most likely reason for this may be the non-stable nature of the wave propagation. The dependencies of the wave propagation velocities on relative density are different for the low and high N_2 pressures. Under a pressure of 0.1 MPa the velocity decreases from 3.0 mm·s⁻¹ to extinction as the density changed from 23 to 42. In the 6.0 MPa case it increases from 2.0 to 10 mm·s⁻¹ as the density changed from 23 to about 45% and then decreased as the density increased further due to lower gas permeability. Thus a pressure of 0.1 MPa is not sufficient to provide the necessary supply of nitrogen to the combustion zone in the higher density samples, while a pressure of 6.0 MPa supports the combustion reaction, even for the pressed (high density) samples.

Fig. 10 shows the X-ray patterns of the reactants and products. The raw SiC powder had mainly the 3C structure, although its hexagonal modifications along with free silicon were also present as shown in Fig. 10(a). The presence of one sharp peak near 60 ° indicates the formation of a solid solution (ss) between SiC and AlN with 2H structure. This type of diffraction pattern was observed

Fig. 8. Effect of packing density on combustion temperature.
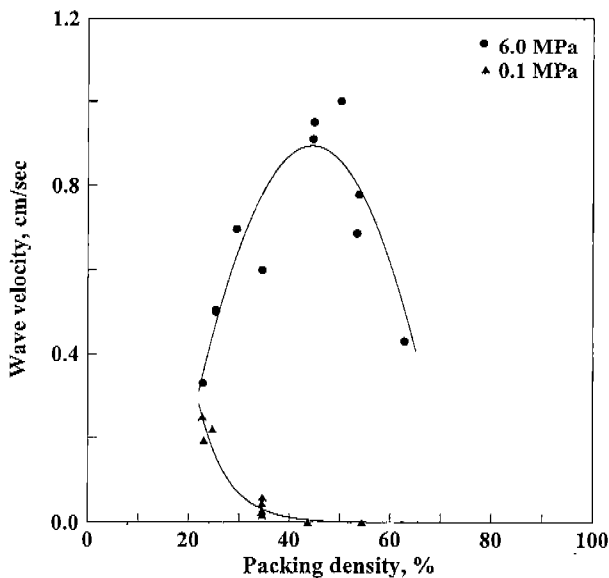
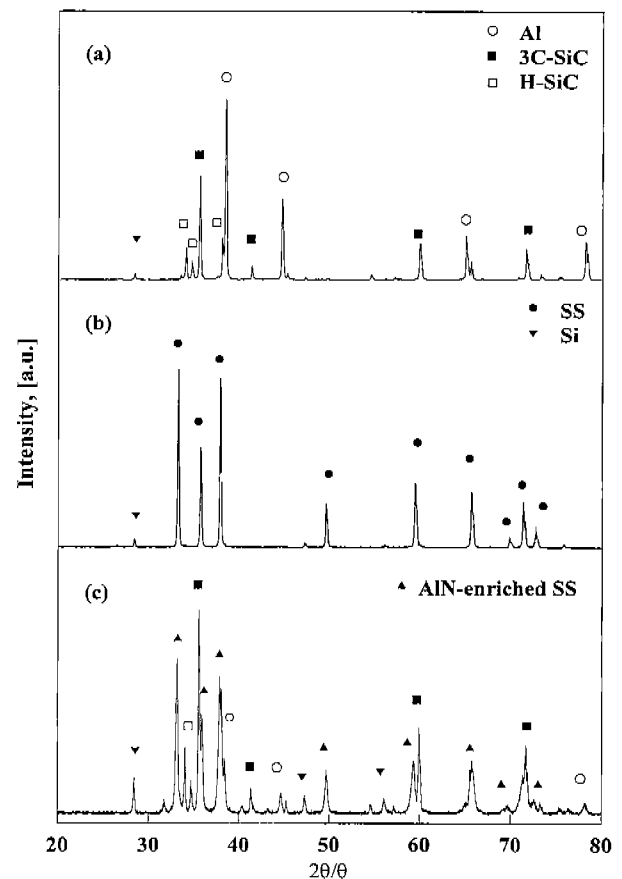Fig. 9. Effect of packing density on combustion wave velocity.

Fig. 10. X-ray diffraction patterns for the green mixture (a) and SHS products for initial density 45%, 6 MPa (b) and 35%, 0.1 MPa (c); SS-solid solution.
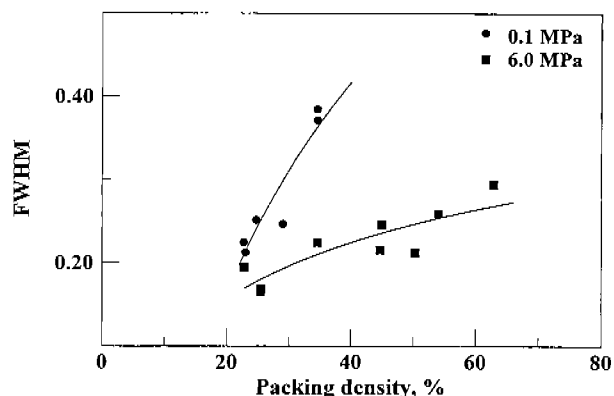
Fig. 11. Effect of packing density on FWHM of the X-ray line near 60 degrees.
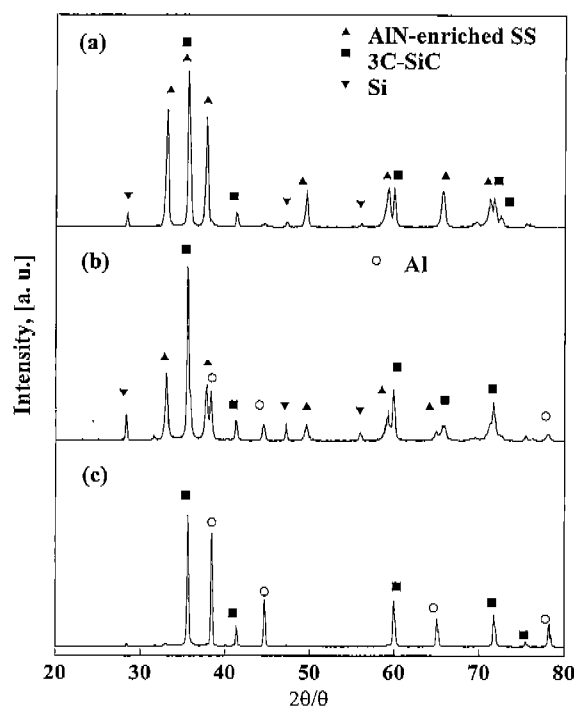

Fig. 12. XRD patterns for the sample after extinguishing the wave propagation, (a) very top layer close to the ignition point, (b) middle layer of combustion zone just behind the extinguished wave propagation and (c) bottom layer of preheat zone without burning.

for samples prepared with combustion temperatures above 2300 °C. Fig. 10(b) shows the peaks corresponding to a solid solution which formed at 6.0 MPa and green mixture density of 45 % with a maximum combustion temperature of 2420 °C. In the case of 0.1 MPa nitrogen pressure and 35% relative density (T_c=2200 °C) Al was converted to its nitride, but the formation of a solid solution was not complete: two peaks are distinctly visible at 60 ° in the X-ray patterns as shown in Fig. 10(c).

Free silicon peaks were observed after combustion in all cases. Its amount was evaluated as about 2-3 mol % when the solid solution formation was complete, and up to 8 mol % in the case of no solution formation. Ths amount of Si in the starting powders was about 1-2 mol%. The increase in the amount of Si (over the initial value) is taken as an indication of the decomposition of SiC during the synthesis reaction.

The value of the full width at half maximum (FWHM) of the XRD peak near 60 ° is an indication of the homogeneity of the solid solution. In Fig. 11, the FWHM values are plotted against the green density. With synthesis under a pressure of 0.1 MPa, the FWHM increases from 0.188 to 0.367, with increasing density splitting into two distinct lines. With a pressure of 6.0 MPa, it increases from 0.165 to 0.254 and remains roughly as a single line. These observations indicate that a homogeneous solid solution is formed at higher values of T_c and lower values of green density.

To understand the reaction mechanism between Al, SiC and N_2, wave propagation was arrested by the following procedure: The green powder mixture was pressed slightly and ignited under an N_2 pressure 0.1 MPa. The combustion wave propagated halfway through the sample and stopped. The sample was then carefully divided layer by layer and analyzed by XRD and SEM. The XRD patterns and the micrographs of the very top layer (close to the ignition point), the middle layer (the combusted zone just behind the extinguished wave), and the bottom layer (the preheat zone) are shown in the sequence, (a), (b), (c) of Fig. 12 and 13, respectively. The X-ray patterns depict no

solid solution formation. Even in the very top layer (Fig. 12a) with a conversion of Al to AlN of 100%, 3C-SiC remains in the product. The amount of reacted Al increases from the top to the bottom of the sample. Free Si content increases from 4 mol % in the top layer to 8 mol % in the middle layer and then decreases sharply to 0% in the lower layer. These results demonstrate that SiC decomposes during the SHS reaction. SEM studies confirmed this conclusion. In Fig. 13(a) and (b), corresponding to top and middle layers, no SiC whiskers can be seen, although combustion had occurred there. Thus, SiC must have dissolved into the molten Al and then re-solidified but in the form of equiaxed particles as shown in parts (a) and (b) in Fig. 12 and 13. In Fig. 13(c), large particles of re-solidified Al with adhered SiC whiskers are clearly seen.

From the above experimental observations, we propose the following mechanism for combustion synthesis of the solid solutions between AlN and SiC using Al and SiC powders as solid reactants under an N_2 atmosphere. If the formation of AlN in the reaction of Eq. (2) occurs completely before any other reaction, the solid solution is not likely to form during the subsequent short time of the process. If it did form, then a considerably long time is required to form the solid solution, as is experienced in the conventional methods. However, in this reaction we believe that at first heat is generated from the partial nitridation of Al. As the temperature increases, the rem-
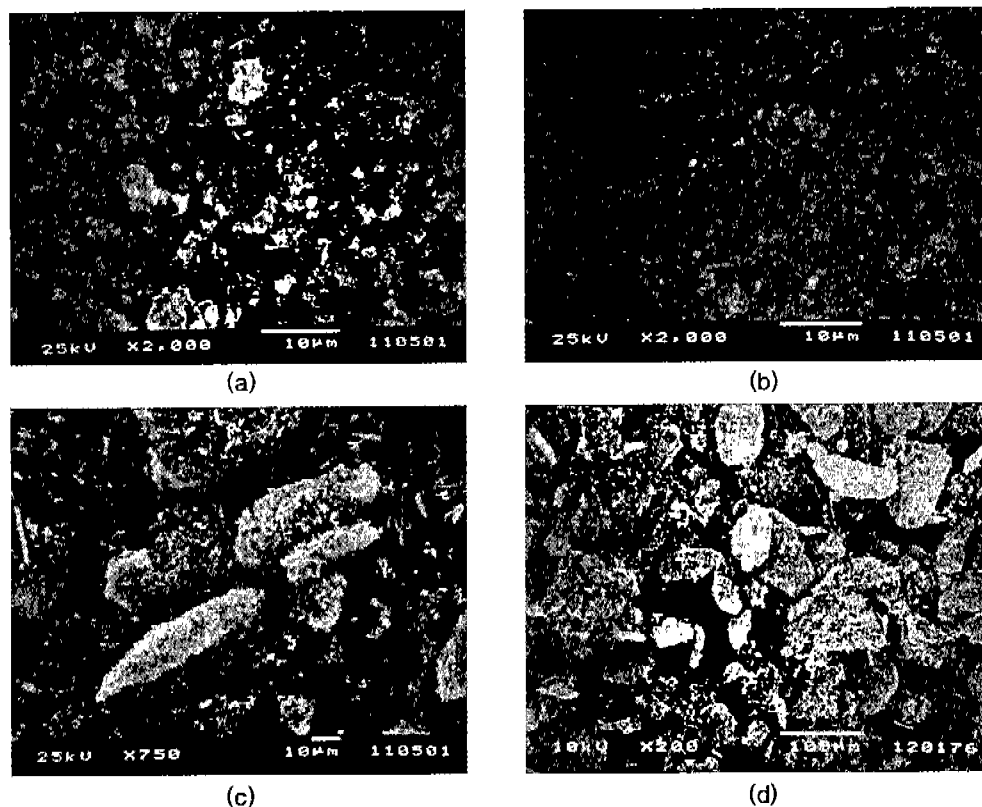
(a)

(b)

(c)

(d)

Fig. 13. SEM micrographs for the sample after extinguishing the wave propagation: (a) - top layer, (b) - middle layer, (c) - bottom layer and (d) - green mixture.

aining unreacted molten Al can dissolve SiC to form an Al-Si-C liquid at about 2150 °C and the previously formed AlN can also dissolve into this liquid to form an Al-Si-C liquid containing dissolved nitrogen at about 2400 °C, as suggested by the Al-Si-C[26] and Al-Si-N[27] phase diagrams. Finally, we propose that a transient liquid solution forms at a temperature close to maximum combustion temperature which, upon cooling results in the formation of the AlN-SiC solid solution.

IV. Conclusion

Composites and solid solutions (57 mol% AlN) of AlN and SiC were synthesized by field-activated combustion. Reactions between silicon nitride, aluminum, and carbon were self-sustaining only in the presence of fields above a threshold value of 8 V/cm. Products obtained under the influence of fields $8<E<25$ V/cm are composites of SiC-rich and AlN-rich phases. The extent of solubility of AlN and SiC into each other increases with increasing field and at 25 V/cm, the product is a complete solid solution. Synthesis under a higher field (30 V/cm) increased the randomness of the solid solution. The formation of solid solution AlN-SiC by combustion synthesis from Al and SiC powders in N_2 atmosphere was also studied. The dependencies of combustion temperature and wave propagation

velocity were investigated. Nitrogen pressure of 6.0 MPa was found to be sufficient for self-sustaining formation reaction of solid solutions. Formation of such solutions was not possible under a pressure of 0.1 MPa. Synthesis reactions were possible for all relative densities investigated when the pressure was 6.0 MPa. In this case, the combustion temperature did not depend strongly on the density of the reactants. In the case of 0.1 MPa, combustion was not observed for samples with densities above 45 %. Combustion wave velocities depended on the green density: for the 0.1 MPa case, it decreased with increasing density, and for the 6.0 MPa case it did not exhibit a definite trend but had a maximum at a relative density of about 45%. From frozen wave experiments, it was established that SiC decomposes during the reaction. Solid solution is formed during the solidification of a transient Al-N-Si-C liquid phase.

Acknowledgments

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