PII: S0955-2219(97)00075-7

Journal of the European Ceramic Society 17 (1997) 1787–1792

0955-2219/97/$17.00 + 0.00

Synthesis of AlN–SiC Composites and Solid Solutions by Field-Activated Self-Propagating Combustion

H. Xue and Z. A. Munir

Department of Chemical Engineering and Materials Science, University of California, Davis, CA 95616, USA

Abstract

The synthesis of AlN–SiC composites and solid solutions was achieved through the imposition of an electric field in self-propagating high-temperature reactions. Despite its highly exothermic nature, the reaction $Si_3N_4 + 4\,Al + 3C = 4\,AlN + 3\,SiC$ *is not self-sustaining without the imposition of a threshold field (E) of* $8\,V\,cm^{-1}$*. At higher fields, the nature of the product depended on the value of the field. At* $E = 8$ *and* $16{\cdot}5\,V\,cm^{-1}$*, the product is a composite of AlN-rich and SiC-rich phases. The extent of solubility of each phase into the other increased with increasing field. When* $E = 25{\cdot}0\,V\,cm^{-1}$*, the product is a solid solution with the 2H structure. The degree of randomness of the solution increased with a further increase in the value of the imposed field. Compositional analyses of the product phases are in reasonable agreement with the reported tentative phase diagram for AlN and SiC. The work demonstrates the use of an electric field as a processing parameter in self-sustaining combustion synthesis of nitride composites and solid solutions. © 1997 Elsevier Science Limited.*

1 Introduction

The relatively high thermal conductivity and high electrical resistivity of aluminum nitride has been the primary reason for its use as a substrate material in electronic devices, and more recently as a potential insulator in high performance spark plugs.[1] Silicon carbide has a comparable thermal conductivity but is substantially more attractive with regards to its mechanical properties (e.g. microhardness and flexural strength). In its high temperature (α) modification, SiC forms a complete solid solution with AlN. The solution has the 2H structure and is stable at temperatures above about 1960°C.[2] When annealed at temperatures below this, the solid solutions undergo a spinodal decomposition and result in a modulated nanocomposite structure with a preferred orientation.[3] The fracture toughness and flexural strength of the spinodal decomposition product depends on the composition (i.e. AlN content). The enhancement in mechanical properties of the spinodally decomposed AlN–SiC solid solutions is attributed to energy absorption due to the presence of the modulated structure.[3]

The synthesis of AlN–SiC solid solutions has been successfully accomplished through a variety of methods, all requiring high temperatures (up to 2300°C) and long reaction times (up to 8 h). Solid solutions have been formed through furnace heating or hot-isostatic pressing of mixtures of AlN and α or β-SiC,[2–8] through the carbothermal reduction of silica and alumina in a nitrogen atmosphere,[9] and through a reaction between Si_3N_4, AlN, carbon black and CaO.[10]

The use of the energy-efficient method of the self-propagating high-temperature synthesis (SHS) has not been previously attempted and it is the focus of this investigation. An ideal approach would be to synthesize AlN–SiC composites and solid solutions according to

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

The above is a highly exothermic reaction ($\Delta H^{\circ}_{298} = -746{\cdot}8\,kJ\,mol^{-1}$) and, as such, it is expected to be self-sustaining. The adiabatic combustion temperature of eqn (1) is 2502 K which considerably exceeds the empirically established minimum of 2000 K for SHS reactions. However, this expectation is not experimentally realized. When powder mixtures of Si_3N_4, Al, and C are exposed to an ignition heat source, no self-sustaining reaction can be initiated. Such a case represents an example of a kinetic limitation of the SHS method, as is the case in the synthesis of TaC.[11] It has been recently demonstrated that kinetically and thermodynamically limited SHS reactions can be activated through the application of an electric field.[12]

The concept of field-activated combustion synthesis has recently been developed[13] and its utility was demonstrated in the synthesis of a variety of materials.[14–20] The use of this method has made it possible to prepare materials which heretofore could not be synthesized by SHS (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.

Field-activation is realized by the simultaneous imposition of an electric field and an ignition source on compacted reactant powders. In the absence of either, no self-sustaining wave can be initiated. In the presence of a field, ignition generates a wave whose velocity is found to be directly proportional to the magnitude of the applied field.[17] The field was also shown to change the mode of wave propagation (i.e. non-steady state to steady-state)[17] and to increase the combustion temperature and hence the degree of melting and consolidation of the product.[18] Experimental results and modeling studies have led to the conclusion that the effect of the field is to provide Joule heating. This heat is confined to the narrow combustion zone ($\sim$1 mm) in systems with electrically low-conducting products (e.g. SiC).[17,19] By contrast, for systems with relatively high conductivity products, the field effect is not localized and for any given applied field value, the degree of activation (as indicated, for example, by wave velocity) decreases as the wave propagates through the reactants.[11,21] Field-activation was also investigated with regard to the relationship between the directions of the applied field and the advancing wave.[22] Enhancement of the combustion process by field-activation was found to be confined to the case where the two directions are perpendicular.

2 Experimental

Powders of Si_3N_4, Al, and C, mixed according to the stoichiometric ratios of eqn (1), were uniaxially pressed into orthorhombic pellets with dimensions of 21 × 12 × 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) 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 0·4 MPa atmosphere of nitrogen. Each sample was placed between two graphite electrodes and a tungsten ignition coil was placed near a free surface as shown schematically in Fig. 1. In the presence of a field (above a threshold value) the activation of the ignition coil causes the initiation and propagation of a combustion wave. The wave velocity was measured by a time-coded video recorder and its temperature was measured by a two-color optical pyrometer with a response time of 0·01 s. Experimental details of the process of field-activated synthesis have been provided in previous publications.[16,17]

The products were analyzed by X-ray diffraction (XRD) using CuKα with a nickel filter. Phase identification was made through scans at a set rate of $2\theta\,\mathrm{min}^{-1}$. For curve fitting, the (1 1 0) peak pattern near $2\theta = 60°$ was examined in a step-scan mode with $\Delta 2\theta = 0{\cdot}02°$ and a collecting time of 10 s. Peak curve fitting was made through the use of a Scintag 2000 diffractometer computer program.

3 Results and Discussion

In order to initiate a self-sustaining reaction for eqn (1), the imposition of a field equal to or greater than a threshold of $8\,\mathrm{V\,cm^{-1}}$ was found necessary. As the field strength is increased, the velocity of the combustion wave also increased (Fig. 2), in agreement with previous observations on other systems.[15–18] A more significant aspect of the effect of

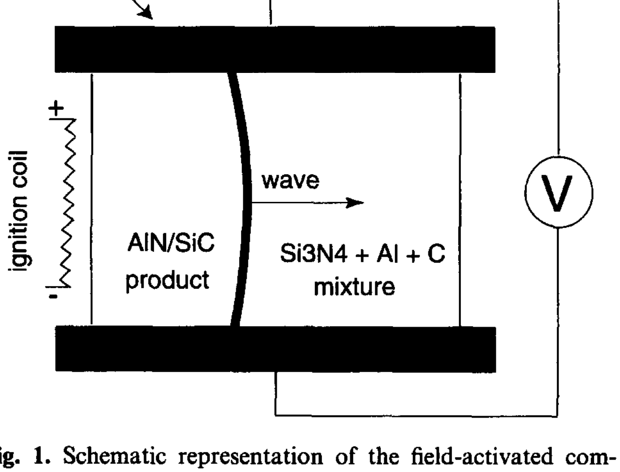

Fig. 1. Schematic representation of the field-activated combustion apparatus.

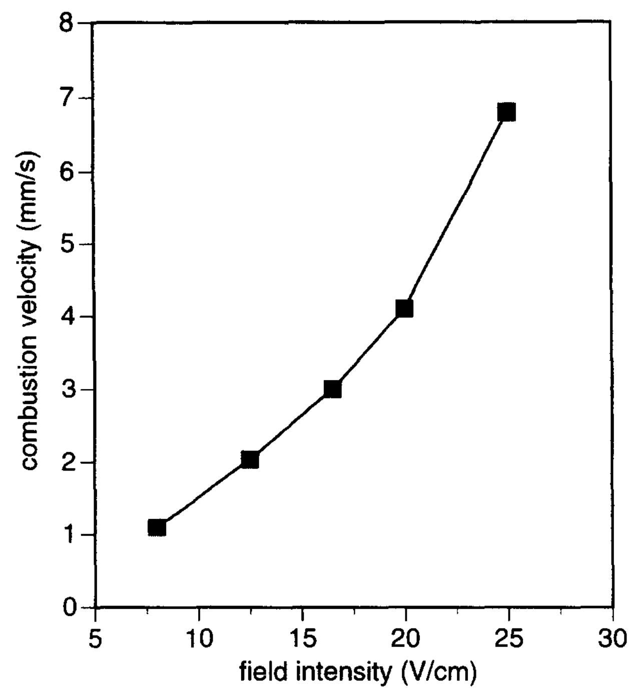

Fig. 2. Effect of field on the wave velocity.

field strength is the nature of the product obtained at the end of the process. Figure 3 shows the X-ray diffraction patterns of products obtained with fields of 8, 16·5 and 25·0 V cm^{-1}. The product obtained at the threshold field (part (a) in Fig. 3) is a mixture of unreacted Si, C, and a 2H phase. The latter can be either AlN, α-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 25·0 V cm^{-1}, the product contained peaks corresponding to the 2H-structure only, i.e. the reaction is complete, as shown in Fig. 3.

In order to determine the exact nature of the 2H-phases observed in the XRD analysis, the diffraction lines of the (1 1 0) planes were carefully examined. These lines provide the largest 2θ difference (0·64°) for the two sets of the 2H structures of AlN and α-SiC. The diffraction line of the (1 1 0) planes of α-SiC is at $2\theta = 59{\cdot}996°$ and the corresponding line for AlN is at $2\theta = 59{\cdot}350°$. Diffractions of the (1 1 0) lines of products of eqn (1) are shown in Fig. 4. Figure 4 also shows the (1 1 0) 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^{-1} (parts (b) and (c) in the figure) are relatively broad but can be deconvoluted to provide two peaks representing AlN and α-SiC. As the field increases from 8 to 16·5 V cm^{-1}, the resultant peaks move closer to each other. This indicates that each represents a solid solution of one phase into the other, as will be discussed later. When the field is increased to 25 V cm^{-1}, the peak is relatively narrow (part (d) in Fig. 4) and cannot be deconvoluted to give two peaks as in the above cases. In this case, it represents a solid solution of AlN and α-SiC. When the

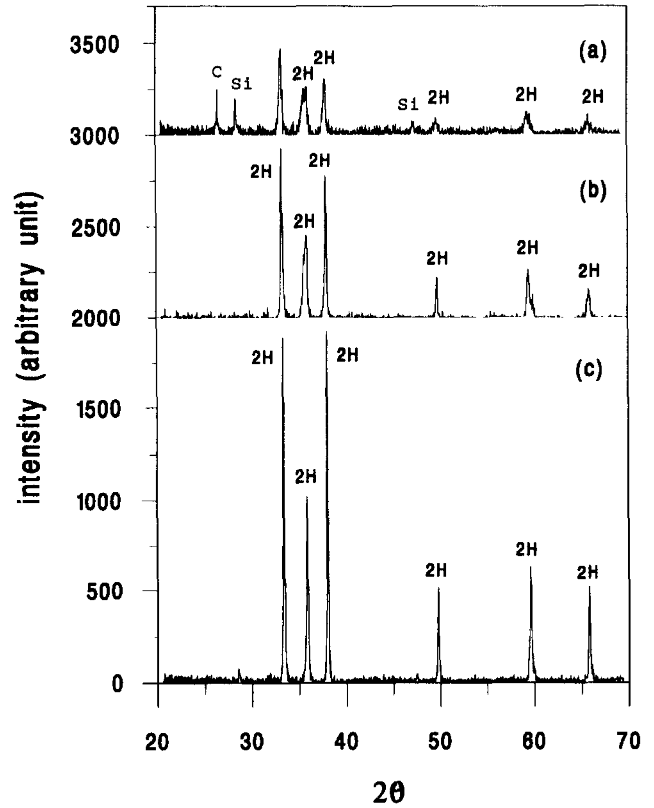

Fig. 3. X-ray diffraction patterns of products obtained with E = 8·0 (a), 16·5 (b), and 25·0 (c) V cm^{-1}.

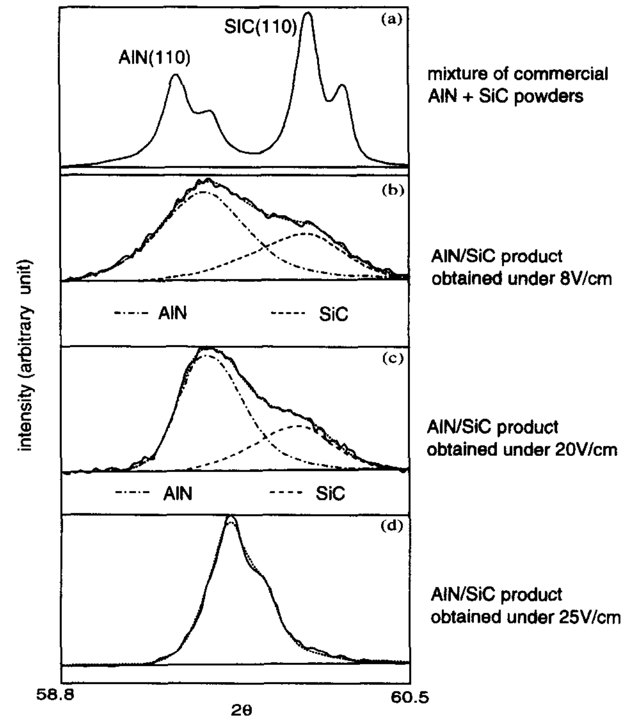

Fig. 4. X-ray diffraction peaks of the (110) planes of a random mixture of AlN and SiC and products of synthesis under different fields.

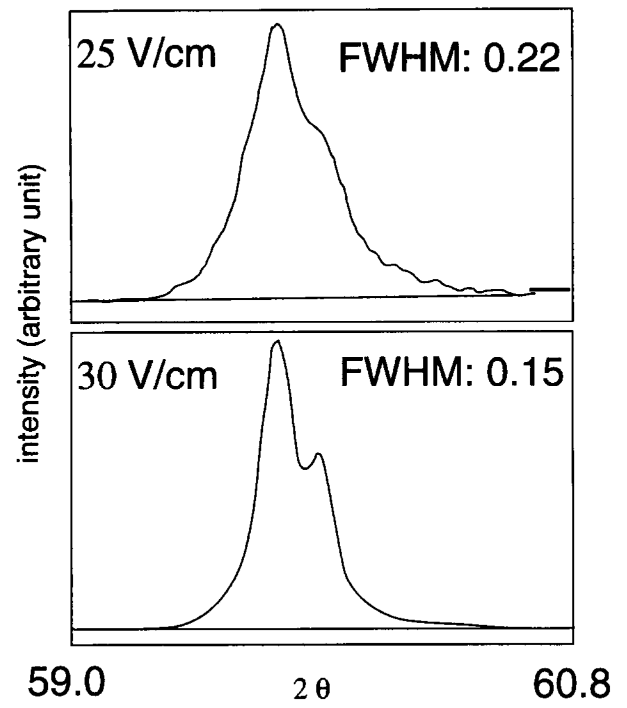

Fig. 5. X-ray diffraction peaks of AlN–SiC solid solutions synthesized under 25·0 and 30·0 V cm^{-1}.

field is further increased to 30 V cm^{-1}, the (1 1 0) diffraction peak is similar to that obtained at 25 V cm^{-1}, except that it is significantly narrower, as seen in Fig. 5. The widths of the peaks at half heights are 0·22 and 0·15 for the products obtained at 25 and 30 V cm^{-1}, 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 ($>1\ \mu$m), 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^{-1} systems are approximately the same and thus the thermal history for both cases should provide no significant difference in microstrain.

Careful determination of the deconvoluted peaks provided information on the extent of solubility in each phase. Using Vegard's law, the composition of the SiC-rich and the AlN-rich phases were calculated as a function field, as shown in Fig. 6. The validity of Vegard's law for the AlN–SiC system had been experimentally established.[5,9] Examining the curve for the SiC- rich phase (Fig. 6(b)) shows that its AlN content increases slightly as the field is increased from 8 to 16·5 V cm^{-1} but rises markedly as the field is increased to 25 V cm^{-1}. A somewhat similar trend is observed for the AlN-rich phase, Fig. 6(a).

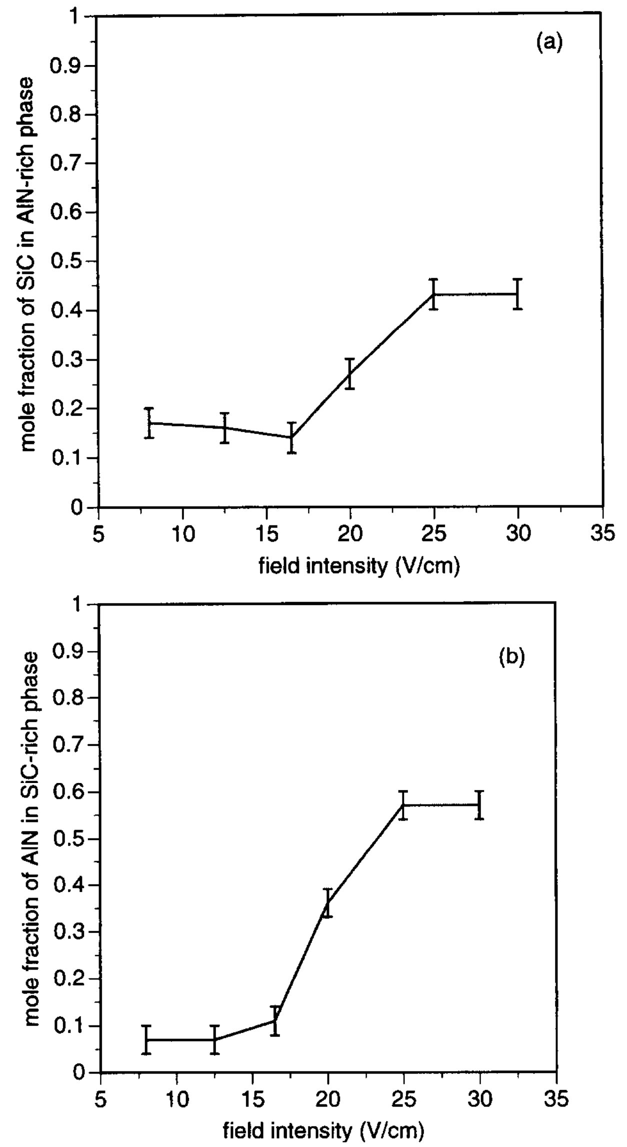

Fig. 6. Compositions of the SiC-rich and AlN-rich phases as a function of field.

We now examine these results in light of reported phase equilibria between AlN and SiC. Figure 7 shows a tentative phase diagram for these two ceramics.[2] According to this diagram, a solid solution with a composition of 57 mol% AlN (corresponding to the product of eqn (1)) can be obtained if the temperature is above about 1960°C. Below this temperature, the product is a mixture of two phases whose compositions depend on temperature according to the diagram. It is therefore instructive to relate the information of Fig. 6 to the observed combustion temperatures. Figure 8 shows the effect of the applied field on the combustion temperature of reaction eqn (1). The temperature increases from 1660°C at the lowest applied (8 V cm^{-1}) to 1980°C at a field of 25·0 V cm^{-1}. At 1660°C, the composites of the SiC-rich phase according to Fig. 7 are about 10 mol% AlN which is in reasonable agreement with the calculated composition from the experimental results,

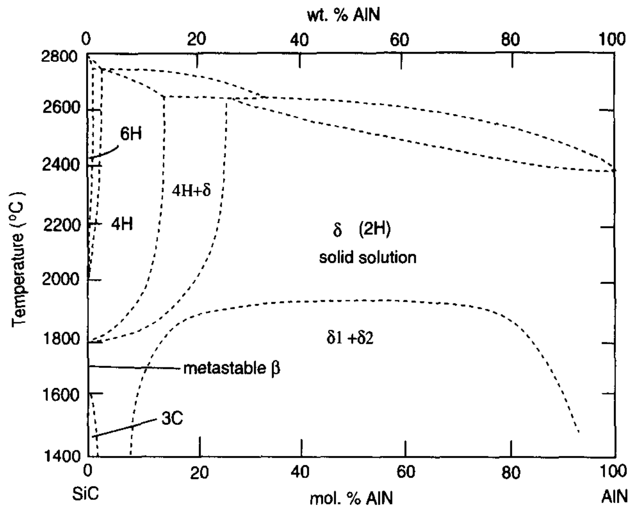

Fig. 7. Binary diagram of AlN–SiC.[2].

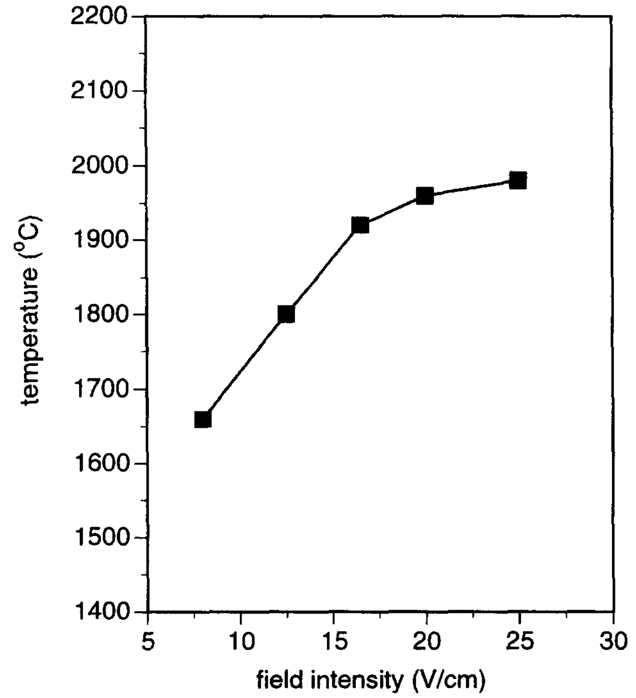

Fig. 8. Effect of field on the combustion temperature.

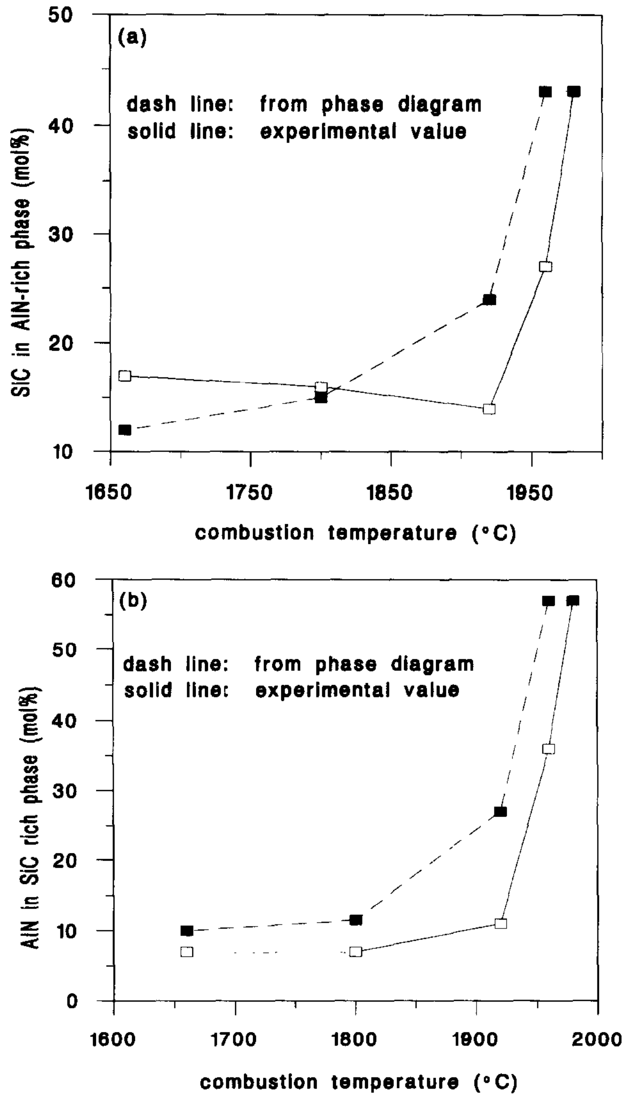

Fig. 9. The dependence of composition on temperature: experimental and phase diagram data: (a) SiC-rich phase, (b) AlN-rich phase.

Fig. 6(a), ~7 mol%. At a field of 16·5 V cm^{-1}, 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^{-1}, the combustion temperature is 1980°C, a temperature corresponding to a complete solid solution on the phase diagram and consistent with the experimental observations. The dependence of the composition of the SiC-rich phase on combustion temperature is shown in Fig. 9(b) for the experimental results and those obtained from the tentative diagram, Fig. 7.

The corresponding results for the AlN-rich phase have a generally similar trend but with some deviation at fields between 8 and 16·5 V cm^{-1}, although the combustion temperature increased as the field was increased in this range. The calculated composition of this phase (in mol% SiC) decreased slightly, probably due to experimental uncertainties. At higher fields, however, the results are consistent with the trend for the SiC-rich phase, as can be seen in Fig. 9(a).

To understand the mechanism of formation of the AlN–SiC composites, experiments were carried out in which the field was interrupted after the wave had partially advanced through the sample. Five visually distinguishable regions are seen in a sample partially combusted at 16·5 V cm^{-1}, Fig. 10. Results of X-ray diffraction analysis on these regions are given in Table 1.

Region 1, (ahead of the frozen wave) is composed of reactant phases only. Region 2 was found to have the same phases and thus its distinction from Region 1 is only visual, probably due to the presence of Al in the form of a solidified melt.

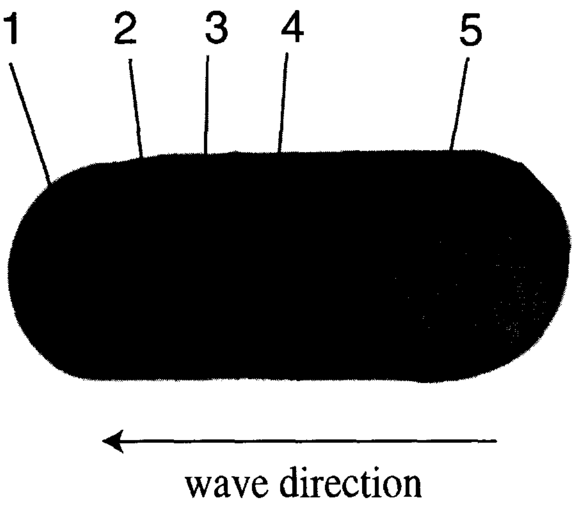

Fig. 10. Quenched reaction front in the synthesis of AlN–SiC composites; numbered zones correspond to the regions in Table 1.

Table 1. X-ray analysis of regions of electrically quenched sample (Fig. 10) E = 16·5 V cm^{-1}

Region	*Phases*
1	C, Al, Si_3N_4
2	C, Al, Si_3N_4
3	C, Al, Si_3N_4, Si, AlN
4	C, Si, SiC/AlN (ss), Si_3N_4(tr)
5	SiC/AlN (ss)

ss = solid solution; tr = trace.

Although no reaction has taken place in this region, the temperature exceeded the melting point of aluminum. The first evidence of a reaction is seen in Region 3 where, in addition to the three reactant phases, minor amounts of AlN and Si phases are detected. Region 4 contained SiC-rich and AlN-rich phases along with carbon and silicon and a trace of Si_3N_4. Finally, behind the combustion front, Region 5, a product forms containing the SiC-rich and AlN-rich 2H phases. At this field value (16·5 V cm^{-1}) the product did not form a complete solid solution, as indicated earlier. The above results suggest that the process begins with the dissociation of the silicon nitride as the first step in the synthesis of the composite. This is followed, first, by the formation of the AlN phase and subsequently by the formation of the AlN-rich and the SiC-rich phases.

4 Summary and Conclusions

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^{-1}. Products obtained under the influence of fields $8 < E < 25$ V cm^{-1} 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^{-1}, the product is a complete solid solution. Synthesis under a higher field (30 V cm^{-1}) increased the randomness of the solid solution. X-ray analysis on an 'electrically' quenched sample revealed the sequence of the field-activated reaction between Si_3N_4, Al, and C. The process begins with the dissociation of silicon nitride and the formation of AlN, this is followed by the formation of the AlN-rich and SiC-rich phases of the composite. The results of this investigation demonstrate the use of the electric field as a processing parameter in the synthesis of nitride composites and solid solutions.

Acknowledgement

This work was supported by a grant from the Materials Science Division ARO.

References

1. Ebbinghans, B. B., Lawrence Livermore National Laboratory, Personal Communication, 1996.
2. Zangvil, A. and Ruh, R., *J. Amer. Ceram. Soc.*, 1988, **71**, 884.
3. Miura, M., Yogo, T. and Hirano, S., *J. Mater. Sci.*, 1993, **28**, 3859.
4. Watanabe, R., Kawasaki, A., Tanaka, M. and Li, J. F., *Int. J. Refract. Metals Hard Mater.*, 1993, **12**, 187.
5. Landon, M. and Thevenot, F., *Ceram. Intern.*, 1991, **17**, 97.
6. Kuo, S. Y. and Virkar, A. V., *J. Amer. Ceram. Soc.*, 1990, **73**, 2640.
7. Ruh, R. and Zangvil, A., *J. Amer. Ceram. Soc.*, 1982, **65**, 260.
8. Rafaevich, N. B., Tsvetkov, V. F., Komov, A. N. and Losevskaya, S. G., *Inorganic Materials*, 1990, **26**, 818.
9. Rafaniello, W., Plichta, M. R. and Virkar, A. V., *J. Amer. Ceram. Soc.*, 1983, **66**, 272.
10. Li, J. and Watanabe, R., *J. Mater. Sci.*, 1991, **26**, 4813.
11. Xue, H. and Munir, Z. A., *Int. J. SHS*, 1996, **5**, 229.
12. Munir, Z. A., *Ceram. Trans.*, 1995, **56**, 39.
13. Munir, Z. A., Lai, W. and Ewald, K., US Patent No. 5,380,409, 1995.
14. Feng, A. and Munir, Z. A., *J. Appl. Phys.*, 1994, **76**, 1927.
15. Gedevanishvili, S. and Munir, Z. A., *Scripta Metall. et Mater.*, 1994, **31**, 741.
16. Shon, I. J. and Munir, Z. A., *Mater. Sci. Eng.*, 1995, **A202**, 256.
17. Feng, A. and Munir, Z. A., *Metall. Mater. Trans.*, 1995, **26B**, 587.
18. Gedevanishvili, S. and Munir, Z. A., *J. Mater. Res.*, 1995, **10**, 2642.
19. Feng, A. and Munir, Z. A., *Metall. Mater. Trans.*, 1995, **26B**, 581.
20. Xue, H. and Munir, Z. A., *Metall. Mater. Trans.*, 1996, **27B**, 475.
21. Feng, A. and Munir, Z. A., unpublished results.
22. Feng, A. and Munir, Z. A., *J. Amer. Ceram. Soc.*, 1996, **79**, 2049.