

Combustion synthesis of AlN–SiC solid solution particles

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Abstract

The feasibility of synthesising AlN–SiC solid solution ceramics by combustion synthesis (CS) reaction is demonstrated through igniting the mixtures of aluminium, silicon and carbon black under different nitrogen pressure values. The effects of the nitrogen pressure and the atomic ratio of (Si + C)/Al on the crystalline phases formed in the reaction product and on the characteristics of combustion behaviour were investigated. Combining thermodynamic analysis and the combustion characteristics, the reaction sequence and the formation of AlN–SiC solid solution by CS were explained. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Aluminium nitride (AlN) has recently become an attractive ceramic material because of its excellent properties such as low density, high thermal conductivity, electrical resistivity, mechanical strength and good oxidation and thermal shock resistance. It has been considered for many applications, such as electronic substrates, cutting tools, heat sinks, and many high temperatures structural components.^{1–3} However, its potential use in load-bearing applications, is limited by its lack of toughness and reliability. AlN and SiC have similar 2H crystal structures, and crystal patterns. Culter et al.⁴ have proposed that AlN and SiC could form a complete solid solution, which could improve the mechanical performance of the ceramic materials so obtained because of their similar structures and high temperature properties.

Numerous laboratory-scale methods for the synthesis of AlN–SiC solid-solution have been reported.^{5–9} However, the development and application of AlN–SiC solid solution has been restricted because of its fabricating conditions are very rigorous, requiring temperatures higher than 2000°C.

Combustion synthesis has many advantages in comparison with solid state reaction synthesis such as the simplicity of the process, lower cost, higher purity of the products, and so on, which has attracted the interest of many researchers recently. Z.A. Munir et al.^{10,11} fabricated the AlN–SiC solid solution through igniting a mixture of Al, C and Si₃N₄ powders in a nitrogen atmosphere assisted by an electric field.

In this paper, the fabrication of AlN–SiC solid solution is proposed through igniting a mixture of Al, Si and C powders in nitrogen atmosphere but without any assisted electric field, and investigated in an attempt to overcome the usual barrier of rigorous fabricating conditions of AlN–SiC solid solution. Al/N₂ is a highly exothermic reaction system (–318kJ/mol), without preheating. In nitrogen atmosphere, Al powder can realise self-propagating combustion that can originate very high temperatures. The addition of AlN powder in the reactant solid/gas mixture is required to decrease the combustion temperature for complete reaction and avoid excessive melting of Al. On the other hand, Si/C is a low exothermic reaction system (–69.5 kJ/mol) that requires preheating of the reactants up to about 1200°C for realising propagating combustion. Therefore, the combination of these two different reaction systems together could superimpose their complementary characters. The quantity of heat generated from the Al/N₂ system can support self-propagating combustion of the

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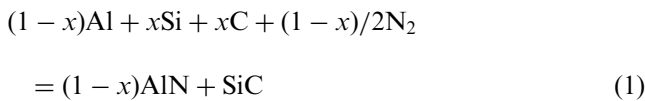
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Si/C system and, at the same time, the addition of AlN as diluent can be avoided.

2. Experimental procedure

The CS assembly was formed by a combustion chamber, temperature acquiring system, power supply, gas supply and vacuum system as schematically shown in Fig. 1. A steel cylinder (out diameter 150 mm, inner diameter of 110 mm, height 360 mm) formed the outer housing of the reactor. The structure of CS reactor has been reported in a previous paper.¹²

The combustion synthesis reaction in this paper can be described as



The Al, Si and C powders, with the properties listed in Table 1, were mixed according to the proportions of $x = 0.00; 0.30; 0.50; 0.60;$ and 0.85 (atomic fraction) in ethanol followed by ball milling for 8 h and then dried in air. The mixture of powders was put into a porous crucible, which was then placed into the CS chamber. Evacuation was performed up to a vacuum of 10^{-4} MPa was reached. The mixed powders were then ignited by passing an electric current of 20 A through a tungsten coil at required nitrogen pressure values. The combustion reaction temperature and velocity were measured

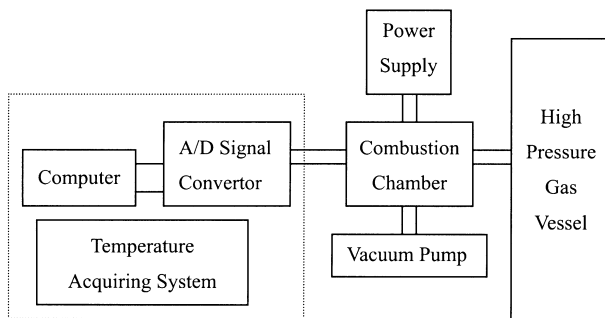


Fig. 1. Schematic drawing of the CS assembly.

Table 1
Properties of the starting reactant powders

Powders	Purity	Average diameter	Impurity			
			Fe wt%	Si wt%	C wt%	O wt%
Al	>99%	20 μm	<0.2	<0.15	—	—
AlN	>99%	1 μm	<0.03	—	<0.01	<0.5
C	>99%	0.01 μm	<0.02	<0.05	—	—

through the voltage of W/3%Re–W/25%Re thermocouples, which were directly inserted into the samples. The phase formation and microstructure of combustion products were identified by XRD (Cu target, K_{α}) and SEM [SCAN360 (Cambridge S-360, England)] respectively.

3. Results and discussion

3.1. Effect of nitrogen pressure on combustion reaction

The influence of nitrogen pressure on the crystalline phases formed was studied for $[x = 0.30$ in Eq. (1)]. Fig. 2 shows the XRD spectra from the reaction products obtained under different nitrogen pressure values. It can be seen that the peaks of Al and Si were weakened gradually as the nitrogen pressure increased. The peaks of Al and Si disappeared completely when the nitrogen pressure increased to 12 MPa. In these conditions, the combustion products are composed of AlN–SiC solid solution, which was confirmed by measuring the lattice parameters with the approximate a_0 values of about 3.102 under different nitrogen pressures. This value is in agreement with 3.1025 of a homogeneous solid solution of SiC and AlN, calculated from Vegard's law. Si_3N_4 and Al_4C_3 were not detected by XRD in the reaction products.

Both combustion temperature and velocity of combustion wave increased with increasing of nitrogen pressure, Table 2. This is a typical phenomenon observed in gas–solid CS reaction systems. The possible reason is

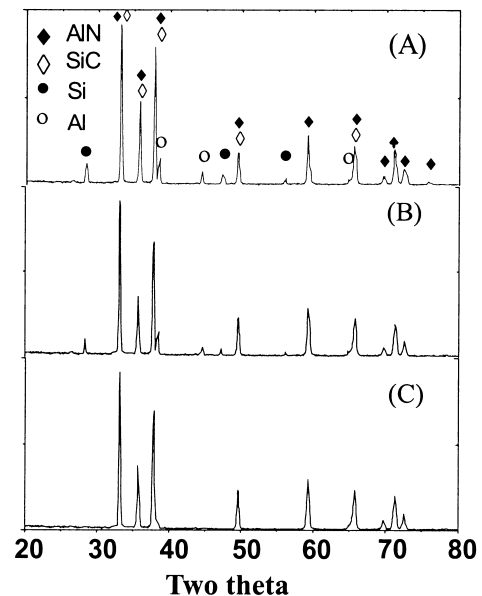


Fig. 2. XRD patterns of the combustion products obtained under different nitrogen pressure values for $x = 0.30$ (A) 3 MPa; (B) 8 MPa; (C) 12 MPa.

that the nitrogen permeability was improved with increasing the nitrogen pressure, accelerating the nitridation of aluminium and increasing the quantity of heat dispersed. The net energy for driving the reaction was enhanced. This explains why the peaks of Al and Si were weakened with the increasing of the nitrogen pressure, and disappeared under 12 MPa, Fig. 2.

3.2. Effect of composition on combustion reaction

The influence of the starting composition on the kinetics of the combustion reaction, temperature reached and crystalline phase formation was carried out under 8 MPa nitrogen pressure. The products obtained were composed of AlN–SiC solid solution with a small amount of Si, Fig. 3. For $x=0.30$, a small amount of Al was also detected, besides Si, Fig. 3 (a). The velocity of combustion wave and the combustion temperature decreased with the increasing values of x , Table 3.

Table 2
Effect of nitrogen pressure on the combustion temperature combustion wave velocity ($x=0.30$)

N ₂ pressure (MPa)	Combustion temperature (°C)	Velocity of combustion wave (mm/s)
3	1810	0.98
8	1940	1.70
12	2090	2.31

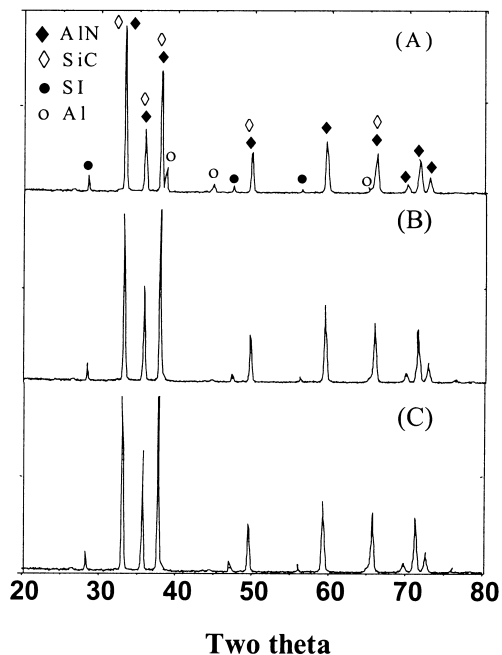


Fig. 3. XRD patterns of the combustion products obtained under 8 MPa nitrogen pressure for: (A) $x=0.30$; (B) $x=0.50$; (C) $x=0.60$.

When the atomic ratio of (Si + C)/Al increases, the proportion of low exothermic system becomes more important in detriment of high exothermic system, Al and N₂. As a consequence, the combustion temperature decreases, reducing of driving energy for propagating the combustion wave and the velocity of the combustion reaction decreases. Increasing of the proportion of Si and C is equivalent to increasing the amount of diluent in the starting composition, which is beneficial for nitridation of Al powder. Therefore, the peaks of Al vanished completely in Fig. 3 (b) and (c).

3.3. Thermodynamic and mechanism analysis of the CS reactions

There are two possible reactions among Si, C and N₂:



Combining Eqs. (2) and (3) gives:



Whether the Si₃N₄ or the SiC is formed is determined by the free enthalpy variation of Eq. (4). It is well known that the free enthalpy of a solid or a liquid substance SiC, Si₃N₄ and C does not change with pressure, while the enthalpy of nitrogen gas changes with pressure as follows:

$$G_{\text{N}_2} = G_{\text{N}_2}^0 + RT \ln P_{\text{N}_2} \quad (5)$$

Then, the free enthalpy variation of Eq. (4) can be determined from the balance

$$\Delta G = 3G_{\text{C}}^0 + G_{\text{Si}_3\text{N}_4}^0 - 2G_{\text{N}_2}^0 - 2RT \ln P_{\text{N}_2} - 3G_{\text{SiC}}^0 \quad (6)$$

The reaction reaches equilibrium conditions when $\Delta G=0$. This enables the rewriting of Eq. (6) as follows:

$$\ln P_{\text{N}_2} = \frac{3G_{\text{C}}^0 + G_{\text{Si}_3\text{N}_4}^0 - 2G_{\text{N}_2}^0 - 3G_{\text{SiC}}^0}{2RT} \quad (7)$$

The free enthalpy in the above equation can be obtained from literature,¹³ and the dependence of $\ln P_{\text{N}_2}$ on the temperature can be shown in Fig. 4. For

Table 3
Velocities of the combustion wave under different x values

x	0 atm%	30 atm%	50 atm%
Combustion temperature (°C)	2120	1940	1800
The velocity of combustion wave (mm/s)	2.94	1.70	1.57

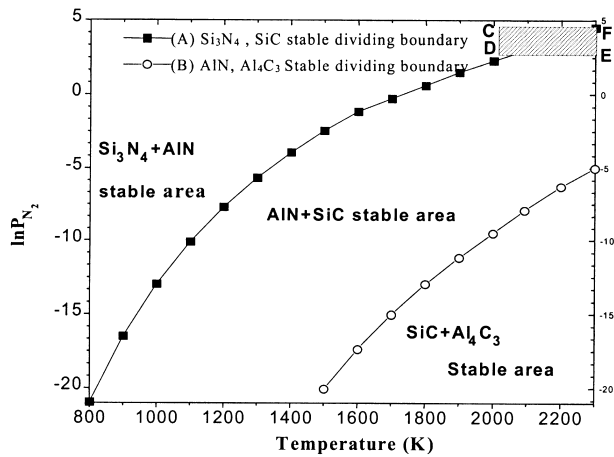


Fig. 4. Stability diagram of the phases formed in the CS reaction products at different nitrogen pressures and temperatures.

values of $\ln P_{N_2}$ located above the curve A, $\Delta G < 0$ in the Eq. (6), and the reaction (4) would go towards the right leading to the formation of Si_3N_4 . While the $\ln P_{N_2}$ values are located below the curve A, the reaction (4) would go towards the left, and SiC would be formed. In the same way, when the values of $\ln P_{N_2}$ are located above the curve B in Fig. 4, would result in the formation of AlN, otherwise, Al_4C_3 would be formed.

Under the experimental conditions used in this research work, the range of the highest combustion temperature varied from 2070 to 2300 K; while the nitrogen pressure values varied from 3 to 12 MPa. These conditions correspond to the CDEF rectangle shadow area near the boundary of SiC and Si_3N_4 stable area. The actual combustion temperatures were higher than the melting points of Al and Si. Therefore, Al and Si would melt during the combustion reaction, which hindered the permeating of nitrogen towards the inside of the sample. So, the nitrogen pressure inside the sample should be lower than outside. In this case, the ranges of temperature and pressure are dislocated to the stable area of AlN and SiC, Si_3N_4 and Al_4C_3 would not be formed.

It can be found from Fig. 4 that under low temperature and high nitrogen pressure, ΔG in reaction (4) is less than zero. Under these conditions it is easier to form Si_3N_4 , than SiC.

The relationship between combustion temperature and reaction time is shown in Fig. 5 for different starting compositions and under a constant nitrogen pressure of 8 MPa. Following the highest point of combustion temperature, an approximate platform area appears in Fig. 5 (curves B and C). At the decreasing stages of combustion temperature, the curves B and C dropped slowly. This indicates that an after-burning phenomenon has occurred. In the combustion reaction of pure Al powders in the nitrogen gas (curve A), this phenom-

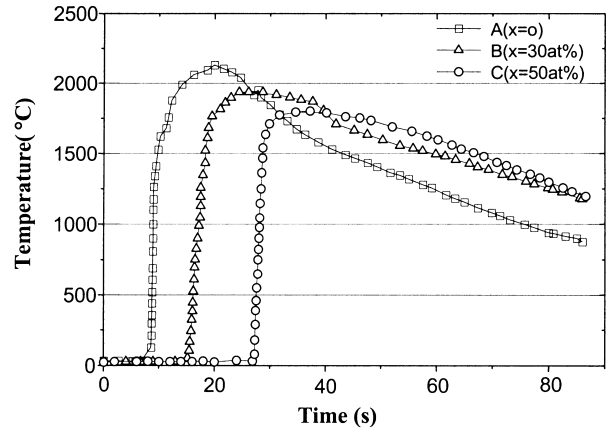


Fig. 5. Dependence of combustion temperature on time under 8 MPa for $x = 0.00$; $x = 0.30$; $x = 0.50$.

enon does not appear. From the above experimental observations and thermodynamic analysis, the formation of AlN–SiC solid solution is proposed to occur at the stage of after-burning combustion. Similar results were obtained by Osama Yamada¹⁴ in the research of formation of SiC from Si and C under 3–12 MPa nitrogen pressure. He proposed that Si powder would firstly react with N_2 , giving out a lot of heat. The combustion temperature could reach about 1800°C, and then Si_3N_4 would decompose and Si vapour would react with C to form SiC. Therefore, the combustion reaction sequence of Al, Si, C and N_2 system can be proposed as follows. Firstly, AlN and Si_3N_4 would be formed, with the combustion temperature reaching about 1800°C. At this temperature the rate of temperature increase slows down due, probably to the induced decomposition of Si_3N_4 , and then the AlN–SiC solid solution starts to be formed. The formation of AlN–SiC solid solution has two possible ways: (1) SiC formed firstly, then reacted with AlN to form AlN–SiC solid solution; (2) Si and C entered into the AlN crystal lattice directly to form AlN–SiC solid solution. In the first way, more energy would be required than in the second way because the Si–C bond must rupture before Si and C entered into the AlN crystal lattice. In the present experiments, Si was found in the combustion products, while no SiC was detected. Therefore, it is confirmed that AlN–SiC solid solution would be formed according to the second way. As AlN–SiC solid solution is being formed, the quantity of heat will continue to be given out by the nitridation of unreacted aluminum powder. At this time, the sum of releasing heat from nitridation of aluminium and formation of the AlN–SiC solid solution was more than the sum of absorption heat from decomposing of Si_3N_4 and radiating heat to the environment. The temperature of the reaction system kept on increasing, although at a lower speed up to reaching maximum values of 1940 and 1810°C, for the curves B

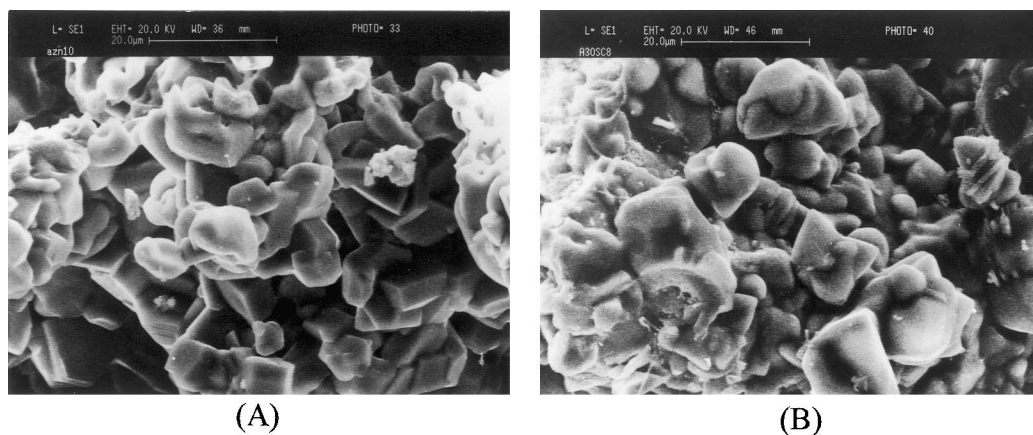


Fig. 6. Micrographs of the combustion products obtained for $x=0.30$, under different nitrogen pressure values: (A) 3 MPa; (B) 8 MPa.

and C, respectively, (Fig. 5). With the continuous nitridation of aluminium powders, the quantity of unreacted aluminium decreases, and the quantity of aluminium participating in nitridation reaction became less per unit time. It means that the quantity of releasing heat decreased gradually. Accordingly, an approximate platform area appears on B and C curves in Fig. 5 where the sum of releasing heat from nitridation of aluminium and formation of the AlN–SiC solid solution is of the same magnitude as the sum of the heat consumed on decomposing Si_3N_4 and radiating to the environment. Whereafter, the combustion temperature began to decrease gently. This gently decreasing suggest that the atomic diffusing of Si and C into the AlN crystal lattices experience a little more time than that required for the formation of crystalline AlN from Al and N_2 . When the temperature decreases to a certain value, Si and C can not diffuse any more into AlN crystal lattice to form the AlN–SiC solid solution because of lacking enough energy. As a consequence, the Si and C will remain in the combustion products, as observed. Increasing and keeping high combustion temperature would be very important for removing the residual Si and C in final combustion products.

3.4. The effect of nitrogen pressure on the microstructure of combustion products

The final products are very loose and could be easily milled into powders. The crystalline degree of combustion product obtained under 3 MPa is more perfect than that formed under 8 MPa as shown in Fig. 6. The change of nitrogen pressure from 3 to 8 MPa means an increasing concentration of one reagent involved in the CS reaction. This would lead to faster kinetics of the crystal growth. In these conditions, the species added to the crystal lattice might not have enough time to search for the more stable positions at the surface of the crystal and some defects would result. This explains why the

crystal surfaces of the powders obtained at 8 MPa are less well defined than those formed at 3 MPa.

4. Conclusions

1. When the atomic proportion of Si and C to Al is 3–7, the combustion temperature and combustion propagating wave velocity increased with increasing of nitrogen pressure. The amounts of Al and Si in the reaction products decreased gradually, and at last vanished under 12 MPa of nitrogen pressure.
2. When the nitrogen pressure was 8 MPa, the combustion temperature and the combustion propagating wave velocity decreased with increasing of the atomic ratio (Si + C)/Al. Concomitantly, the amount of Al in the reaction products decreased gradually, even vanished for $x \geq 0.50$, while the amount of Si in the reaction products almost did not change.
3. The results suggest the following sequence for the formation of the AlN–SiC solid solution from Al, Si, C and N_2 through CS process: Firstly, Al and Si reacted with N_2 to form AlN and Si_3N_4 increasing the combustion temperature rapidly to about 1800°C . At this temperature level Si_3N_4 starts to decompose to Si vapour, then Si and C atoms diffuse into the AlN crystal lattice to form AlN–SiC solid solution.
4. Increasing and keeping the combustion temperature at a relatively high level are the key to decrease the unreacted Si in the combustion products.

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