

PREPARATION OF BN-Si₃N₄ NANOSTRUCTURED COMPOSITES

L.F.Krushinskaya, G.N.Makarenko, I.V.Uvarova,
I.I.Timofeeva, L.P.Isayeva
Institute for Problems of Materials Science NAS of
Ukraine
3, Krzhizhanovsky str, 03142, Kyiv, Ukraine
tel: (+440)424-1533,
e-mail: uvarova@materials.kiev.ua

Abstract

The process of boron silicide nitration in nitrogen and ammonia media has been studied. The composite powders of boron and silicon nitrides were established as the products of nitration. By using the boron silicide compounds instead of boron and silicon powder mixture it can be possible to decrease the temperature of BN and Si₃N₄ formation up to 1200 and 1400 °C, correspondingly. Without using the catalytic additions, the BN and Si₃N₄ are generated at 1500 and 1700 °C, correspondingly over a long period of time. Decreasing the temperatures and time of nitration one can increase the dispersity of final products.

The nitration by ammonia occurs more intensive than that by nitrogen and the boron and silicon powder nitrides are more dispersive and have the specific surface area about 20 m²/g.

The dispersity of BN and Si₃N₄ composites can be increased by preliminary mechanical activation of boron silicide by intensive milling. In this case the temperature of nitration decreases up to 1100 °C and as a result of this the composite powders of boron and silicon nitrides have a size of particles about 50-70 nm.

INTRODUCTION

High-temperature composite materials of the BN-Si₃N₄ system are of great interest due to a wide range of applications such as automobile components, refractory nozzles, sliding gates, break rings for the horizontal continuous casting of steel, friction assemblies operating at high temperatures in aggressive media. In a number of works [1-2], it has been shown that the use of boron nitride as a minor phase increases significantly the fracture toughness and thermal shock resistance, which are sensitive to the grain size of ceramics.

RESULTS AND DISCUSSION

In the present work, the nitration process of boron silicide in a nitrogen and ammonia atmospheres was investigated with the aim of preparing nanocrystalline powders of the BN-Si₃N₄ system. The influences of the nitration temperature, exposure time, nitration atmosphere, compositions and dispersion of initial boron silicide powders on the nitride formation process and nitrogen content in products of nitration were investigated.

As a starting material, boron silicide having a rhombohedral lattice and characterized by a wide region of homogeneity from B_{2,8}Si to B₄Si [3] was

chosen. Boron silicide, compared to phases that were expected to form during nitration, is much less stable, which follows from thermodynamic characteristics presented in Table 1.

Table 1. Thermodynamic characteristics of the strengths of the chemical bonds of BN, Si₃N₄ и B₄Si [4,5]

Characteristic	Compound		
	BN	Si ₃ N ₄	B ₄ Si
Melting point, T _m , K	3240 (under pressure of N ₂)	2250 (dissociation at a pressure of N ₂ =100 kPA)	1600 (decomposes)
Heat of formation, -Δ _f H ⁰ (298 K), kJ/mole	250.5	757.8	86.56
Atomization energy, Δ _{at} H ⁰ (298 K), kJ/mole (kJ/g-atom)	1286.92 643.45*	40285.53 575.50*	2701.16 540.32*

*calculation

The comparative investigation of nitration of boron silicide powders of different dispersion and composition was performed on the initial and mechanically activated powder with the B₄Si B_{2,8}Si compositions. Both powders were prepared by synthesis from elements. The chemical compositions and specific surface areas of the powders are given in Table 2.

Table 2. Characteristics of initial boron silicide powders

Boron silicide	Content, mass %				Specific surface area, m ² /g
	B	Si	Si _{cb}	Fe	
B ₄ Si	62.45	35.9	0.9	-	7.09
B _{2,8} Si	52.0	48.1	-	0.9	2.99

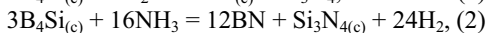
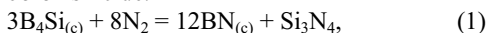
The initial B₄Si powder was mechanically activated in a planetary mill in a liquid nitrogen atmosphere. The total time of the operation was 40 min. After mechanical activation, the powder contained 5.12 mass % of iron and 0.65 mass % of oxygen; its specific surface was 10.46 m²/g.

The nitration of the initial boron silicide powders was performed in a resistance furnace in a nitrogen and an ammonia flow in the temperature range 1200—1450°C with isothermal exposures for 1-5 h, and the activated powder was nitrated in the temperature range 1000-1400 °C with exposures for 1-5 h.

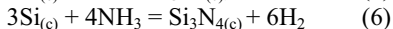
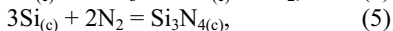
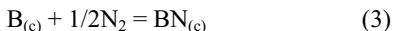
The compositions of the reaction products were assessed on the base of the data of the chemical and X-ray phase analyses using standard procedures. The

specific surfaces were determined by the thermal nitrogen desorption method.

From the change of the Gibbs free energy ($\Delta_r G^0(T)$) in the temperature range 1000–2000 K the probabilities of development of nitration reactions of boron silicide.



and, for comparison, the probabilities of development of the nitration reactions of boron and silicon were evaluated



In the calculation, the following equations were used:

$$\Delta_r G^0(T) = \Delta_r H(298) - T\Delta_r \Phi'(T)$$

$$\Delta_r H(298) = \sum \Delta_f H^0(298)_{\text{prod.}} - \sum \Delta_f H^0(298)_{\text{init.}}$$

$$\Delta_r \Phi(T) = \sum \Phi(T)_{\text{prod.}} - \sum \Phi(T)_{\text{init.}},$$

where $\Delta_f H^0(298)$ is the standard enthalpy of formation; $\Phi(T)$ is the reduced isobari-isothermal potential at a temperature T ; subscripts: r – reaction, prod. – reaction products, init. – initial substances, c – condensed state.

The thermodynamic characteristics of the components were taken from [4–7].

The results of the thermodynamic calculation are shown in Fig. 1. The results of the experimental investigation of nitration are presented in Table 3. The chemical analysis of the products of nitration of the initial boron silicide powders shows that the intensity of the nitride formation process depends on the ratio of boron to silicon.

The nitration of the $B_{2,8}Si$ powder in a nitrogen flow proceeds somewhat more intensively (despite of its smaller specific surface) than the nitration of the initial B_4Si powder at temperatures to 1450 °C. The nitrogen content in the nitration products of $B_{2,8}Si$ obtained at 1300 и 1400 °C and an exposure for 3 h is higher than that in the nitration products of B_4Si obtained using the same conditions by 4 and 10 mass %, respectively (Table 3). The difference between these powders in the nitrogen content decreases to 1 mass % as the nitration temperature is raised to 1450 °C.

The nitration of the $B_{2,8}Si$ и B_4Si powders proceeds more intensively in ammonia, since the chemical reactivity of dissociated ammonia is larger than that of nitrogen and, moreover, ammonia cleans the surface of particles. These results are substantiated by the thermodynamic calculations (Fig. 1).

According to the X-ray analysis data, boron forms first. It is identified in the nitration products at a temperature of 1200 °C. The formation of silicon nitride begins at temperatures higher by 100–200 °C, which agrees with a significant difference between these compounds in the heat of formation (Table 1). In the whole investigated temperature range, in the reaction products, silicon is present; its amount increases near the temperature of peritectic decomposition of B_4Si and then decreases to traces at the maximal one.

The nitration behavior of the mechanically activated powders during in nitrogen and ammonia is somewhat different. The mechanochemical treatment leads not only to the increase in the dispersion, but also to a rise in the energy of the lattice. As a result, B_4Si becomes more chemically active, and all processes occurring during its nitration shift in the direction of lower temperatures and proceed much more intensively. Moreover, after the treatment of the initial B_4Si powder in the planetary mill, the iron impurity exerts a catalytic influence on the nitration processes.

According to the results of the chemical analysis (Table 3), the nitration of the activated powder begins at a temperature of 1000 °C. Lines of boron nitride were identified in the X-ray diffraction patterns of specimens nitrated at 1100 °C. The formation of silicon nitride begins at 1000 °C. A rise in the temperature to 1400 °C and an increase of the exposure time at the maximal temperature from 1 to 5 h leads to an abrupt increase in the nitrogen contents in the reaction products.

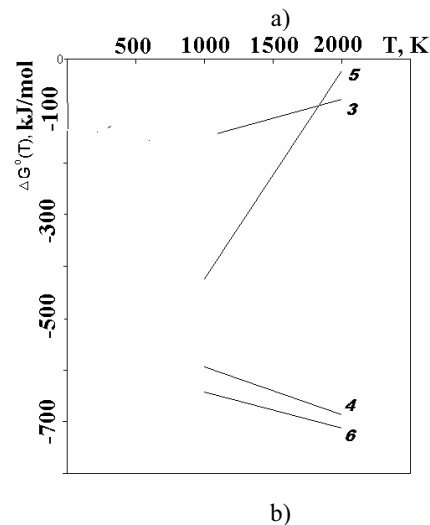
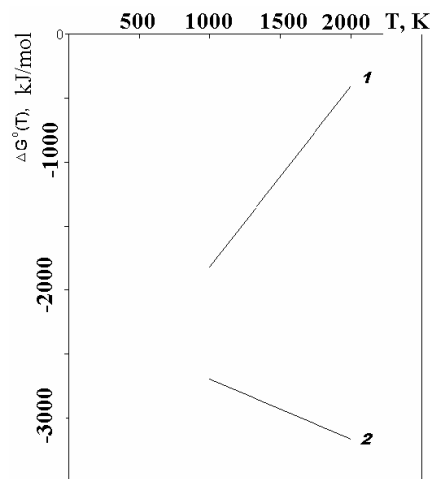


Figure 1. Temperature dependences of Gibbs free energies a – reactions 1, 2; b – reactions 3, 4, 5, 6

Table 3 Data of chemical analysis of nitration products of boron silicide

Boron silicide	Conditions of nitrating			N ₂ content mass %	Specific surface area, m ² /g
	Media	T, °C	Time, h		
Initial powders					
B _{2,8} Si	N ₂	1200	3	8.22	3.07
		1300	3	19.1	2.63
		1400	3	43.4	7.59
		1450	1	-	6.42
		1450	3	47.4	-
	NH ₃	1300	1	19.7	20.31
		1300	3	35.7	16.20
B ₄ Si	N ₂	1300	3	15.7	8.04
		1400	3	33.5	15.13
		1450	1	43.4	15.71
		1450	3	48.7	16.67
		1450	5	49.5	16.92
	NH ₃	1300	3	19.5	21.8
		1400	3	48.8	-
		1450	1	-	17.06
Mechanically activated powders					
B ₄ Si	N ₂	1000	1	1.77	8.42
		1100	1	5.3	8.81
		1200	1	11.0	10.60
		1300	1	35	20.30
		1400	1	44.4	25.7
		1400	3	45	24.33
		1400	5	44.8	24.85
	NH ₃	1300	3	26.9	13.17
		1400	1	42.8	43.56
		1400	3	45.2	31.9

Such an intensive process of formation of boron and silicon nitrides is connected both with the increased activity of the mechanically activated B₄Si [8] and with the catalytic influence of iron [9]. It should be noted that, during the nitration of the mechanically activated boron silicide, silicon nitride first formed in the form of the α-phase, and when the nitration temperature and exposure time were increased, the formation of β-Si₃N₄ was observed; the amount of which rose in comparison with that of α-Si₃N₄. This agrees with data of [8, 10], according to which, in the process of formation of silicon nitride, the α-phase forms in the first minutes of nitration, and then, in the course of the isothermal exposure, annealing of the powders, accompanied by α→β transition, occurs. In the nitration products of the mechanically activated B₄Si powder, besides the basic phases of BN and Si₃N₄, iron boride and iron silicide phases are present in small amounts. As the nitration temperature is raised, the formed iron borides and silicides interact with nitrogen and partially form BN и Si₃N₄ [11]. As this take place, iron silicide phases transform from higher to lower phases.

The nitrogen contents in the powders obtained by nitration of mechanically activated boron silicide in

nitrogen and ammonia differ insignificantly. It is evident that, against the background of the catalytic effect of iron and the increased reactivity of the activated boron silicide, the influence of ammonia does not manifest itself.

To assess the degrees of dispersion of the formed composite powders, the measurement of their specific surface area was carried out. An essential increase in S_{уд.}, which corresponds to a rise in the dispersion of powders (Fig. 2), occurs after the beginning of their intensive nitration. In this case, the preliminary activation of the initial B₄Si powder exerts a particular influence on the dispersion process, which agrees well with data of [10]. The authors of [10] showed that, in the nitration of silicon powder with a highly defective lattice, the failure of coherence on the Si—Si₃N₄ interface occurs in the certain stage of nitration. This results in the fracture of the formed silicon nitride layer, which facilitates the access of nitrogen to the new-formed surface of silicon. According to electron microscopy data, the consequence of this is the much smaller particle of the formed silicon nitride against that of the initial silicon powder. It is assumed that an analogous situation takes place in the formation of boron nitride obtained from mechanically activated B₄Si.

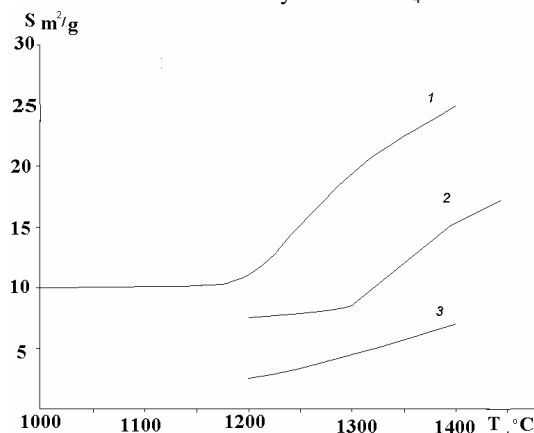


Figure 2 Specific surface area of boron silicide against temperature under nitration in nitrogen:

1 – B₄Si (after mechanical activation); 2 – B₄Si; 3 – B_{2,8}Si

An analysis of measured specific surface area data of the obtained powders (Table 3) indicate that S_{уд.} of the powders nitrated in ammonia are higher than those of powders nitrated in nitrogen. According to [9], this can be connected with the participation of reactions in a gaseous phase, that proceed during interaction of silicon and boron with products of incomplete dissociation of ammonia, in the processes of formation of nitride phases.

In the comparison of the specific surface area of all powders, much higher values for powders obtained by nitration of the mechanically activated boron silicide powders in ammonia attract attention. Their specific surface area 32—43 m²/g, which corresponds to a particle size of 70–50 nm of powders of the 60 BN—40 Si₃N₄ composite material.

Conclusions

1. It is shown that the nitration products of boron silicide powders in a nitrogen and ammonia atmospheres are composite powders of boron and silicon nitride. In this case, the temperatures of formation of BN и Si₃N₄ are substantially lower than those in the case of nitridation of elementary boron and silicon, which makes it possible to obtain nanosized powders of these nitrides.

2. In ammonia, the nitride formation process is more intensive than in nitrogen and allows to obtain thin powders with a specific surface area above 20 m²/g.

3. It was established that the preliminary mechanical activation of boron silicide powder increased significantly its nitration rate, lowered the temperatures of formation of BN и Si₃N₄, and, as a consequence, made it possible to obtain this composition in the nanocrystalline state.

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