

## The Melting Parameters of High-Temperature Nonmetallic Nitrides

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The ranges of temperatures and pressures for the existence of condensed boron, aluminum, and silicon nonmetallic nitrides in thermodynamic equilibrium with an ambient gas were calculated on the basis of reference data. The melting parameters of the high-temperature nitrides mentioned above were investigated experimentally in the nitrogen pressure range of 5–200 MPa. The 99% purity nitride samples were prepared in the form of 4 × 4-mm plates with a thickness of 1 mm. The surfaces of samples were heated with stationary laser beam and analyzed by X-ray technique. The brightness temperature of nonmetallic nitrides was measured at 0.633- $\mu\text{m}$  wavelength using the optical pyrometry method. The apparent melting temperatures were found from the analysis of heating and cooling thermograms. Based on the available literature data on normal spectral emissivity, the true melting temperatures of nonmetallic nitrides were estimated as 3370 K for BN, 3025 K for AlN, and 2775 K for Si<sub>3</sub>N<sub>4</sub>.

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**KEY WORDS:** aluminium; boron; high pressure; high temperature; melting parameters; nitrides; silicon; thermogram.

### 1. INTRODUCTION

High-temperature nonmetallic nitrides (HTNN) of boron, aluminum, and silicon are known to possess high values of electrical resistivity, thermal conductivity, mechanical strength, thermal stability, and resistance to the influence of many chemically aggressive media at high temperatures [1], which may be practically realized only for a poly- or monocrystalline material. Such samples may be produced by growing the crystals from the

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melted initial substance. However, the indicated HTNN decompose on heating under normal conditions before the melting point is reached.

The available literature data give evidence that there are no experimental investigations where parameters (temperature and pressure) corresponding to congruent HTNN melting are investigated. The attempts to melt congruently BN in a graphite cell at pressures of 30,000–80,000 MPa [2] and AlN inside a graphite heater at nitrogen pressures from 10 to 20 MPa [3] were also unsuccessful. The present paper describes the results of investigation of HTNN melting parameters in the temperature range 1300–4000 K at nitrogen pressures in the range 1–200 MPa.

## 2. MEASUREMENTS

### 2.1. Apparatus and Specimens

The computerized experimental facility used for these investigations has been described in detail previously [4]. We note only (see Fig. 1) that BN and AlN samples were heated by a 800-W CO<sub>2</sub> laser with a generated radiation wavelength to 10.6  $\mu\text{m}$  and the Si<sub>3</sub>N<sub>4</sub> sample was heated by a 250-W YAG laser at a wavelength of 1.06  $\mu\text{m}$ . The laser beam was focused onto the sample surface so that the heating spot diameter was about 2 mm.

The equipment for controlling the atmosphere in the high-pressure chamber consists of a vacuum pump, a compressor, and gas cylinders, which makes it possible to maintain inside the chamber the required gas composition under a pressure ranging from 10 Pa to 200 MPa.

The brightness temperature of the sample at 0.633  $\mu\text{m}$  wavelength was measured at the sighting spot (0.6 mm in diameter) by means of an automatic micropyrometer with a time resolution of 10<sup>-4</sup>s; accuracy in

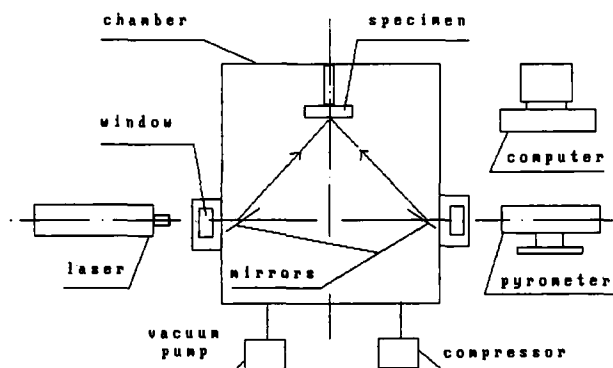


Fig. 1. Principle scheme of the installation.

temperature measurement was 0.5%. The samples were placed in a high-pressure chamber on springy tungsten holders to prevent them from cracking during heating. The laser radiation was introduced into the chamber through a zinc selenide window for the case of BN and AlN and a quartz window for  $\text{Si}_3\text{N}_4$ .

The nitride samples were prepared in the form of  $4 \times 4$  mm plates with a thickness of 1 mm. Pyrolytical BN had a 99.8% purity. We used 99.5% purity AlN with a density of  $2.15 \text{ g} \cdot \text{cm}^{-3}$  and 98.9% purity  $\text{Si}_3\text{N}_4$  with the density of  $2.45 \text{ g} \cdot \text{cm}^{-3}$ .

## 2.2. Procedure

The brightness temperatures of melting for nitrides were measured according to a procedure which has been tested in materials with well-known properties and described in detail previously [5]. The investigation process involved two stages. In the first stage heating and cooling thermograms of nitrides were obtained at a preset nitrogen pressure in the chamber. The aim was to measure the levels of the horizontal plateaus obtained in the thermograms. The specific values of pressure were set in the second stage, in which the sample was heated to a predefined temperature below or above the revealed plateau. After cooling, X-ray structure analysis of the sample was made to determine the composition of the material and ascertain whether it had melted.

## 3. RESULTS AND DISCUSSION

The melting parameters of nitrides were investigated in the following nitrogen pressure range: 1–50 MPa for BN and AlN, and 10–200 MPa for  $\text{Si}_3\text{N}_4$ .

### 3.1. Melting Parameters of BN

The typical thermogram for the variation of brightness temperature of the sample surface, recorded at pressures above 5 MPa, where melting of pyrolytical BN is discovered is shown in Fig. 2 (curve 1).

The thermogram is characterized by the following special features: the horizontal part (plateau) is the temperature level A on the heating curve, which is independent of the nitrogen pressure; the part with the maximum temperature is the temperature level C, which increases with increasing nitrogen pressure.

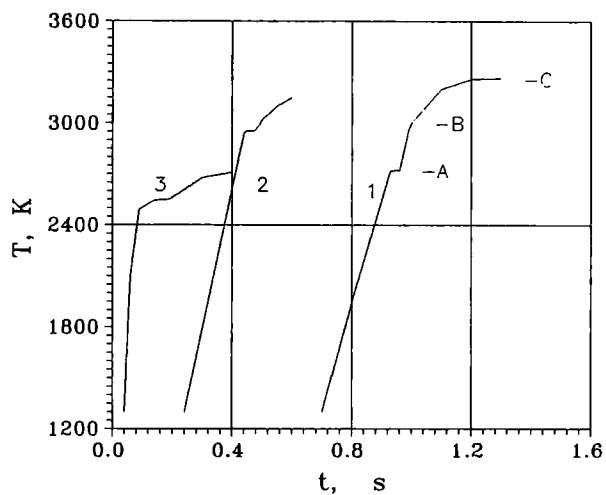


Fig. 2. The heating thermograms of HTNN.  $T$  is the brightness temperature;  $t$  is the time. (1) BN (49 MPa); (2) AlN (32.5 MPa); (3)  $\text{Si}_3\text{N}_4$  (198 MPa).

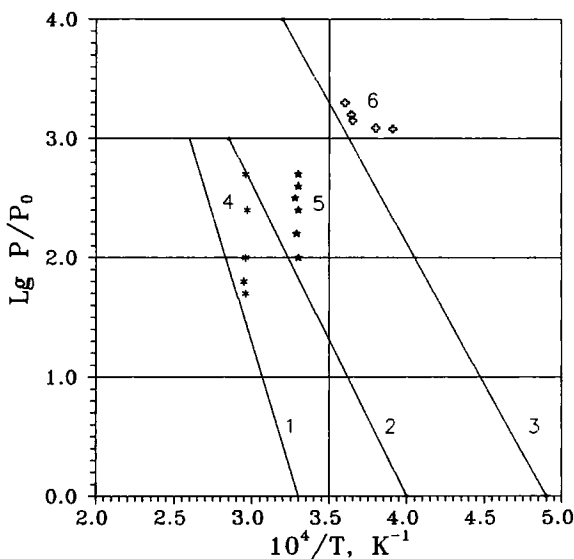


Fig. 3. Dissociation line (solid) and melting (points) of HTNN (1, 4) for BN, (2, 5) for AlN, and (3, 6) for  $\text{Si}_3\text{N}_4$ .  $P$  is the total gas pressure,  $P_0$  is the standard pressure of 1 atm (101,325 Pa), and  $T$  is the temperature.

X-ray investigations show that melting of the sample reveals itself when the heating is stopped in the temperature range between level A and level B. Over  $T_B$  as the brightness temperature increases, the sample surface is covered with boron droplets up to the formation of a solid boron film. The true melting temperature calculated with the use of normal spectral emissivity for pyrolytical BN [6] was 3370 K. In the range of nitrogen pressures 5–50 MPa, the melting temperature is practically unchanged (Fig. 3, cluster of points indicated as 4).

### 3.2. Melting Parameters of AlN

The experiments have shown that quite an appreciable (about 50  $\mu\text{m}$  thick) fused layer of a solid AlN sample can be reliably obtained only if the nitrogen pressure reaches 10 MPa.

Ceramic samples of a fairly high porosity were used for the investigations. Thus, during the initial heating of the sample when its melting temperature was attained, the resulting heating thermogram was strongly affected by the density increase in the material and associated variations of emissivity of the material. This produced a distortion in the heating pattern. During the second and subsequent heating, clearly defined plateaus were obtained at a brightness temperature of 2950 K in the heating thermograms (curve 2 in Fig. 2). As the nitrogen pressure increased, the maximum possible temperature of heating the AlN surface increased, while the plateau level remained practically unchanged. X-ray investigation of samples after the experiments showed that the resultant material was an AlN melt.

The brightness temperature of melting for aluminum nitride at 0.633  $\mu\text{m}$  wavelength is 2950 K at a nitrogen pressure of from 10 to 50 MPa. As for the true melting temperature, its calculation appears to be rather difficult owing to the absence of data on the spectral emissivity of aluminum nitride at these high temperatures. The extrapolation of lower-temperature data [7] leads to values of normal spectral emissivity of about 0.80–0.85 for aluminum nitride at 0.633  $\mu\text{m}$ . Using the value of brightness temperature of melting obtained in the present work, one can obtain the true melting temperature of aluminum nitride to be 3025 K (Fig. 3, cluster of points indicated as 5).

### 3.3. Melting Parameters of $\text{Si}_3\text{N}_4$

The first indication that the silicon nitride sample melted was noted at nitrogen pressures over 120 MPa.

A typical heating thermogram of a silicon nitride sample obtained at a nitrogen pressure in the chamber above 120 MPa is shown in Fig. 2 (curve 3). The temperature characterizing the plateau increases as the nitrogen pressure in the chamber is increased. This plateau cannot be explained by silicon nitride melt formation as was done for other nitrides: the plateau is observed in the thermogram, but no melted silicon nitride is noted. Apparently, the thickness of the melted layer is small and it evaporates completely after heating is turned off.

After the experiment, a crater with crystallized black color formation occurs. X-ray investigation of the samples performed after the experiments has shown the existence of small crystals of silicon nitride on the surface of the crater. The size of the particles is 10–15  $\mu\text{m}$ . The main phase in the layer of thickness up to 85  $\mu\text{m}$  is silicon (probably the solid solution of nitrogen in silicon). It may be considered that in the investigated range of nitrogen pressures, melting of silicon nitride proceeds incongruently. The increase in brightness temperature with increasing nitrogen pressure indicates the same.

Evaluation of the true melting temperature of silicon nitride was made with the use of a value of normal spectral emissivity (about 0.68). This value was obtained from the measurements based on the laser reflectometer method utilizing an integrating sphere [8]. The change in nitrogen pressure in the chamber over 120 MPa causes a variation in the true melting temperature of silicon nitride; at 198 MPa (the upper limit of these experiments) it is 2775 K (Fig. 3, cluster of points indicated as 6).

#### 4. CONCLUSION

Plateaus have been observed in cooling thermograms for all the nitrides. X-ray investigations have shown that under our experimental conditions for BN and  $\text{Si}_3\text{N}_4$ , characterized by noncoordinated evaporation of the compound elements, crystallization of boron and silicon, respectively, took place. In the case of AlN, which has coordinated evaporation, crystallization of AlN was observed.

The position of the experimentally measured melting temperatures with respect to the calculated temperatures of dissociation (according to the method given in Ref. 6 for HTNN under study is shown in Fig. 3.

From the standpoint of crystal growing from the melt of the initial material, which was mentioned above, the most favorable material is AlN. This is due to the fact that a difference of hundreds of degrees between the temperature of melting and that of dissociation for AlN that exists even at 20 MPa and above this pressure provides the possibility of producing AlN melt with a thickness of hundreds of microns.

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## REFERENCES

1. C. V. Samsonov (ed.), *Nitrides* (Naukova Dumka, Kiev, 1968), p. 264.
2. R. H. Wentorf, *J. Phys. Chem.* **63**:1934 (1959).
3. W. Class, NASA-CR-1171 (1968).
4. A. V. Kirillin, A. V. Kostanovsky, and V. L. Vinogradov, *Teplofiz. Vys. Temp.* **22**:1200 (1984).
5. A. V. Kirillin, A. V. Kostanovsky, and V. L. Vinogradov, *High Temp. High Press* **19**:473 (1987).
6. V. L. Vinogradov and A. V. Kostanovsky, *Teplofiz. Vys. Temp.* **29**:1112 (1991).
7. A. E. Sheindlin (ed.), *Radiation Properties of Solid Materials* (Energiya, Moscow, 1974), p. 471 (in Russian).
8. G. I. Daniliants and A. V. Kirillin, Preprint. 1-265. ed. (IVTRAN, Moscow, 1989), p. 33.