

THERMOANALYTICAL STUDY OF THE POLYMORPHIC TRANSFORMATION OF CUBIC INTO GRAPHITE-LIKE BORON NITRIDE

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The polymorphic transformation of cubic into graphite-like boron nitride was studied by using DTA, high-temperature calorimetry and dilatometry over the temperature range 1000–2500 K. The transformation enthalpy was determined to be $+22_{-11}^{+5}$ kJ/mol.

Keywords: boron nitride, high-temperature calorimetry, polymorphic transformation

Introduction

An analysis of papers on studies of the polymorphic transformation of cubic (cBN) into graphite-like boron nitride (gBN) in an inert atmosphere or in vacuum, given in [1], reveals the considerable differences between the experimental data obtained by different authors. This is evidently caused by differences in the structural state and dispersivity of the samples studied, and also in the experimental conditions. It can be concluded from the results that the onset temperature of the polymorphic transformation $cBN \rightarrow gBN$ can vary from 1350 K [2] to 1800 K [3], while the process observed goes on in a wide temperature interval and is fully completed only at temperatures of the order of 2100 K [3].

It should be noted that thermoanalytical investigations of the process have not been made. However, the use of thermal analysis would allow determination not only of the polymorphic transformation temperature range, but (particularly important) also of the sign and value of the corresponding thermal effect. The latter is very topical for corroboration of the new conception of the phase p, T -diagram for BN suggested by one of the present authors [4], which was based on the new

value of the enthalpy of the polymorphic transformation $\text{cBN} \rightarrow \text{gBN}$ given in [5]*

The foregoing situation led us to study this polymorphic transformation by thermoanalytical methods.

Experimental

Samples

As the subjects of the studies, we used 100–200 μm cBN monocrystals grown in the spontaneous crystallization field under high pressure and temperature in the well-known gBN-Mg growth system [7] (cBN-1), and cBN polycrystalline samples (discs 5 mm in dia. and 1–3 mm thick) produced both by using high-pressure – high-temperature sintering of cBN monocrystals (cBN-2) and as a result of direct phase transformation of high-order pyrolytic gBN under similar conditions (cBN-3). X-ray diffractometry showed that the gBN content in the samples studied did not exceed 0.1 mass%. The microimpurity compositions of the samples, established by mass-spectrometry, spectral analysis and X-ray microanalysis, are given in the Table. Ti (0.01%), Ni (0.005%), P (0.003%) and Cr (0.003%) were found only in the cBN-2 samples.

Table 1 Impurities compositions of the cBN samples (Mass %)

	C	O	Si	Ca	Al	Mg	Fe
cBN-1	0.1	0.1	0.05	0.01	0.01	0.2	0.002
cBN-2	0.4	0.3	0.1	0.1	0.09	0.04	0.001
cBN-3	0.04	0.08	0.02	0.005	0.002	0.004	0.002

Differential thermal analysis

DTA of the polymorphic transformation $\text{cBN} \rightarrow \text{gBN}$ was carried out in the temperature range 1000–2500 K, using a VDTA-8M3 thermoanalyser in a static high-purity He atmosphere (less than 0.0006 vol.% of oxygen) at a pressure of 0.12 MPa and a heating rate of 80 deg/min. A sensor with a W-W20%Re string thermocouple was used. This was calibrated for temperature with the procedure described in [8], using the temperatures of polymorphic transformation and melt-

* $\Delta_{\text{tr}}H^{\circ}(298.15\text{K}) = +16.3 \pm 2.7 \text{ kJ/mol}$, and differs essentially from the earlier accepted value, -3.5 kJ/mol [6].

ing of high-purity iron and rhodium (99.999%) and α - Al_2O_3 monocrystals as reference points. The accuracy of the temperature measurements in the range 1500–2500 K was ± 5 deg. 400 mm³ cylindrical crucibles of aluminium or magnesium oxides were used as the sample holders for 200–250 mg cBN-1 samples. In the case of cBN-2 and cBN-3 samples of about 200 mg, 100 μm molybdenum foil plate holders were used. Powdered (for cBN-1) or pellet-like pressed (for cBN-2 and cBN-3) gBN obtained as a result of the total transformation of cBN-1 at 2100 K in dry nitrogen served as the reference in the DTA experiments.

Simultaneous thermal analysis (TG-DTA)

The TG-DTA of cBN-1 samples in the temperature range 300–2450 K was carried out by using an STA 429 NETZSCH thermoanalyser in a static He atmosphere ($p=0.1$ MPa) at a heating rate of 50 deg/min. A sensor with a W3%Re–W25%Re thermocouple and 150 mm³ graphite crucibles were used; metallic tungsten was taken as a reference; the mass of each sample was of the order of 90 mg.

Dilatometry

The thermal expansion of a cBN-3 sample (a 7.49·2.42·1.23 mm³ parallelepiped, cut from a standard disc) was studied in a DL-1500 H SINKU-RIKO high-temperature dilatometer in the temperature range 300–1700 K and in a static He atmosphere ($p=0.1$ MPa) at a heating rate of 5 deg/min. The sample temperature was measured with a Pt-Pt13%Rh thermocouple; the load on the sample was 2.0 g. A single crystal of α - Al_2O_3 ($l_0=10.18$ mm) was taken as a standard.

High-temperature calorimetry

The enthalpy of the studied polymorphic transformation in the temperature range 1300–2000 K was determined experimentally using a KADS-2000 high-temperature heat flux calorimeter [9] in a static high-purity Ar atmosphere (less than 0.0007 vol.% of oxygen) at a pressure of 0.105 MPa. The study was performed in the stage-heating regime with a scanning rate of 50 deg/min; the temperature intervals between isothermic stages (ΔT) were taken equal to 80 deg; the isothermic exposure time was 100 s. A high-temperature calorimetric sensor with a W-W20%Re string thermocouple was used. The sensor was calibrated for temperature using a procedure similar to that described above; the error in the temperature measurements in the range 1300–2000 K was ± 5 deg. 300 mm³ cylindrical crucibles of melted aluminium oxide were used as both sample and standard holders. As the standard, a 180 mg gBN disc (identical in form to the 200–230 mg cBN-2 and cBN-3 samples) was used, which was produced by sinter-

ing at 5 GPa and 2000 K from powdered gBN (99.9%) previously annealed in dry nitrogen at 2100 K for 3 hours.

To take into account the thermal asymmetry of the calorimetric sensor, an experiment with empty crucibles was performed according to the program described. Calibration experiments with high-purity metals (copper, iron, platinum) and α -Al₂O₃ monocrystals as standards showed that the error in the enthalpy measurements was no more than 5% over the entire experimental temperature range.

The equation for calculation of the studied sample enthalpy increment in the temperature interval between two isothermic stages is as follows:

$$\Delta H_s = \Delta H_r \frac{m_r}{m_s} \frac{\int_{\tau_1}^{\tau_2} (T_x - T_s) d\tau - \int_{\tau_1}^{\tau_2} (T_x - T_x') d\tau}{\int_{\tau_1}^{\tau_2} (T_x - T_r) d\tau - \int_{\tau_1}^{\tau_2} (T_x - T_x') d\tau}$$

where ΔH_r is the enthalpy increment for the standard in a given temperature interval; m_r and m_s are the masses of the standard and the studied sample; T_x , T_r and T_s are the temperatures of the empty crucible, the crucible with the standard, and the crucible with the sample studied; T_x' is the temperature of the empty crucible where the standard or a sample is then placed; and τ_1 and τ_2 are the completion times of the corresponding isothermic stages.*

X-ray diffractometry

The degree of polymorphic transformation cBN \rightarrow gBN in the studied cBN samples after the thermoanalytical experiments**, and the structural peculiarities of the gBN formed, were investigated in a DRON-4-07 X-ray diffractometer (CuK α radiation), using the procedure described in [1]. The relative error in the phase composition evaluation did not exceed 10%.

* The mathematical description of the heat balance in a high-temperature calorimetric sensor is given in [10].

** On attainment of the finite temperature in the TA experiment, the sample was quenched by rapid cooling (of the order of 30 deg/s) down to the ambient temperature.

Results and discussion

The results of examination of the cBN-1 samples in the interval 300–2450 K with the STA 429 thermoanalyser showed the absence of any effects in the recorded curves over the temperature interval in which the studied polymorphic transformation occurs (1840–2080 K according to X-ray study of hardened samples). The sample weight loss observed at temperatures above 2100 K is caused by the dissociation of gBN ($P_3=0.6-0.7$)* formed as a result of the studied transformation. It should be noted that the absence of thermal effects in the DTA curves over the whole experimental temperature range examined is apparently caused by the fact that the sensitivity of the sensor used was not sufficient, as both the processes studied (the polymorphic transformation and dissociation) occur in wide temperature ranges and accordingly the corresponding heat flows are extremely small. It should also be taken into account that the heat contact between the sample undergoing polymorphic transformation and the crucible walls and bottom is disturbed owing to the great volume effect of the transformation (+51.5% [1]). Further, this is accompanied by a thermal resistance increase in a thermoanalytical cell, which results in a considerable reduction in the registered DTA signal.

Therefore, the further DTA study of the polymorphic transformation cBN → gBN was performed by using a VDTA-8M3 thermoanalyser, which allows variation of the size and shape of the sample holder and optimization of the thermo-physical parameters of the DTA cell, with an essential increase in the sensitivity of the method.

The results of investigation of different cBN samples indicate that the polymorphic transformation under consideration is endothermic (Fig. 1). The observed difference in the temperature ranges of the transformation under study in dispersive (cBN-1) and compact (cBN-2 and cBN-3) samples is caused by the difference in the conditions of the processes of mechanical stress relaxation at the cBN/gBN interface, due to the great volume effect of transformation mentioned above. Naturally, the relaxation of the generated stresses, preventing the further growth of new phase nuclei, is essentially facilitated in dispersive samples. This makes the polymorphic transformation proceed at temperatures (1910–2100 K) lower than in the case of compact polycrystalline samples (2120–2470 K). It should also be noted that for cBN polycrystalline samples a distinct dependence of the transformation onset temperature (T_0) on the heating rate is observed.

* The 3-dimensional ordering degree, calculated according to the procedure in [11].

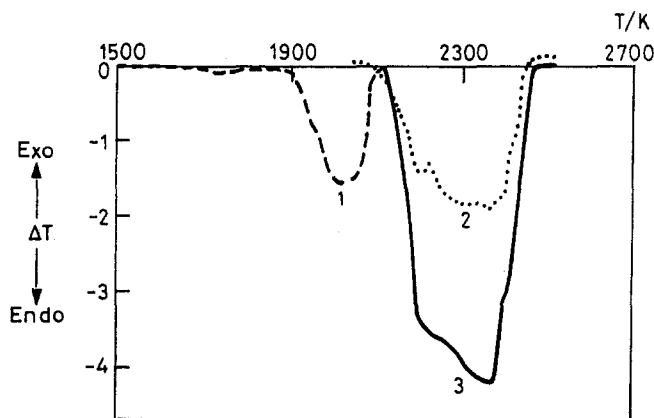


Fig. 1 DTA curves of cBN \rightarrow gBN phase transformation for cBN-1 (1), cBN-2 (2) and cBN-3 (3)

Thus, according to the results of the dilatometric study on cBN-3 at a scanning rate of 5 deg/min^{*}, the transformation starts at 1670 ± 5 K, while the DTA data indicate that the corresponding T_0 at a heating rate of 80 deg/min is 2160 ± 5 K.

For evaluation of the enthalpy of the polymorphic transformation under study, the calorimetric examination of polycrystalline samples of cBN-2 and cBN-3^{**} was performed in the range 1300-2000 K. The transformation enthalpy was evaluated as the excess of the cBN sample enthalpy over the corresponding enthalpy for standard gBN, normalized to the transformation degree determined on the basis of an X-ray study of hardened samples.

Figure 2 shows the temperature dependences of the average heat capacity $\bar{C}_p(T) = \Delta H_s / \Delta T$ for both the cBN samples studied and standard gBN. The average heat capacity anomaly observed for the cBN is caused by the endothermic nature of the polymorphic transformation cBN \rightarrow gBN, and the difference in the \bar{C}_p curves is attributed to the kinetic peculiarities of the process for cBN-2 and cBN-3^{***}.

On the basis of the experimental data, we calculated $\Delta_t H^0(1800\text{K}) = +11$ kJ/mol. However, the real enthalpy of the transformation is undoubtedly higher than the calculated one, as the process under study occurs in isothermal stages as

* DTA registration of the thermal effect of the transformation is impossible at such a low heating rate.

** Use of cBN-1 in these experiments is impossible for the above reasons.

*** The transformation degrees in the calorimetric experiment at $T=1970$ K are 0.5 ± 0.05 for cBN-2 and 0.25 ± 0.03

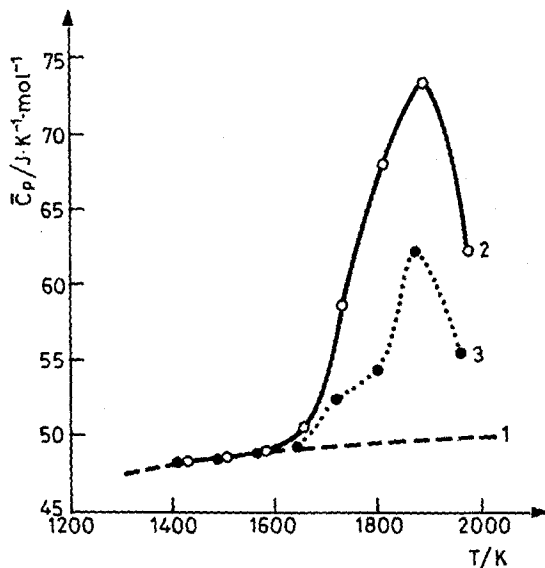


Fig. 2 Temperature dependences of $\bar{C}_p(T)$ for gBN (1), cBN-2 (2) and cBN-3 (3)

perwell. As the duration of the latter is equal to the scanning time for the interval ΔT , the $\Delta_{tr}H^\circ$ component that has not been allowed for can comprise up to +11 kJ/mol. The occurrence of the process in the isothermal stages is accompanied by an isothermal base-line offset. Therefore, one more $\Delta_{tr}H^\circ$ component exists that has likewise not been allowed for. Its value can also reach +11 kJ/mol. However, as the polymorphic transformation is a thermoactivated process, under the isothermal conditions it proceeds at a lower rate than during temperature interval scanning. Therefore, the enthalpy of the transformation considered can be evaluated as $\Delta_{tr}H^\circ(1800\text{ K}) = +22_{-11}^{+5}$ kJ/mol, which agrees well with the value of $+19 \pm 3$ kJ/mol calculated by using a new standard enthalpy value for the transformation $\text{cBN} \rightarrow \text{gBN}$ [5] and enthalpy dependences for cBN [12, 13] and gBN [14] at high temperatures.

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Zusammenfassung — Mittels DTA, Hochtemperaturkalorimetrie und Dilatometrie im Temperaturbereich 1000–2500 K wurde die polymorphe Phasenumwandlung von kubischem Bornitrid in graphitähnliches untersucht. Die Umwandelungsenthalpie wurde mit $+22_{-1}^{+5}$ kJ/mol bestimmt.