Journal of Thermal Analysis, Vol. 44 (1995) 97-103

THERMOANALYTICAL STUDY OF THE POLYMORPHIC TRANSFORMATIONS OF WURTZITIC BORON NITRIDE MODIFICATION INTO GRAPHITE-LIKE ONES

V. L. Solozhenko

V. Bakul Institute for Superhard Materials of the Ukrainian Academy of Sciences, Kiev, 254153, Ukraine

(Received December 5, 1993; in revised form January 5, 1994)

Abstract

The polymorphic transformations of wurtzitic modification of boron nitride into graphite-like ones have been studied using DSC, inverse drop-calorimetry and dilatometry over the temperature range of 500 to 1400 K. The transformation enthalpies at 1380 K were determined to be +14±2 kJ/mole and +17±3 kJ/mole for wBN→hBN and wBN→rBN transformations, respectively.

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

Introduction

Wurtzitic boron nitride (wBN) synthesized by shock-wave compression has a highly imperfect structure and is characterized by a high (of the order of 10^{12} cm^{-2}) dislocation density, the presence of stacking faults and oriented distortions of coordination tetrahedron as well as small grit sizes, and this is responsible for the low thermal phase stability of wBN. Earlier [1], it has been found that as a results of prolonged heating wBN in a vacuum at a gradual temperature increasing at a rate of 1 deg·min^{-1} between 500 and 1300 K, the wBN phase stabilization occurs, which manifests itself in an essential increase of the starting temperature (T_0) of its transformation into hBN.

The analysis of the results of X-ray diffractometry, transmission electron microscopy and EPR-spectroscopy of wBN samples of different stabilization degrees has shown [2], that the rise of starting temperature for wBN→hBN transformation due to phase stabilization is accompanied by the decrease in point defect concentration and in c/a ratio of wurtzite structure lattice parameters. It allows us to explain the observed effect of wBN phase stabilization in the framework of Lavaets' conception [3], by the c/a ratio decrease and approxima-

0368–4466/95/ $ 4.00

John Wiley & Sons, Limited
Chichester

tion to the value of 1.633 for perfect wurtzite structure as a result of the annihilation of wBN lattice point defects during annealing [4].

The analysis of literature on the processes of polymorphic transformations of wurtzitic boron nitride (wBN) into the graphite-like hexagonal modification (hBN) indicates that experimental data obtained by different authors vary widely [5, 6]. Evidently, this is caused by differences in both the structural state and dispersity of the samples being studied as well as in the experimental conditions.

Summarizing the results, it can be concluded that the starting temperature for wBN→hBN polymorphic transformation can vary between 500 to 1300 K. The process under study occurs over a wide temperature range and is fully completed only at temperatures of the order of 1600 K. And finally, any data on wBN polymorphic transformation into the rhombohedral modification (rBN) were unavailable in the literature.

It should be noted, that until recently attempts have not been made of thermoanalytical study of the processes, though the usage of thermal analysis in this case would allow us not only to make more exact the temperature ranges for studied transformations, but to define the sign and values of the corresponding thermal effects. Earlier [7], the thermoanalytical methods were successfully used by us for studying the polymorphic transformation of cubic boron nitride into the graphite-like one.

The foregoing has aroused our interest in a thermoanalytical study of the wBN polymorphic transformations.

Experimental

Samples

As the subjects of the studies, we used samples of wurtzitic boron nitride, produced in shockwave compression of graphite-like hexagonal modification (wBN-1) and obtained in the wBN-1 thermal phase stabilization [1] (wBN-2).

The grit size of both wBN samples as estimated by granulometry and electron microscopy lies in the range 0.1–3.0 μm; the average particle size of 1.4 μm corresponds to the maximum in the mass distribution curve. The specific surface values of studied samples were estimated from the absorption isothermal of nitrogen at 77 K by the BET-method to be 16.5 m^2/g for both wBN-1 and wBN-2.

X-ray diffractometry (HZG-4A Carl-Zeiss) and IR-spectroscopy (Perkin-Elmer 1600 FTIR) have shown that graphite-like BN modification contents of the samples under study do not exceed 0.1 mass%.

The impurity contents of the wBN samples being studied, according to the data of mass-spectrometric and emission spectral analyses as well as X-ray microanalysis are given in Table 1.

Table 1 Impurity content of wurtzitic boron nitride samples (mass%)

	C	O	Si	Al	Ca	Cr	Fe
wBN*	0.1	0.1	0.01	0.02	0.01	0.01	0.01

*impurity contents of wBN-1 and wBN-2 are identical

From the results of TMA-study (990 DuPont) the values of starting temperature $T_0(\alpha = 0.001)$[1] of the wBN →hBN polymorphic transformation were determined to be 680±5 K and 1310±5 K for wBN-1 and wBN-2, respectively.

Differential scanning calorimetry

DSC-study of the polymorphic transformation wBN→hBN was carried out in the temperature range 500–1400 K, using a ATD 2000 SETARAM thermoanalyzer in a static high-purity Ar atmosphere (less than 0.0006 vol.% of oxygen) at pressure of 0.12 MPa and heating rate of 30 deg·min^{-1}. A calorimetric sensor with a Pt–Pt10%Rh thermocouple was used. It was calibrated for temperature with the procedure described in [9], using the melting points of high-purity (99.999%) zinc, aluminum and copper. The accuracy of the temperature mea-surements in the 500–1400 K temperature range was ±3 K. The temperature dependence of calibration coefficient for DSC cell at experimental conditions in the 500–1750 K range was determined by use the standards (Zn, Al, Cu and Ni); and it was shown that the error in the enthalpy measurements was not more than 8% over the temperature interval under study. 100 μm platinum foil plates were used as the sample holders for 100–150 mg disk-like pressed wBN samples. hBN obtained as a result of the total transformation of wBN-1 at 1500 K in Ar, was used as the reference in the DSC experiments.

Inverse drop-calorimetry

The method was realized using a HT 1500 SETARAM high-temperature heat flux calorimeter[2] and consists in the following: a sample (2–5 mg) thermostated at 298.15 K was dropped by a special solid specimen introducer into the upper cell of calorimetric detector placed in the isothermal zone of a high-temperature furnace without seal failure of the system. The computational equation for the heat content value is as follows:

$$[H^\circ(T) - H^\circ(298.15\text{K})] = \frac{k(T)}{m_s} \cdot \int \Delta T \mathrm{d}\tau,$$

1 $T_0(\alpha=0.001)$ values were calculated according to [8].

2 The principle and specifications were described in details earlier [10,11].

where $k(T)$ – the calibration coefficient at the experimental temperature calculated from the equation:

$$k(T) = [H(T) - H(298.15\text{K})]_r \cdot m_r / \int \Delta T d\tau,$$

m_s and m_r - masses of the sample studied and the standard; ΔT - the calorimeter signal; τ - time.

The area under the registered curve in coordinates ΔT *vs.* τ was determined using ITC SETARAM electronic integrator. Calorimetric detector was calibrated directly during the experiment by samples of material under study and the standard (monocrystalline α-Al_2O_3 and high-purity (99.999%) molybdenum) being dropped one after another. Values of the calibration coefficient $k(T)$ were calculated for each sample using an equation approximating the $k(T)$ dependence on the degree of filling the calorimetric cell at an experimental temperature, which allowed to raise considerably the accuracy of the method used.

The calorimetric cell temperature was taken using a Pt–Pt10%Rh thermocouple and F-283 digital voltmeter. The thermocouple was calibrated according to the method [9]; the melting temperatures of high-purity Zn, Al and Cu were used as reference points. The temperature measurements' error in the experiment did not exceed ±1 K over the temperature range under study.

To improve the stability of a calorimeter signal a voltage stabilizer was used, and the temperature of the furnace shell was kept constant by controlling the water flow rate in the cooling system. The deviations of calorimetric detector temperature in the isothermal experiment did not exceed ±0.5 K.

The measurements were taken in the high purity argon atmosphere with oxygen content less then 0.0007 vol.% at the pressure of 0.105 MPa. A calorimetric detector with Pt–Pt10%Rh thermocouple and crucibles of melt alumina were used.

X-ray diffractometry

The degrees of the studied polymorphic transformations in the wBN samples after the thermoanalytical experiments were determined in a DRON-4-07 diffractometer (CuK_α radiation), using the procedure described in [12]. The relative error in the phase composition evaluation did not exceed 10 mass%. High-temperature X-ray diffraction analysis in the 1000–2100 K range was carried out using a DRON-1/UVD-2000 diffractometer in a high-purity Ar atmosphere.

Results and discussion

wBN→hBN

According to the data obtained by differential scanning calorimetry, the polymorphic transformation under study is the endothermic one, and its enthalpy at 1500 K can be evaluated as +13±4 kJ/mole irrespective of the degree of sample's phase stabilization. The value is in good agreement with the $\Delta_{tr}H^0(1500\ K)=+15\pm3$ kJ/mole value calculated from wBN and hBN formation enthalpies [13] as well as from temperature dependencies of their enthalpies at high temperatures [14, 15]. Figure 1 gives characteristic DSC curves for the studied transformation at the scanning rate of 30 deg·min^{-1} on correction of the basic line.

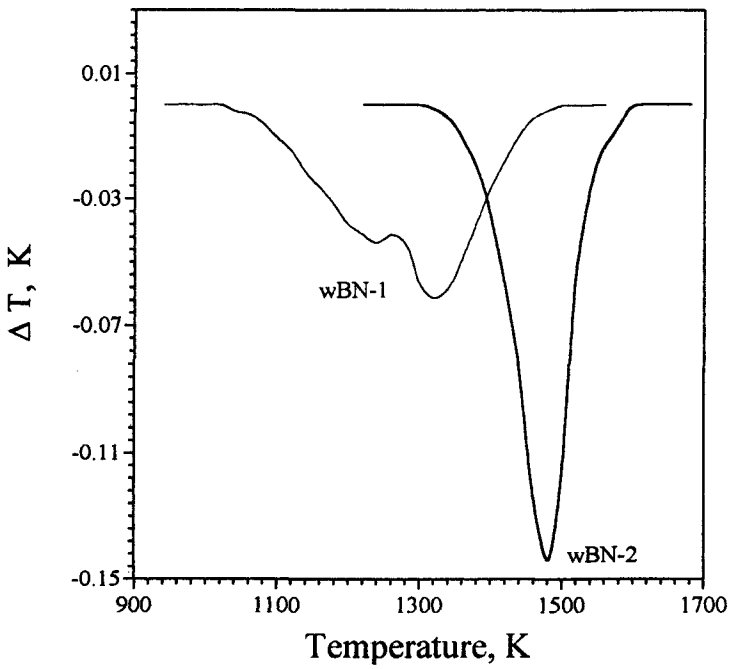

Fig. 1 DSC curves of wurtzitic boron nitride around its polymorphic transformation into hBN

The transformation enthalpy over the 1250–1400 K temperature range was measured by the inverse drop-calorimetry. A typical curve of a calorimeter signal after a wBN-1 sample dropping is given in Fig. 2. The *a–b* region of the curve corresponds to heat absorption by the dropped sample in the process of heating up to the calorimeter temperature, and the *b–c* region corresponds to the endothermic process of wBN→hBN transformation in a calorimetric cell. In

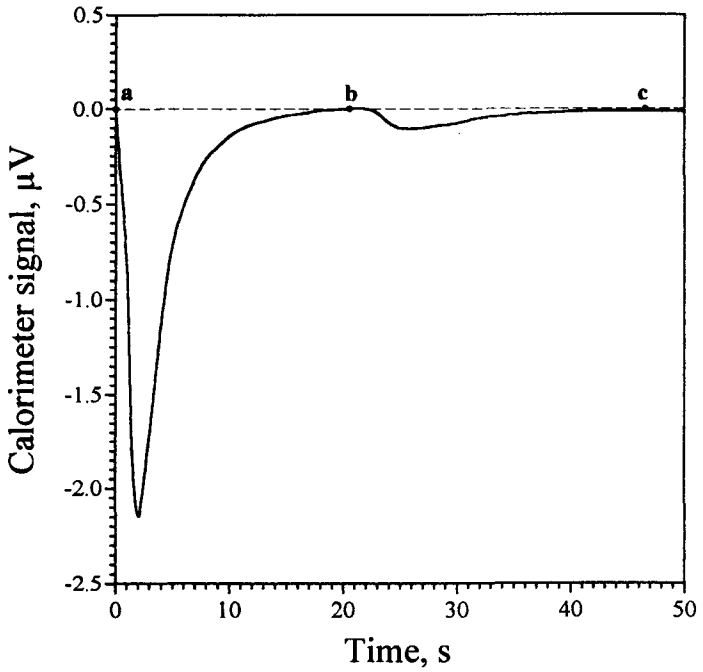

Fig. 2 The curve of wBN heat absorption at 1380 K, obtained by using inverse drop-calorimetry

a set of 7 measurements at 1380 K, the $\int \Delta T d\tau$ integral values in *b–c* regions of corresponding experimental curves have been determined, and allowing for the transformation degree ($\alpha = 0.40 \pm 0.05$), a value of $\Delta_{tr}H^0$ at this temperature has been found to be +14±2 kJ/mole. The obtained transformation enthalpy value is in good agreement both with the $\Delta_{tr}H^0(1380\ K) = +15 \pm 3$ kJ/mole value, calculated using experimental wBN and hBN formation enthalpies, and with the $\Delta_{tr}H^0(1500\ K) = +13 \pm 4$ kJ/mole value obtained by DSC method.

wBN→rBN

It is highly unexpected, that under the conditions of the above calorimetric experiment, the phase transformation of the wBN-2 thermostabilized sample occurs mostly to form the rhombohedral modification, which content of transition products can reach 90 mass%. In a set of 5 measurements at the temperature of 1380 K, the $\int \Delta T d\tau$ integral values in *b–c* regions of the curves obtained (Fig. 2) have been determined, and with regard to the transformation degree ($\alpha = 0.30 \pm 0.05$) and rBN content (85±5%), an enthalpy value for wBN→rBN transformation at the temperature of the experiment has been found to be +17±3 kJ/mole.

The experimental data on the transformation enthalpies of wBN into graphite-like modifications have allowed to evaluate the enthalpy of rBN→hBN transformation, which makes −3.0±2.8 kJ/mole at 1380 K, and calculate for the first time the standard value of the formation enthalpy of rhombohedral boron nitride to be equal $\Delta_f H^0$(rBN, 298.15 K)=−247.6±3.5 kJ/mole[3].

The high-temperature X-ray diffractometry of the process of rBN→hBN transformation has shown that the temperature of its beginning can vary from 1500 K for a highly dispersed rBN, obtained at high pressure – high temperature interaction of amorphous boron with ammonia [16], to 2100–2300 K for a highly ordered pyrolytic rBN. The transformation occurs in a wide temperature range, which makes impossible the direct calorimetric determination of the corresponding thermal effect due to small values of the respective heat flows.

References

1 V. L. Solozhenko, Reactivity of Solids, 7 (1989) 371.
2 W. B. Zelyavsky, A. V. Kurdyumov and V. L. Solozhenko, Sov. Phys.-Doklady, 35 (1990) 911.
3 G. Lavaets, Phys. Rev. B, 5 (1972) 4039.
4 A. V. Kurdyumov, V. L. Solozhenko, W. B. Zelyavsky and I. A. Petrusha, J. Phys. Chem. Solids, (1993) in press.
5 A. V. Kurdyumov and A. N. Pilyankevich, Phase transformations in carbon and boron nitride. Kiev: Naukova Dumka, 1979, 188 pp. (in Russian).
6 R. R. Will, Int. J. High Techn. Ceram., 1 (1985) 139.
7 V. L. Solozhenko and V. Z. Turkevich, J. Thermal Anal., 38 (1992) 1181.
8 V. M. Gorbachev, J. Thermal Anal., 19 (1980) 377.
9 E. M. Barrall, Thermochim. Acta, 5 (1973) 377.
10 I. Arpshofen, B. Predel, E. Schultheiss, M. Hoch, Thermochim. Acta, 33 (1979) 197.
11 R. Naumann and D. Petzold, J. Thermal. Anal., 20 (1981) 319.
12 A. V. Kurdyumov, Sov. Phys.-Crystallography, 17 (1972) 534.
13 V. Ya. Leonidov, I. V. Timofeev and V. L. Solozhenko, In: 'Thermodynamics of Chemical Compounds'. Gorky, 1988, p.16 (in Russian).
14 V. L. Solozhenko, Thermochim. Acta, (1993) in press.
15 V. L. Solozhenko, Rus. J. Phys. Chem., 67 (1993) 2137.
16 V. L. Solozhenko, V. A. Mukhanov and N. V. Novikov, Doklady Chem., 312 (1990) 125.

Zusammenfassung — Mittels DSC, inverser Dropkalorimetrie und Dilatometrie im Temperaturbereich von 500 bis 1400 K wurden die polymorphen Umwandlungen der Wurtzit-Modifikation von Bornitrid in die Graphit-Modifikation untersucht. Die Umwandlungsenthalpien bei 1380 K für die Umwandlungen wBN→hBN und wBN→rBN wurden mit +14±2 kJ/mol und mit +17±3 kJ/mol bestimmt.

3 The experimental data [15] on hBN and wBN enthalpies in 298-1400 K range were used in calculations.