Journal of Thermal Analysis and Calorimetry, Vol. 60 (2000) 661–665

FORMATION OF B–C–N CERAMICS INVESTIGATED BY EMANATION THERMAL ANALYSIS, TG AND DTA

T. Sato[1]*, M. Hubáček*[2]*, V. Balek*[3,4]*, J. Šubrt*[4] *, O. Kriz*[4] *and T. Mitsuhashi*[1]

[1]National Institute for Research in Inorganic Materials, 1-1 Naimiki, Tsukuba, Ibaraki 305-0044
[2]Okayama Ceramic Research Foundation, 1406 Nishi Katakami, Bizen, Okayam 705-0021, Japan
[3]Nuclear Research Institute Ře plc, CZ-25068 Ře
[4]Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, CZ-25068 Ře
Czech Republic

Abstract

Processes taking place during formation of B–C–N ceramics by thermal treatment of organic precursors were investigated using emanation thermal analysis (ETA), differential thermal analysis (DTA) and thermogravimetry (TG). An additional information about thermal behavior of precursors used for preparation of BC_4N, BN and CN_x ceramic systems by heating in argon up to 1100°C was obtained. The ETA enabled us to characterize microstructure changes in the samples at in situ conditions of thermal treatment. A good agreement of ETA, TG and DTA results was found.

Keywords: B–C–N ceramics, boron carbonitride, emanation thermal analysis

Introduction

One of the typical characteristics of B–C–N ceramics is its resistance towards crystallization. Accordingly, the precursor of BC_4N investigated in this paper was turbostratic. The structure of the intermediate products remained turbostratic throughout the heating until 1400°C, whereas a separation of boron nitride and carbon was observed in the material heated over 1800°C [1]. It was also observed [1] that the chemical composition of the heat-treated samples gradually changed with temperature during the heat treatment. Considering this fact it is rather difficult to characterize the thermal behaviour of the BC_4N intermediate products using traditional chemical and structural methods. Therefore, emanation thermal analysis [3–5] as a non-traditional method was used in this paper to characterize microstructure changes taking place during formation of B–C–N ceramics. This information is important for the assessment of the properties of the ceramics intermediate products as well as for determination of the optimal conditions to obtain the ceramics of required properties. DTA and TG curves were measured for comparison with the ETA results.

1418–2874/2000/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Experimental

Preparation of precursors

The precursor of BC_4N was prepared as follows [2]: Urea, boric acid and saccharose were mixed in the ratio 1:2.2:2.56 in a porcelain mortar; the ratio was empirically found in order to obtain the BC_4N compound without formation of free BN and free carbon by heating at 1500°C. The mixture was heated in a Pyrex beaker at 130–150°C for 1 h and at 250°C for additional 2 h. The pressure in the system was kept at 6–8 torr to remove volatile exhausts. The reaction began with complete melting of the mixture. The melt gradually lost its transparency, turned to a brown viscous liquid with foaming and finally solidified.

The BN and CN_x precursors were prepared by heating the mixture of boric acid and saccharose in the 1:2.2 ratio and the mixture of saccharose and urea in the ratio 1:1, respectively. The mixtures were heat-treated similarly as in the case of the BC_4N precursor. The precursors thus obtained as solidified foams were pulverized in an agate ball mill to be used for the characterization by means of ETA, TG and DTA.

Three weeks prior to ETA measurements the precursors were labelled by adsorption of ^{228}Th and ^{224}Ra radionuclides from acetone solution on the sample surface. Atoms of radon ^{220}Rn were formed by the spontaneous alpha decay of ^{228}Th and ^{224}Ra. The thorium nuclide ^{228}Th used for labelling samples has suitable half-life (1.9 years) to be used as a quasi-permanent source of radon ^{220}Rn (half-life 55 s). The ^{224}Ra and ^{220}Rn atoms were incorporated into the sample to the depth of max. 120 nm due to the recoil energy (85 keV atom^{-x}) which the atoms gained by the alpha spontaneous decay. The specific activity of a sample was 10^5 Bq per g. For one measurement approx. 0.05 g of the sample was used.

Methods

Emanation Thermal Analysis (ETA) [3–5] is based on the measurement of radon release rate from samples previously labelled. During ETA measurement the sample situated in a corundum crucible was heated in a furnace being purged with a constant flow of argon, which carried out the radon gas released from the sample into the measuring chamber of radon atoms radioactivity [3, 4]. The ETA apparatus was constructed on the bases of the NETZSCH DTA 409 equipment. Heating rate of 5 K min^{-1}, and the argon flow rate of 40 ml min^{-1} were used in the measurements.

The TG/DTA measurements were carried out simultaneously during heating in argon flow (the heating rate 5 K min^{-1}, the flow rate 40 ml min^{-1}) using RIGAKU TAS 300 apparatus.

Results

Properties of organic B–C–N compounds to be used as precursors for preparation of B–C–N ceramics were described by Hubáček and Sato [2]. Scanning electron microscopy and X-ray diffraction patterns were found not sufficient to characterize microstructure of intermediate products of thermal treatment of the B–C–N ceramics precursors because of their turbostratic character. The emanation thermal analysis used in this paper enabled us to investigate microstructure changes in the intermediate products during formation of new phases, under in situ conditions of heat treatment. We shall present here results of ETA, TG and DTA measured during heating of the precursors of the three ceramics systems, namely BC_4N , BN and CN_x.

Formation of turbostratic BC_4N

From TG and DTA results (full lines in Fig. 1) it follows that in the temperature range 50–1100°C a loss of the sample mass took place, due to the thermal decomposition of the precursor. The major portion of volatile products of thermal decomposition was released in the temperature range 100–600°C [6]. From the ETA curve (full line in Fig. 2) measured parallel in the same experimental conditions it follows that in the temperature interval from 50 to 380°C an intense increase of the radon release rate, *E*, took place corresponding to the increased mobility of radon along surface defects and micropores existing in the BC_4N precursor prepared at 250°C, as well as along micropores additionally formed as the result of thermal decomposition of the precursor. During further heating of the sample above 400°C a decrease of the radon release rate was observed on the ETA curve (full line in Fig. 2). This indicates that recovering of porosity and surface took place in this temperature range. Formation of an intermediate glassy state is supposed in the temperature interval 600–700°C. As it follows from DTA results (full line in Fig. 1) this process was accompanied by an exothermal effect.

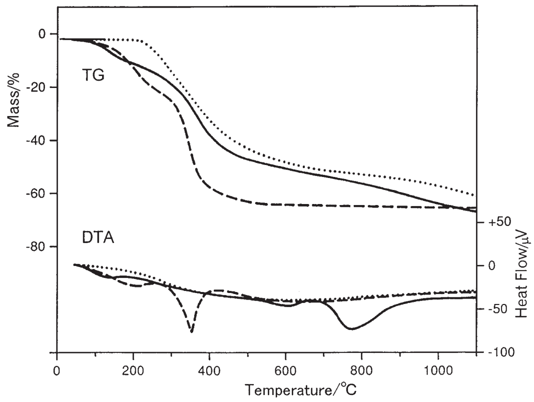

Fig. 1 TG and DTA results measured during heating of BC_4N, BN and CN_x ceramic systems precursor in argon. Full lines correspond to BC_4N, dashed lines to BN and dotted lines to CN_x ceramic systems precursors

The decrease of the radon release rate continued during heating up to 650°C, i.e. to the temperature at which the melting of the bulk sample is supposed. This interpretation

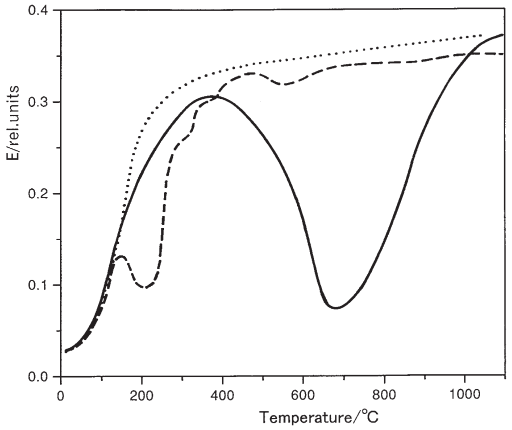

Fig. 2 Results of Emanation Thermal Analysis measured during heating of BC_4N, BN, and CN_x ceramic systems precursors in argon. Full lines correspond to BC_4N, dashed lines to BN and dotted lines to CN_x ceramic systems precursors

is supported by ETA results of other glassy systems [3]. When interpreting the ETA results, we should keep in mind that a part of the radon atoms formed by the spontaneous alpha-decay of radium was directly released from the sample by recoil, reflecting surface area of the sample. Another part of the radon atoms trapped at lattice defects, vacancy clusters, grain boundaries and pores was released by diffusion. The defects in the solids served both as traps and diffusion paths for radon. Consequently, the radon release rate measured in the ETA, reflected at every temperature surface area and radon diffusivity in the samples labelled with the radon parent nuclides. Consequently, we can suppose that the increase of E values observed on sample heating from 700 to 1050°C reflects the formation of open pores, due to the thermal decomposition of the glassy intermediate product of the BC_4N ceramics. The TG results (Fig. 2, the full line) indicates that the mass loss continued in this temperature interval, due to the release of volatile products of the thermal decomposition (mainly CO, CO_2) [6]. From the results published in [2] it follows that the intermediate product of BC_4N ceramics heated to 1050°C was turbostratic.

Formation of turbostratic BN

From TG and DTA results (Fig. 1, the dashed lines) it follows that the loss of the sample mass takes place in two steps in the temperature intervals 40–220°C and 220 to 420°C, respectively. The thermal decomposition of the precursor was accompanied by endothermal effects (the DTA dashed line in Fig. 1). The release of CO, CO_2 and other volatiles was reported in these temperature intervals [2].

The ETA curve (the dashed line in Fig. 2) reflected an enhanced radon release in the temperature range 40–130°C which can be ascribed to the increase of surface area and porosity of the sample. The radon release rate increase was interrupted at 130°C, probably due to the formation of a glassy intermediate product. On further heating above 220°C the increase of the radon release indicated again the formation of micropores due to the release of volatile products of thermal decomposition from partially vitrified sample. Moreover, the effect observed on the ETA curve (Fig. 1, the dashed line) in the temperature range 450–520°C revealed the existence of a process resulting in the ordering of the structure of the intermediate products (the process analogous to graphitization). No microstructure changes of the partially graphitized sample were reflected by the ETA curve during heating from 600 to 1100°C. The turbostratic BN resulted after the thermal treatment.

Formation of CN_x

From TG and DTA results (Fig. 1, the dotted lines) it follows that the thermal decomposition of the sample took place in the broad temperature range 200–1100°C. The main thermal decomposition step, however, took place from 200 to 500°C. Another decrease of the sample mass, observed in the TG curve (Fig. 1, the dotted line) in the interval 800–1100°C can be ascribed to a delayed release of hydrocarbons formed during thermal decomposition of the sample [6].

The continuous increase of radon release rate in the temperature range 100–400°C (ETA curve in Fig. 2, the dotted line) reflected additional formation of micropores due to decomposition of the CN_x precursor. The increase of radon release rate was continuous, i.e. not interrupted as in case of the heating of BC_4N and BN precursors, where the formation of intermediate glassy products was supposed. The slow and steady increase of radon release during sample heating in the temperature range 400–1100°C, corresponded to the diffusion of radon in the porous intermediate product. We can suppose that no microstructural changes took place in this sample in the range 400 to 1100°C.

Conclusions

The processes taking place during formation of BC_4N , BN and CN_x ceramic systems were characterized by means of ETA, TG and DTA. Temperature intervals of microstructure changes of the intermediate products of ceramics powders were in situ determined by means of ETA. A good agreement between ETA,TG and DTA results was found.

References

1 T. Sato, Research on boron carbonitride, Research Report of NIRIM (Ed. NIRIM, Tsukuba) 89 (1996), Ch. 3 p.12 (in Japaneese).
2 M. Hubáček and T. Sato, J. Solid State Chem., 114 (1995) 258.
3 V. Balek and J. Tölgyessy, `Emanation Thermal Analysis and other Radiometric Emanation Methods', in: Wilson and Wilson's Comprehensive Analytical Chemistry, Part XII C., (Ed. G. Švehla), Elsevier, 1984, p. 304.
4 V. Balek, J. Thermal Anal., 96 (1990) 179.
5 V. Balek, Thermochim. Acta, 192 (l991) 1.
6 M. Hubáček, T. Sato, V. Balek and E. Klosová, J. Solid State Chem., in print.