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Stages of the synthesis of gallium nitride with the use of urea

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Abstract

Experimental studies have enabled the suggestion of a scheme of the reaction stages of gallium with urea in the temperature range 20–1000°C. During studies on the formation of boron nitride with the use of urea and products of its thermal condensation, we have discovered that cyanamide (H_2CN_2) plays a substantial role in those processes [Z. Gontarz and S. Podsiadło, Pol. J. Chem, 58 (1984) 3; A. Górski and S. Podsiadło, Pol. J. Chem., 58 (1984) 13]. As shown in these works cyanamide, formed in the course of the thermal decomposition of urea, is the main nitriding agent in the reactions. We have decided to investigate the processes of the reactions of urea with gallium to form gallium nitride.

Keywords: Gallium nitride; Synthesis

1. Experimental

The course of the reactions was studied by thermal analysis on a MOM derivatograph (Budapest, Hungary). The syntheses of characteristic temperatures were carried out in tube furnaces under the required atmosphere. The reaction products were studied after freezing, by means of IR absorption of the solid and gaseous products (apparatus Specord IR, Germany), X-ray phase analysis (TUR M 62, Germany) and quantitative analysis (Microanalyser CHN 240 Perkin-Elmer and classical analysis).

The following substances were used in the work: urea, pure for analysis, produced by POCh (Poland); gallium, pure for analysis, produced by SNT (Czech Republic).

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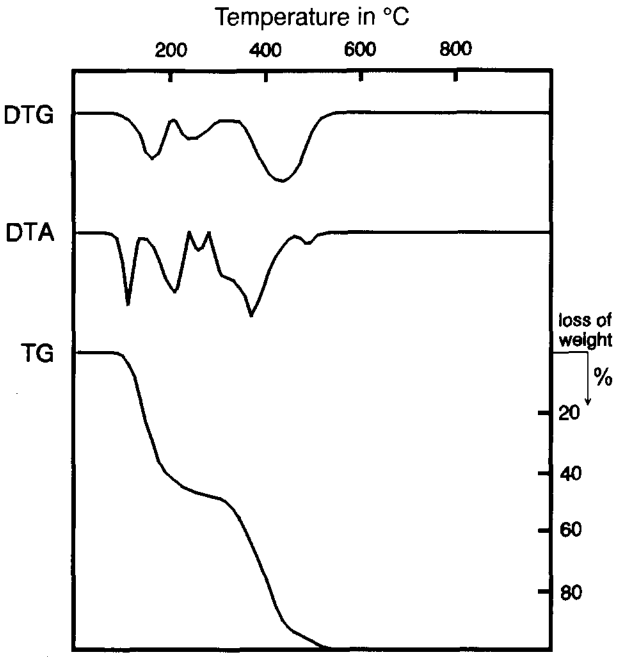

Fig. 1. Thermogravimetric analysis of urea; $m = 0.144$ g, $V = 2.5$ K min^{-1}, N_2 atmosphere.

2. Results and discussion

In the first part of this study the experiments performed previously were repeated under conditions that enabled their correlation with the main part of the work. Fig. 1 shows the results of the urea decomposition. Pure urea decomposes endothermically in several stages [1–3]:

$$H_2NCONH_2 \rightarrow HCNO + NH_3 \ (140°C) \qquad (1)$$

$$H_2NCONH_2 \rightarrow H_2CN_2 + H_2O \ (140°C) \qquad (2)$$

$$H_2NCONH_2 + HCNO \rightarrow H_2NCONHCONH_2 \ (180°C, \text{biuret}) \qquad (3)$$

$$H_2NCONHCONH_2 + HCNO \rightarrow H_2NCONHCONHCONH_2 \ (210°C, \text{triuret}) \qquad (4)$$

$$2H_2CH_2 \rightarrow H_4C_2N_4 \ (210°C, \text{dicyandiamide}) \qquad (5)$$

$$3H_2CN_2 \rightarrow H_6C_3N_6 \ (300°C, \text{melamine}) \qquad (6)$$

At higher temperature the reaction products were ammelide, ammeline, melame, meleme and melone [4]. In an ammonia atmosphere, non-oxygen containing products were mainly obtained [1]:

$$H_2NCONH_2 \rightarrow H_2CN_2 + H_2O \ (140°C) \quad (7)$$

$$2H_2CN_2 \rightarrow H_4C_2N_4 \ (210°C) \quad (8)$$

$$3H_2CN_2 \rightarrow H_6C_3N_6 \ (300°C) \quad (9)$$

and at higher temperatures the presence of melame, meleme and melone was established.

Fig. 2 gives a tabulation of the decomposition temperature of some compounds of the urea group. Fig. 3 shows a thermogram of a 1:3 molar mixture of gallium and urea taken in a nitrogen atmosphere.

The reaction is a multistage process in which weight loss begins at 130°C. At 130°C the weight loss is 30%, corresponding approximately to the formation of biuret from urea (reactions 1, 2 and 3). The main gaseous products of this reaction were ammonia, as identified by IR absorption in the gas phase, and cyanic acid (HCNO), identified both in the gas phase by IR absorption and as a solid product of its condensation — cyanuric acid $(HCNO)_3$ — in the cool parts of the furnace [5,6]. Elemental analysis of a solid product obtained at 210°C gave: Ga, 44.2%; H, 0.77%; C, 13.42%; N, 27.47%; O, 24.2%. These results correspond to a stoichiometry of Ga:H:C:N:O = 1:2:2:3:2. The formation of a phase of the given stoichiometry was also confirmed by the weight loss (32%). The compound formed was crystalline. Its X-ray diffraction data (different from those of the starting materials [6]) are shown in Table 1.

Other products of the decomposition were gaseous NH_3 and H_2O, identified by IR absorption in the gas phase, and HCNO identified both in the gas phase and as

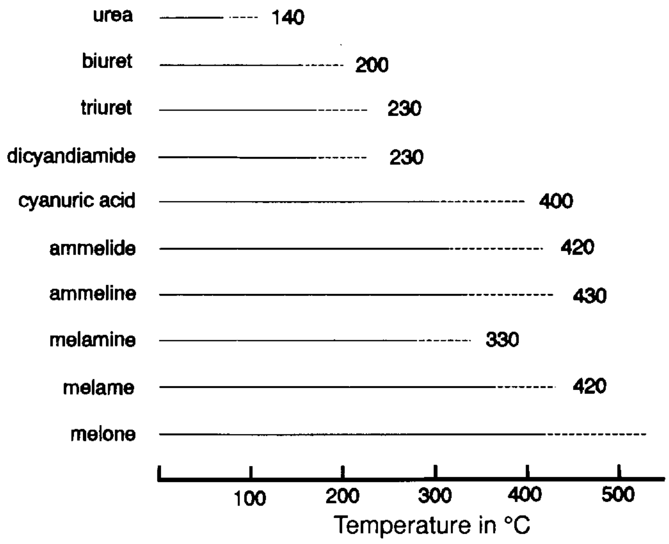

Fig. 2. Decomposition temperatures of nitriding agents (temperatures of maximum rate of decomposition are given).

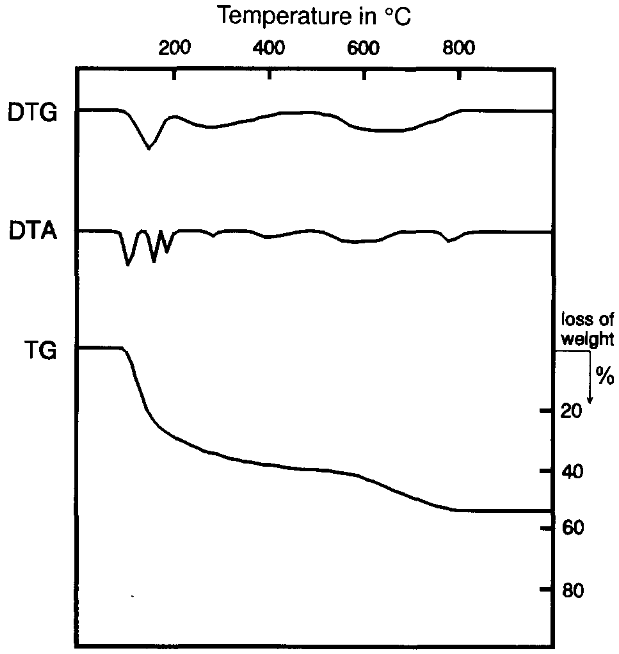

Fig. 3. Thermogravimetric analysis of mixtures of gallium and urea (molar ratio 1:3); $m = 0.14$ g, $V = 2.5$ K min^{-1}, N_2 atmosphere.

a solid product of condensation in the cool parts of the installation. The crystals formed were identified as polymeric HCNO — the cyanuric acid $(HCNO)_3$ [6]. In the mixture of gaseous products hydrogen was identified by mass spectroscopy. Fig. 4 shows the IR spectrum of the phase $GaH_2C_2N_3O_2$. This spectrum does not contain absorption bands characteristic of C–N bonds in urea or biuret, and there

Table 1
X-ray identification data for $GaH_2C_2N_3O_2$

d in Å	I/I_0	d in Å	I/I_0
7.451	5	3.436	5
5.286	3	3.360	5
5.155	10	3.010	3
5.030	8	2.912	4
4.843	9	2.874	5
4.734	100	2.675	4
4.568	12	2.574	6
4.072	5	2.2094	8
3.994	5	2.1023	8
3.905	5	2.0566	6
3.700	20		

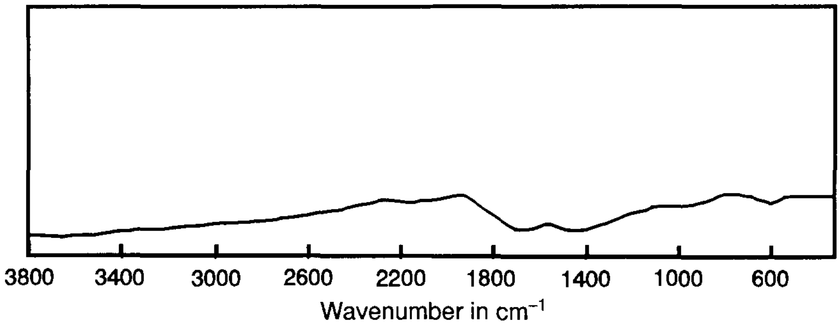

Fig. 4. IR spectrum of the $GaH_2C_2N_3O_2$ phase.

is no free gallium in this material. We assume, therefore, that the product is a polymeric compound. The structure of the new phase has not been examined. Above 210°C weight loss is observed, reaching the value of 48% at 500°C. Elemental analysis of the solid state product corresponds approximately to the stoichiometry $GaHCN_2O$. The product was amorphous and its IR spectrum did not contain absorption bands characteristic of Ga–N, Ga–O, C–O or C–N bonds. IR spectroscopy indicated the presence of HCNO, H_2CN_2 and CO_2 in the gaseous products of the reaction [5]. Above 500°C continuous weight loss is observed. At 800°C a solid product is obtained with a composition corresponding to a mixture of crystalline Ga_2O_3 and crystalline GaN (molar ratio about 1:1) [7]. Other products of the reaction were gaseous dicyanide (C_2N_2), identified by IR spectroscopy of the gas phase, and cyanamide (H_2CN_2), identified both in the gas phase by IR spectroscopy and as a crystalline product of its condensation (dicyandiamide) in the cool parts of the installation.

The results obtained lead to a conclusion that in the process under study the formation of gallium nitride in the reaction of gallium with urea in a nitrogen atmosphere proceeds in several stages:

$$\begin{aligned} \mathrm{Ga} + 3\mathrm{H_2NCONH_2} \rightarrow\ & \mathrm{Ga} + \mathrm{H_2NCONHCONH_2} \\ & + \mathrm{HCNO} + 2\mathrm{NH_3}\ (<180°\mathrm{C}) \qquad (10) \end{aligned}$$

$$\mathrm{Ga} + \mathrm{H_2NCONHCONH_2} \rightarrow \mathrm{GaH_2C_2N_3O_2} + \tfrac{3}{2}\mathrm{H_2}\ (>180°\mathrm{C}) \qquad (11)$$

$$2\mathrm{GaH_2C_2N_3O_2} \rightarrow 2\mathrm{GaHCN_2O} + \mathrm{HCNO}\ (<500°\mathrm{C}) \qquad (12)$$

Some of the HCNO probably decomposes to CO_2 and H_2CN_2 in the reaction:

$$2\mathrm{HCNO} \rightarrow \mathrm{H_2CN_2} + \mathrm{CO_2}$$

$$24\mathrm{GaHCN_2O} \rightarrow 4\mathrm{Ga_2O_3} + 4\mathrm{GaN} + 6\mathrm{H_2CN_2} + 3\mathrm{C_2N_2} + \mathrm{N_2}\ (<800°\mathrm{C}) \qquad (13)$$

(in the last reaction nitrogen has not been identified, because the process was carried out in a stream of N_2). The weight loss at 800°C (64%) corresponds to the formation of gallium nitride and gallium oxide (molar ratio 1:1). We have not

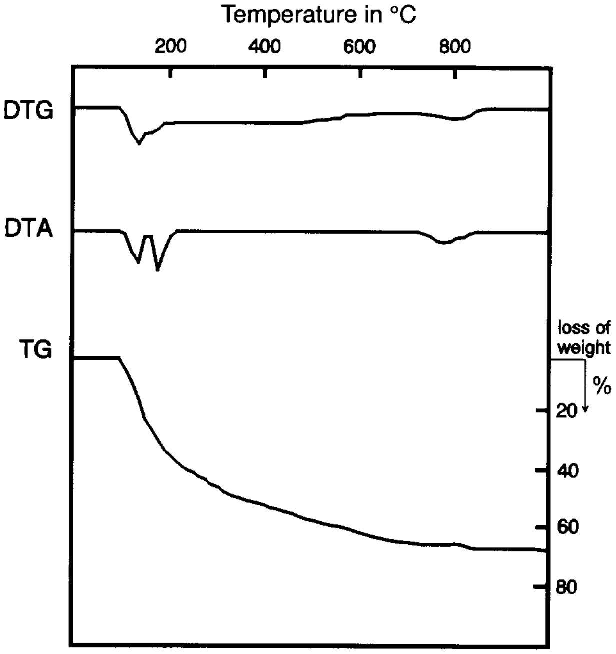

Fig. 5. Thermogravimetric analysis of mixtures of gallium and urea (molar ratio 1:3); $m = 0.138$ g, $V = 2.5$ K min^{-1}, NH_3 atmosphere.

managed to obtain single crystals of the crystalline phase $GaH_2C_2N_3O_2$ to determine its structure.

Similar studies of the reaction of gallium with urea were carried out in an ammonia atmosphere. Fig. 5 shows a thermogram of a 1:3 molar mixture of gallium with urea taken in an ammonia atmosphere.

A comparison of the thermogravimetric curves of the reactions of gallium and urea in nitrogen and ammonia atmospheres (Figs. 2 and 3 respectively) shows that their first stages are identical. Weight loss begins at 130°C, reaching 30% at 180°C which corresponds to the production of biuret from urea in reaction (10). The product of the reaction at 210°C gives a diffraction pattern identical to that presented in Table 1. Elemental analysis of a solid product formed at 210°C gave results corresponding approximately to a stoichiometry of Ga:H:C:N:O = 1:2:2:3:2 ($GaH_2C_2N_3O_2$). The IR spectrum of the product is identical to that presented in Fig. 4 (for the phase obtained in a nitrogen atmosphere). The formation of a product of the given stoichiometry was also confirmed by the weight loss (32%). We have not identified ammonia as a gaseous product because the process was carried out in a NH_3 atmosphere. Another reaction product was HCNO, identified as a solid product of its condensation — cyanuric acid $(HCNO)_3$ — in the cool parts of the installation. The IR spectrum of gaseous ammonia is very rich and it is practically impossible to identify other gaseous substances in its atmosphere. Above 210°C, slow, permanent weight loss is observed, reaching 56% at 500°C. Elemental analysis of solid products formed at this temperature gave: Ga, 65.73%; C, 5.87%; N, 9.81%; O, 18.59%; corresponding to a stoichiometry of Ga:C:N:O = 2:1:2:2. The phase was amorphous and its IR spectrum was illegible. Cyanic acid HCNO and cyanamide H_2CN_2 were the gaseous products of the reaction. They were identified in the solid state after condensation in the cool part of the furnace tube. Above 500°C, a slow weight loss is observed, and at 850°C crystalline gallium nitride is obtained [8]. The product of this process contains more than 99% GaN [7]. We have not identified the gaseous product of the last stage of gallium nitride formation; it is probably carbon dioxide.

It may be concluded from the results that the formation of gallium nitride by the reaction of gallium with urea in an ammonia atmosphere proceeds as follows:

$$\begin{aligned}\mathrm{Ga} + 3\mathrm{H_2NCONH_2} \rightarrow \mathrm{Ga} + &\mathrm{H_2NCONHCONH_2}\\ &+ \mathrm{HCNO} + 2\mathrm{NH_3}\ (<180^\circ\mathrm{C})\end{aligned} \tag{14}$$

$$\mathrm{Ga} + \mathrm{H_2NCONHCONH_2} \rightarrow \mathrm{GaH_2C_2N_3O_2} + \tfrac{3}{2}\mathrm{H_2}\ (180\text{–}210^\circ\mathrm{C}) \tag{15}$$

$$2\mathrm{GaH_2C_2N_3O_2} \rightarrow \mathrm{Ga_2CN_2O_2} + 2\mathrm{HCNO} + \mathrm{H_2CN_2}\ (<500^\circ\mathrm{C}) \tag{16}$$

$$\mathrm{Ga_2CN_2O_2} \rightarrow 2\mathrm{GaN} + \mathrm{CO_2} \tag{17}$$

The gallium nitride obtained contains less than 0.06% carbon, less than 0.05% hydrogen and less than 0.1% oxygen. These impurities are much smaller than in the synthesis of GaN by previous methods [9–11].

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