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THERMOGRAVIMETRIC STUDY OF YTTRIUM ISOPROPOXIDE AND DISPERSANT BURNOUT IN ALUMINUM NITRIDE CERAMIC PROCESSING

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Abstract

Yttrium isopropoxide, an yttrium oxide precursor, is sometimes used as a sintering aid for producing aluminum nitride ceramics. In the present work, this sintering aid was used with isopropanol as the solvent and polyethyleneimine as the dispersing agent. After initial ball milling and drying steps, the burnout behaviour of samples taken from isostatically pressed pellets was studied by thermal analysis in nitrogen and air. In addition to the milled and pressed pellets, each component was also analyzed separately.

Complete conversion to yttrium oxide, with no residual carbon, would be a desirable property of this system. However, during the preparation of the aluminum nitride pellet, there was only partial yttrium isopropoxide decomposition. The nitrogen burnout residue contained carbon formed from the yttrium isopropoxide and dispersant overlapping thermal decomposition, mostly from an intermediary decomposition stage of the former that occurs between 300 and 550°C. The residual carbon content and the previous yttrium isopropoxide decomposition were estimated by thermogravimetry.

Keywords: aluminum nitride, ceramics, TG

Introduction

Yttrium oxide has been used as a sintering aid in the manufacture of aluminium nitride [1, 2], being directly contained in the "green" (unfired) body composition, or being formed from precursors during processing steps. Organic solvents and binders are also volatilized or decomposed during these steps, which complicates a detailed analysis of the process. The pyrolysis of various organic additives in nitrogen can leave residual carbon [3, 4], which is not de-

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sirable if it is excessive. This can also occur during burnout in air [5]. In the present work, yttrium isopropoxide, an yttrium oxide precursor, was used as a highly effective aluminum nitride sintering aid, with isopropanol as the solvent and polyethyleneimine as the dispersing agent. The use of metal alkoxides results in finer corresponding metal oxide grains and their more homogeneous distribution in the resulting ceramic [6]. However, incomplete conversion to yttrium oxide would be undesirable. Excessive residual carbon would also be undesirable, although Yan *et al.*, have shown [2] that there is an optimum value. This depends on the aluminum oxide content of the composition, because the carbon and oxide can react and form aluminum nitride and carbon monoxide during the sintering cycle in a nitrogen atmosphere.

After initial ball milling and drying steps, samples taken from isostatically pressed pellets were studied by thermal analysis to determine their decomposition behaviour. Flowing nitrogen was used in most of the experiments, since this is commonly used in the pre-sintering step during the production of AlN. Flowing air was also used to further analyze the different thermal decomposition steps. Each of the sample components was also analyzed separately to provide a better understanding of their burnout behaviour, and to aid in estimating the degree of yttrium isopropoxide decomposition in the preceding ceramic processing steps.

Experimental procedure

The AlN powder starting material used in this study was manufactured by Dow Chemical Co., Midland, MI. Chemical analysis data provided by the supplier are 1.20% oxygen, 0.05% carbon, 201 ppm Ca, 53 ppm Si, and 13 ppm Fe. The yttrium isopropoxide used was manufactured by Aldrich Chemical Co., Inc., Milwaukee, WI, and is approximately 95% pure. The Hypermer KD-2 dispersant (a polyethyleneimine) was manufactured by ICI Americas, Inc., Wilmington, DE.

The yttrium containing compositions were formulated to have a desired Y_2O_3% after their burnout in nitrogen atmosphere. For all the cases, 60 g of aluminum nitride powder was mixed with 2 g of KD-2 and the various amounts of yttrium isopropoxide, with 150 ml of isopropanol. The raw materials were mixed together and then ball milled for 24 h. After a drying step at 75°C overnight, pellet samples were prepared by isostatic pressing at 40.000 psi. A Perkin-Elmer TGA 7 System was used for the thermal analyses (The Perkin-Elmer Corp., Norwalk, CT). Heating rates are specified with each analysis. The gas flow rate was 25 $cm^3 \cdot min^{-1}$, using either air or nitrogen. Thermogravimetric (TG) curves and their respective derivative (DTG) curves were used as a study method [7], as was differential thermogravimetric analysis [8]. An Amray 1400

Scanning Electron Microscope with a Princeton Gamma Technology (PGT) Windowless Energy Dispersive X-ray Detector was used for energy dispersive X-ray spectroscopy (EDS) analyses (Amray Inc. Bedford, MA). This apparatus, due to its high vacuum operating conditions and special windowless detector, allows one to identify the elements with an atomic number equal or higher than of carbon, instead of sodium, as is the case with a conventional beryllium window EDS detector.

Results and discussion

The additives

The yttrium isopropoxide can decompose forming yttrium oxide, in two ways [9]. By simple thermal decomposition, yttrium oxide, propene and isopropanol are formed, as in reaction (1). Yttrium oxide can also be formed by hydrolysis with ambient humidity, as in reaction (2), with isopropanol being another product. Either of these reactions would be desirable to provide a uniform coating of yttria around the AlN particles.

$$2Y(OC_3H_7)_3 \rightarrow Y_2O_3 + 3C_3H_7OH + 3CH_3CHCH_2 \qquad (1)$$

$$2Y(OC_3H_7)_3 + 3H_2O \rightarrow Y_2O_3 + 6C_3H_7OH \qquad (2)$$

Figure 1 shows the comparison between TG curves obtained for yttrium isopropoxide samples in air and in nitrogen, with practically the same mass (5.666 mg and 5.640 mg), using a 10 deg·min^{-1} heating rate. Both TG curves

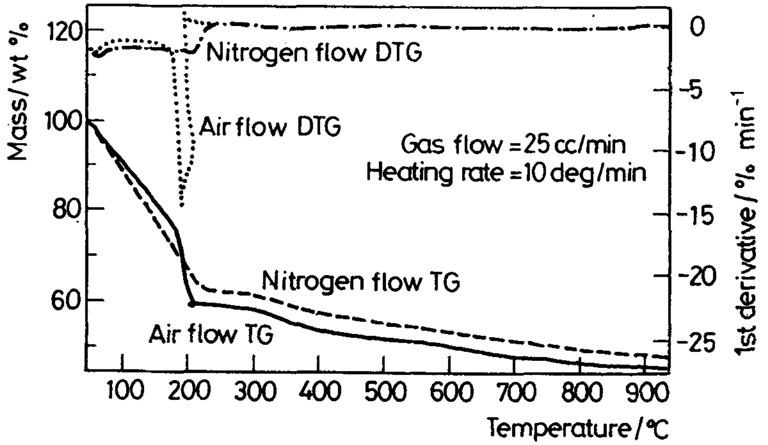

Fig. 1 TG and DTG curves for yttrium isopropoxide in air and in nitrogen. Sample weights: 5.666 mg (in air), 5.640 mg (in nitrogen)

are nearly the same until the 5% weight loss, due to the desorption of residual isopropanol, which is used as a solvent for the isopropoxide.

After that, in the nitrogen case, there is an initial almost-constant weight loss step up to 230°C, where 38.12% of the initial weight is lost. It must be considered that there are two DTG peaks at 65 and at 210°C, the former due to the solvent desorption, and the latter due to some intermediate decomposition stage of reaction (1) between 200 and 230°C. After a constant weight loss rate up to 180°C, this stage occurs with a thermal runaway reaction for the air flow case which ends with an accumulated loss of 40 wt%. A higher apparent DTG peak is probably caused by the additional energy due to the burning of the free radicals formed, and therefore the temperature reading might not be the actual temperature inside the sample.

In both cases, after 270°C, a second multistage decomposition step begins, with similar TG behaviour, and the total decomposition of reaction (1) does not occur. At 930°C, there is a total weight loss of 53.00% in air and 50.32% in nitrogen.

Comparison of thermal decomposition up to 550°C, in air and nitrogen, showed that during the 300–500°C temperature range, black surface compounds are formed. Carbon was identified by windowless EDS, on uncoated specimens burned out to 550°C. Totally white final products are obtained if heated again up to 1100°C in air. This means that in the initial part of the yttrium isopropoxide second decomposition step there is a carbonization of the intermediate residual organic products.

In the previous processing steps of the AlN powder, there is a drying step at 75°C to vaporize the solvent and to hydrolyze the yttrium isopropoxide to the oxide. An isothermal TG run was made with an yttrium isopropoxide sample at 75°C in air. An asymptotic weight loss (30% total) was observed, which corresponds to an equilibrium state with 45.73% yttrium isopropoxide decomposed. The resulting product was burned in air up to 950°C. This time a cumulative weight loss of 59.49% was observed, which is practically equal to the theoretically expected 59.66% weight loss.

Figure 2 shows the TG and DTG curves obtained for KD-2 samples in air and in nitrogen, respectively with 10.862 mg and 9.362 mg starting weights, heated at 10 deg·min^{-1}. As happens with other polymer pyrolyses [10], the decomposition in nitrogen ends at higher temperatures than in air, and it is practically completed at 370°C. The nitrogen derivative TG curve shows a peak at 350°C. In the air flow case, the vaporization begins at 200°C, and the subsequent burning ends at about 300°C. There is a DTG peak at a lower temperature (290°C) due to the additional energy given up by the burning reaction. It is interesting to note that at 300°C there is still 2.94% of the initial mass, which is totally burned out only at about 550°C. Carbon was identified by windowless

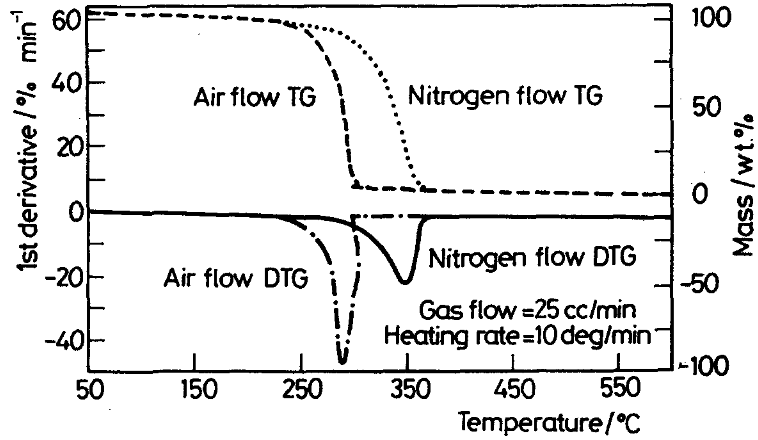

Fig. 2 TG and DTG curves for KD-2 dispersant in air and in nitrogen. Samples weights: 10.862 mg (in air), 9.362 mg (in nitrogen)

EDS on an uncoated residual product obtained in air burnout when it is stopped at 350°C.

The aluminum nitride and its compositions with the additives

Figure 3 shows TG curves (on a residual mass basis) of a 26.806 mg sample of AlN with precursor equivalent to 2 wt% Y_2O_3 and of a 24.699 mg AlN sample without additive in nitrogen heated at 10 deg·min^{-1}. The AlN sample mass was purposely adjusted to be almost the same mass that there was in the former

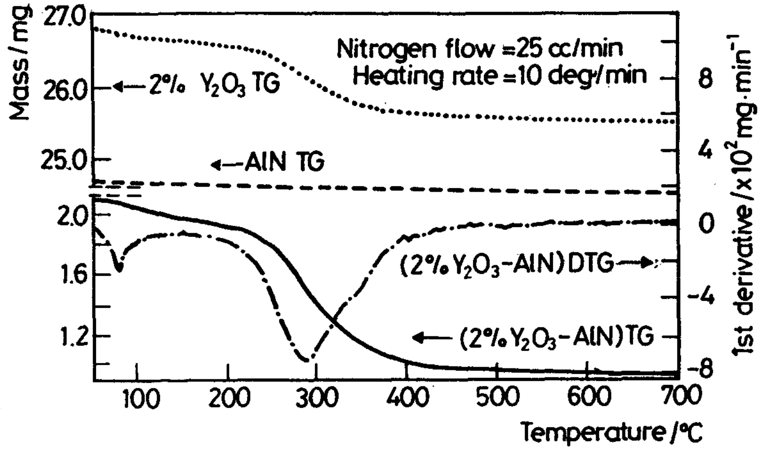

Fig. 3 TG curves of AlN and 2% Y_2O_3 samples and their DTG curve with its derivative. Sample weights: 24.699 mg (AlN), 26.806 mg (2% Y_2O_3 sample)

sample in order to have, by the difference in their respective TG curves, a DTG curve (also shown in the figure), which allows one to see the behaviour due to the additives themselves.

The AlN TG curve shows a total 0.18% weight loss up to 300°C, which is most likely due to adsorbed gases and water. In the 2% yttria TG curve there is a total weight loss of 4.38% that ends at 650°C, less than the expected 5.77 wt% loss (on a solvent free basis). As in other mixtures of organic additives and AlN undergoing pyrolysis in an inert atmosphere [1, 3, 11], the lesser weight loss can be due to any of the following: the residual carbon adsorbed in the final burnout product; to other yttrium isopropoxide residual decomposition products, and/or (as is most probable) to a partial hydrolysis of the yttrium isopropoxide during the previous processing steps.

On the derivative curve of Fig. 3, there is a first peak at 80°C. Considering that the isopropanol boiling point is 82.4°C, and that its 12.6 wt% water azeotrope boiling point is 80.3°C [12], this peak is evidence of the residual isopropanol desorption due to a previous hydrolysis of some yttrium isopropoxide. Between 90 and 190°C there is a practically constant rate of weight loss, due to the first stage of the initial decomposition step for the yttrium isopropoxide, as seen in Fig. 1. This step, as a whole, is shifted to a higher temperature range, as observed in binder burnout cases of other ceramic compositions [1, 11], overlapping the further yttrium isopropoxide multistage decomposition step and the KD-2 pyrolysis. A broad peak in the derivative is observed at 287°C, and although minimal, there is a secondary overlapped peak at 345°C.

TG curves obtained using 2% Y_2O_3 samples heated at both 5 deg·min^{-1} and 20 deg·min^{-1} in flowing nitrogen, with almost the same mass (26.387 mg and 26.961 mg), show practically the same total weight losses (4.55% and 4.51%). The two main yttrium isopropoxide decomposition steps are more overlapped than for the isopropoxide itself, and even at 5 deg·min^{-1} it is difficult to identify the DTG peak due to the dispersant decomposition.

By the DTG curve of a 25.488 mg 2% Y_2O_3 sample, obtained in flowing air at 20 deg·min^{-1}, it can be seen an enhanced initial decomposition of the yttrium isopropoxide due to the additional burning energy as seen in Fig. 1. Consequently, the KD-2 decomposition is less overlapped and it can be identified by a DTG peak occurring at 330°C, by comparison with the DTG decomposition peak of a 4.138 mg KD-2 sample occurring at 325°C, at the same heating rate in air.

Figure 4 shows the TG and DTG curves obtained for a 26.806 mg 2% Y_2O_3 and for a 26.881 mg 5% Y_2O_3 sample in nitrogen, heated at 10 deg·min^{-1}. Before 90°C, the 5% sample shows a higher weight loss than the 2% one, due to a higher initial desorption of residual isopropanol. This indicates a greater hydrolysis in the early stages. In both cases a constant rate loss can be seen, due

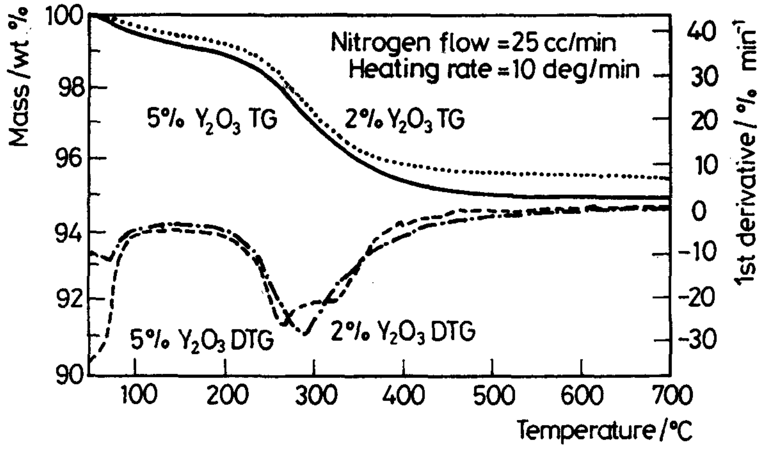

Fig. 4 Effect of the yttrium isopropoxide content on the TG and DTG curves. Sample weights: 26.806 mg (2% Y_2O_3), 26.881 mg (5% Y_2O_3)

to the yttrium isopropoxide initial decomposition step until almost 190°C, which results in a higher weight loss for the 5% Y_2O_3 TG curve. The two next decomposition steps are less overlapped in the 5% case, with better resolved peaks: the former, at 268°C, due to the second stage of the initial yttrium isopropoxide decomposition with a higher weight percent loss, and the second, at 330°C, due mainly to the KD-2 pyrolysis, when compared with its nitrogen flow DTG in Fig. 2. The total weight loss for the 5% case was 4.97 wt%, while for the 2% case it was 4.38 wt%. Considering that theoretically the maximum total loss is 7.40% in the 5% case (on a solvent free and total decomposition basis), these results show that apparently the yttrium isopropoxide has been more hydrolyzed in previous processing steps for the 5% case.

Residual carbon content and previous yttrium isopropoxide decomposition estimation

Complementary analysis

The extent of previous hydrolysis of the yttrium isopropoxide with ambient humidity, as shown, lowers significantly the total TG weight losses of the AlN compositions. As there is the possibility to form carbon during decomposition, complementary KD-2 and yttrium isopropoxide TG analyses were made to estimate maximum carbon contents that could be present after nitrogen burnout.

KD-2 TG analyses were made in flowing nitrogen from ambient temperature to 350°C, at 10 deg·min^{-1}. About 1.6% of the initial mass remains as a carbonaceous residue. Complementary heatings were made with the yttrium isopropoxide in nitrogen flowing to 550°C, obtaining carbonaceous surface products that were then heated in air to 1100°C, obtaining yttrium oxide. About 10.5% of the initially yttrium isopropoxide mass is converted to a carbonaceous organic residue during the nitrogen burnout.

Taking the upper percent values as residual carbon that can be formed from yttrium isopropoxide and KD-2 pyrolysis as a basis for calculation, and assuming that they are proportional to their initial composition, total losses of 5.18 wt% and 7.87 wt% are expected respectively for the 2 and 5% Y_2O_3 samples. As the actual percent weight losses were lower than these, it is an additional indication that a previous partial decomposition of the yttrium isopropoxide had occurred.

Estimation of residual carbon content after nitrogen burnout

The following procedure was made with 2, 3 and 5% Y_2O_3 samples, in order to estimate their residual carbon content after nitrogen burnout. The samples were heated in flowing nitrogen at 10 deg·min^{-1} to 650°C. After having been cooled in nitrogen to ambient temperature to avoid oxidation or hydrolysis reactions with ambient air, the resulting burnout products were immediately heated at 20 deg·min^{-1} in flowing air to 1450°C. Figure 5 shows typical TG and DTG curves obtained for the oxidation step of the 5% Y_2O_3 nitrogen burned-out sample. This behaviour was similar for the other cases. A comparison is made with an AlN sample as received, submitted to the same oxidation conditions.

Essentially, the AlN oxidation of the nitrogen burned out samples begins at about 700°C and is completed at 1300°C. By looking at the DTG curve of Fig. 5, it can be noted that the oxidation rate is lowered by the simultaneous re-

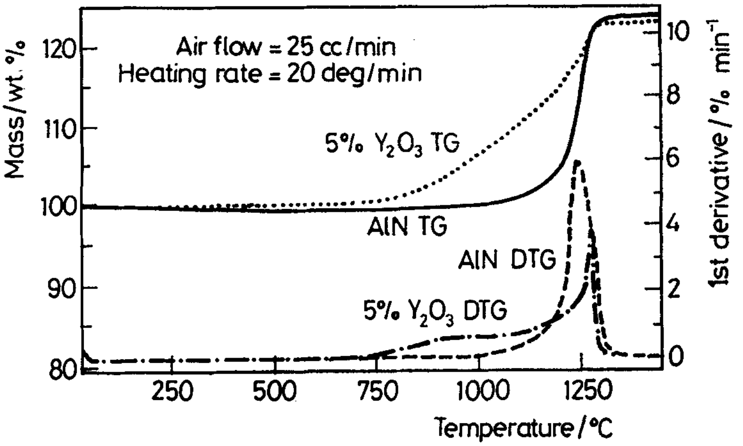

Fig. 5 Oxidation of an AlN sample and of a 5% Y_2O_3 nitrogen burned out sample. Sample weights: 25.552 mg (AlN), 24.688 mg (5% Y_2O_3)

sidual carbon burning between 900 and 1200°C, after which there is the AlN oxidation peak. The as-received AlN sample oxidation begins at a higher temperature and does not show the discontinuity in its DTG curve.

Stoichiometrically, the AlN total oxidation to Al_2O_3 represents a rise of 24.408 wt% referred to its initial mass. Considering for the AlN compositions that:

$M_{1450^\circ C}$ = mass after air oxidation at 1450°C
M_i = initial mass before air oxidation = mass after N_2 burnout
M_c = carbon mass in M_i (completely burned up to 1450°C)
M_{Ai} = initial Al_2O_3 mass in M_i
M_{AlN} = initial AlN mass in M_i = 97.45 M_{Ai}/2.55 (Note: initial AlN has 2.55 wt% of Al_2O_3)
f = Y_2O_3 wt% in $M_{1450^\circ C}$
M_Y = Y_2O_3 mass in M_i = Y_2O_3 mass in $M_{1450^\circ C}$ = $(f)(M_{1450^\circ C})$

$$M_{1450^\circ C} = M_i + 0.24408\, M_{AlN} - M_c \tag{3}$$

$$M_i = M_c + M_{Ai} + M_y + M_{AlN} \tag{4}$$

$$M_{1450^\circ C} = 1.24408\, M_{AlN} + M_Y + M_{Ai} \tag{5}$$

For comparison, in $M_{1450^\circ C}$ there is only Al_2O_3 and Y_2O_3 and their mass rate is fixed by the initial AlN and yttrium isopropoxide masses used to make the pellets, so f is known. Considering the initial yttrium isopropoxide 95% purity and solving the upper system for the 2, 3 and 5% Y_2O_3 sample analysis data, the estimated carbon contents in their respective nitrogen burnout residual products are 0.40%, 0.53% and 0.35%.

Estimation of the extent of previous yttrium isopropoxide decomposition

For all the compositions used to prepare the pellets, 60 g of AlN and 2 g of KD-2 were used. The yttrium isopropoxide initial mass (M), was 2.83 g, 4.24 g and 7.07 g, respectively in the 2, 3 and 5% Y_2O_3 cases.

Considering that in relation to the nitrogen burnout of each AlN composition sample:

a) The initial 5% isopropanol content of the yttrium isopropoxide is lost during the drying step;

b) X = previous decomposition degree of the yttrium isopropoxide;

c) M_{act} = actual mass of yttrium isopropoxide before the nitrogen burnout = $(10-X)(0.95)M$

d) M_{Yi} = stoichiometrical Y_2O_3 mass obtained from the previously decomposed yttrium isopropoxide = $(0.4246)\ (0.95)\ (M)\ (X)$

e) M_{tot} = total mass that will be submitted to the burnout;
f) Y = the total weight percent loss during the burnout;
g) C = the residual carbon weight % in the burnout residue;
h) M_c = residual carbon mass in the burnout residue = $(C)(M_{tot})(1-Y)$
i) L_{Max} = maximum possible mass loss
j) L = actual mass loss during the burnout

$$M_{tot} = 60+2+M_{act}+M_{Yi} = 62+M(0.95-0.5466X) \tag{6}$$

$$L_{Max} = 2+0.5754(1-X)(0.95)M \tag{7}$$

$$L = L_{Max}-M_c \tag{8}$$

$$Y = L/M_{tot} \tag{9}$$

Solving the above system:

$$X = \frac{2+M(0.5466-0.95C)-62C-Y(1-C)(62+0.95M)}{0.5466M(1-C)(1-Y)} \tag{10}$$

The experimental Y values for the 2, 3 and 5% Y_2O_3 cases were respectively 4.45%, 5.63% and 4.85%. The estimated X values are respectively 28.60%, 12.41% and 62.85% for the estimated carbon contents obtained in item 4.2. They would be 45.21%, 27.44% and 68.85%, if there was no carbon residue. If all the carbon from respective KD-2 and yttrium isopropoxide was in the residual burnout product as estimated in item 4.1, the X values would be respectively 28.90%, 7.21% and 60.23%.

As can be seen, the 5% Y_2O_3 sample had the most extensive hydrolysis of the yttrium isopropoxide. It is interesting to notice that for the three carbon residue hypotheses, there was a partial hydrolysis in each case, and the higher its value, the lower the residual carbon content after nitrogen burnout.

Conclusions

There is only a partial yttrium isopropoxide decomposition by hydrolysis with ambient moisture during the processing steps used to prepare the isostatic pressurized AlN pellets.

Both the residual carbon content after the AlN pellet nitrogen burnout, and the degree of yttrium isopropoxide decomposition in their early processing steps can be estimated by thermogravimetric analysis.

The thermal decomposition of the AlN pellets in nitrogen begins from ambient temperature to about 200°C, with an almost constant rate of mass loss where residual isopropanol is volatilized and the first stage of the yttrium isopropoxide decomposition step occurs. Between 200°C and 450°C, there is an overlapping effect of the KD-2 pyrolysis and the multistage yttrium isopropoxide decomposition which ends incompletely at 650°C.

The heating rate is the operating variable that enhances significantly the second stage of the yttrium isopropoxide initial decomposition step.

The thermal decomposition of the dispersant and the yttrium isopropoxide forms carbon in nitrogen atmosphere, but also in air atmosphere. While the carbon from the dispersant can be totally removed in air at 550°C, the residual carbon from yttrium isopropoxide can be completely burned in air only at temperatures higher than 900°C.

The residual product of the burnout in nitrogen contains carbon mostly from the yttrium isopropoxide second decomposition step. The amount of carbon depends on the previous extent of hydrolysis of the yttrium isopropoxide.

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Zusammenfassung — Yttriumisopropoxid, eine Vorstufe von Yttriumoxid, wird in manchen Fällen als Hilfsmittel beim Sintern zur Herstellung von Aluminiumnitrid-Keramik verwendet. Vorliegend wurde dieses Sinterhilfsmaterial mit Isopropanol als Lösungsmittel und mit Polyethy-

lenimin als Dispersionsmittel verwendet. Nach einer anfänglichen Kugelmühlenaufbereitung und Trocknungsschritten wird mittels Thermoanalyse in Stickstoff und Luft das Ausbrennverhalten von Proben aus isostatisch gepreßten Pellets untersucht. Außer den gemahlenen und gepreßten Pellets wurde jede einzelne Komponente auch einzeln untersucht.

Ein vollständiger Umsatz zu Yttriumoxid ohne verbleibenden Kohlenstoff wäre die wünschenswerte Eigenschaft dieses Systemes. Jedoch fand bei der Herstellung der Aluminiumnitridpellets nur eine teilweise Zersetzung von Yttriumisopropoxid statt. Der Ausbrennrückstand in Stickstoff enthält aus Yttriumisopropoxid geformten Kohlenstoff und Dispergiermittel, welches die thermische Zersetzung überlagert, am meisten von einem intermediären Zersetzungsprodukt des ersteren bei 300 und 550°C. Der verbleibende Kohlenstoffgehalt und die vorangehende Zersetzung des Yttriumisopropoxides wurde thermogravimetrisch geschätzt.