ALUMINUM NITRIDE OXIDATION BY SIMULTANEOUS TG AND DTA

J. Dweck[1]*, R. S. Aderne[2] and D. J. Shanefield[3]

[1]School of Chemistry, Federal University of Rio de Janeiro, Bloco E do CT, Sala E-206,
Cidade Universitária, Rio de Janeiro, RJ, Brasil, 21949-900
[2]School of Chemistry, UFRJ and Catalysis Nucleus NUCAT / PEQ / COPPE / UFRJ, Centro de
Tecnologia, Bloco G-115, Cidade Universitária, Rio de Janeiro, Brasil, 219494-900
[3]Department of Ceramic & Materials Engineering, Rutgers University, 607 Taylor Road
Piscataway, NJ 08854-8065, USA

Abstract

This work is a study, by simultaneous thermogravimetry (TG) and differential thermal analysis (DTA), of the oxidation of a water resistant aluminum nitride powder which has a special protective coating, and an uncoated AlN powder which has become partially hydrated during its use. The activation energy for oxidation is estimated by the Kissinger and isoconversional methods. In the former method, the temperatures of the oxidation peaks were obtained from DTA and DTG curves. The activation energies for oxidation of the water resistant AlN, obtained by the Kissinger method, are 357 ±10 kJ mol^{-1}, 392±12 kJ mol^{-1} using respectively DTG and DTA data. For the uncoated AlN, the values are 243±7 and 257±8 kJ mol^{-1}, respectively. By the isoconversional method, the average values obtained for coated and uncoated samples are, respectively, 323±10 and 224 ±7 kJ mol^{-1}. Therefore, the special coating, which protects the aluminum nitride from humidity action, also provides a higher resistance to oxidation.

Keywords: aluminum nitride, DTA, DTG, isoconversional method, Kissinger, oxidation, TG

Introduction

Uncoated AlN powder may hydrolyze in contact with ambient humidity generating ammonia and aluminum hydroxide [1]. A water resistant aluminum nitride powder, which has a special protective coating [2], and an uncoated AlN powder, which has become partially hydrated during its, were characterized by simultaneous thermogravimetry (TG) and differential thermal analysis (DTA). During the analyses, which were performed from ambient temperature to 1723 K using air as the purge gas, two main phenomena may occur: initially any aluminum hydroxide present in the sample is thermally dehydrated to alumina, releasing structural water and, in a second stage, the aluminum nitride is totally oxidized to alumina. This work has as its

---
*   Author for correspondence: E-mail: dweck@h2o.eq.ufrj.br

objective to show how thermal analysis techniques (TG, DTG and DTA) may be used to estimate the aluminum hydroxide and AlN contents of the samples and to study their oxidative behavior by comparing the activation energy for oxidation, which was determined by using Kissinger [3] and isoconversional [5–8] methods.

Experimental

Two AlN samples of different characteristics were studied: an uncoated AlN powder (named as A), type F, manufactured by Tokuyama Soda; a 'water-resistant' AlN manufactured by Advanced Refractories Technology, which has a special protective coating (named as B). A synthetic aluminum hydroxide ($Al(OH)_3$), type OC1000 manufactured by ALCOA, was used as reference for the identification of this substance during thermal decomposition of partially hydrated uncoated AlN samples. A Rigaku, simultaneous TG/DTA, model TAS-100, with TG8110 accessory, was used for the thermal analyses, which were performed from ambient temperature to 1723 K, with an air flow rate of 50 cm^3 min^{-1} at heating rates of 10, 15 and 20 K min^{-1}.

Derivative thermogravimetry (DTG) and TG allow the identification and quantification of the degree of hydration and the actual AlN content in each material. When the sample is partially hydrated, there is a mass loss in the TG curve from 450 to 900 K, which represents stoichiometrically 34.6% of the $Al(OH)_3$ mass in the sample. On the other hand, the total mass rise which occurs during oxidation of the AlN to Al_2O_3 beginning at about 1073 K, represents stoichiometrically 24.41% of the AlN mass in the sample. These relationships were used to estimate the $Al(OH)_3$ and AlN contents of the samples.

Kissinger's method for estimating the activation energy of a reaction [3], considers the temperature of the corresponding DTA peak as the temperature of maximum reaction rate (T_{max}). The temperature of the DTG peak should provide the same information unless the heat released by reaction changes with extent of reaction, or becomes rate controlling. In the Kissinger method, the activation energy E_a (kJ mol^{-1}) is related to the other kinetic and operating parameters by expression (1), and may be estimated from the value of the slope of the straight line obtained by plotting $\ln(\beta/T_{max}^2)$ *vs.* $(1/T_{max})$ [3, 4].

$$\ln\left(\frac{\beta}{T_{max}^2}\right) = -\frac{E_a}{R}\frac{1}{T_{max}} + \ln\left(\frac{AR}{E_a}\right) \tag{1}$$

where β is the heating rate (K min^{-1}), A is the pre-exponential factor (min^{-1}) and R= 8.314 J mol^{-1} K^{-1}, is the gas constant.

The isoconversional method is based on the determination of the activation energy from TG curves obtained at different heating rates, comparing the experimental conditions at the same conversion degree. Thus, several values of the activation energy $E_{a,\alpha}$ may be determined, for each conversion degree α, as the reaction proceeds. These may be estimated by expression (2) [8], from the corresponding straight line

data obtained plotting logβ *vs.* $(1/T_{\beta,\alpha})$, where $T_{\beta,\alpha}$ is the temperature at which a conversion degree α occurs, during the analysis performed at a heating rate β.

$$E_{a,\alpha} \cong -18.2 \left(\frac{\partial \log\beta}{\partial\left(\dfrac{1}{T_{\beta,\alpha}}\right)} \right) \qquad (2)$$

where, α is the oxidation degree, which is calculated as the percentage of the total mass gain during the AlN oxidation step, which was measured from the respective TG curve, as was $T_{\beta,\alpha}$. The factor 18.2 arises from the use of Doyle's approximation for the temperature integral [9].

Results and discussion

Figure 1 shows typical X-ray diffraction patterns for the studied materials, all of them analyzed after a year of intermittent use. Sample B refers to the 'water resistant' AlN, sample C to the uncoated AlN powder, and sample D refers to the synthetic aluminum hydroxide. As can be seen, sample B presents only an AlN phase. Sample D was identified as gibbsite, presenting only an $Al(OH)_3$ phase, while sample C presents two different phases: AlN and $Al(OH)_3$, which indicates that the original uncoated AlN sample (A) was partially hydrated during its use.

Figure 2a, shows typical TG curves obtained at a heating rate of 10 K min^{-1} used for estimation of $Al(OH)_3$ and AlN contents in each sample. The curves of samples A
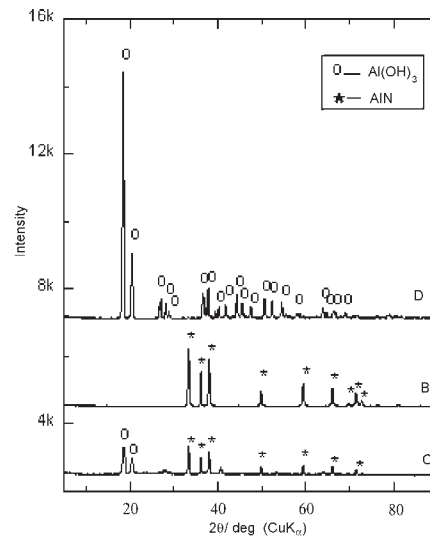
**Fig. 1** X-ray diffraction patterns of samples B, C and D
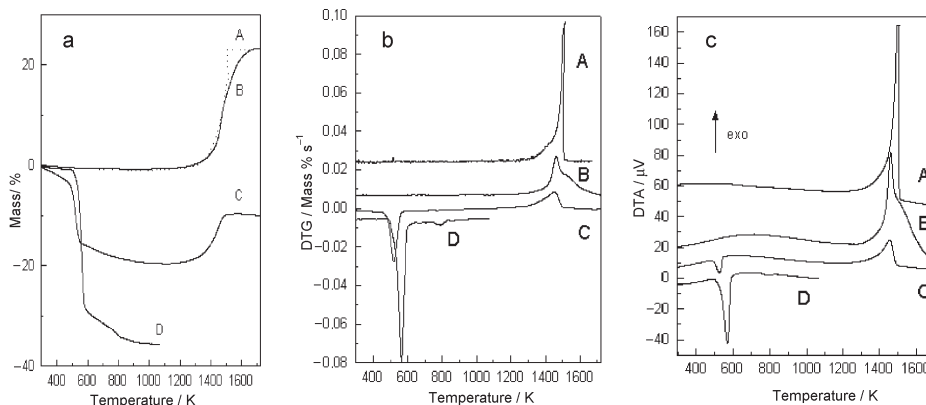
Fig. 2 Thermal analyses of samples A, B, C and D; a – TG curves; b – DTG curves;
c – DTA curves

and B are practically the same from room temperature until the beginning of the oxidation step at 1073 K. This indicates that the original uncoated AlN sample was not hydrated, and did not have any aluminum hydroxide as was also found for the coated 'water resistant' sample B. In both curves, there is small mass loss in the beginning, due probably to some adsorbed gas. It can be seen that the oxidation behavior of the coated, sample B, is different from the uncoated one (A). The 'water resistant', sample B, presents a more delayed reaction with apparently two stages, while the uncoated shows only one. The curve A separates from B at 1380 K and it continues with a much faster oxidation, which ends at 1500 K. The complete oxidation of sample B occurs at 1720 K. The TG curve of sample C shows similar behavior to sample A during AlN oxidation, which occurs from 1077 to 1505 K. The mass loss observed during dehydration of the $Al(OH)_3$ in sample C occurs in the same temperature range as for the reference gibbsite (sample D), indicating that the material was partially hydrated during its use. From the corresponding mass gains during the oxidation step, the estimated AlN contents of sample A, B and C , were respectively, 99.5, 98.5 and 49.7% [10]. The estimated $Al(OH)_3$ content of sample C was 47.5%.

Figure 2b shows the derivative TG curves (DTG) of the samples, which were shifted vertically for comparison. The DTG curve of sample A has only one peak with a maximum at 1511 K, due to the oxidation step. Curve B presents a maximum at 1463 and a shoulder at 1516 K, returning to the base line at 1720 K. The DTG curve of sample C presents a peak with a maximum at 521 K, due to $Al(OH)_3$ dehydration, and an AlN oxidation peak with a maximum at 1460 K, which ends earlier than in the case of sample A, due to a lesser content of AlN.

Figure 2c presents the DTA curves, which have similar profiles to the corresponding DTG curves in Fig. 2b. The original uncoated sample A, during its oxidation, presents a very high exothermic effect, which exceeds the recording limit of the equipment. The 'water resistant' sample B, has an AlN content very similar to sample
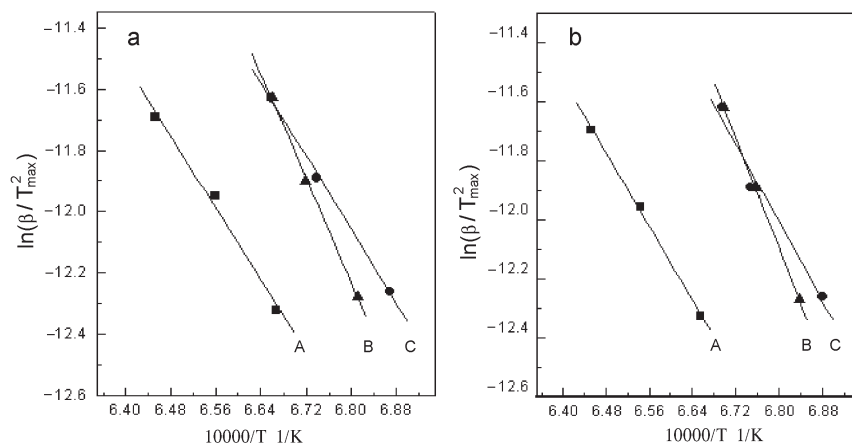
Fig. 3 Kissinger plots for samples A, B, and C; a – from DTG peak data; b – from DTA peak data

A, but presents a DTA curve which shows a more controlled oxidation rate than sample A.

Figure 3a shows the curves obtained by Kissinger's method using DTG peak temperatures to determine the activation energy, and Fig. 3b, using DTA peaks. The curves A and C are practically parallel in both cases. This indicates that for the uncoated samples, the activation energy for their oxidation is independent of their hydration degree. The energies calculated from DTG and DTA data, were respectively, 357 ± 10 and 391 ± 12 kJ mol^{-1} for sample B, 243 ± 7 and 257 ± 8 kJ mol^{-1} for the uncoated sample A, and 249 ± 7 and 277 ± 8 kJ mol^{-1} for sample C. The values obtained for samples A and C from DTG data are practically the same, but those obtained from DTA data show that the activation energy is slightly higher in case of partially hydrated samples, probably due to different heat transfer properties. The highest values
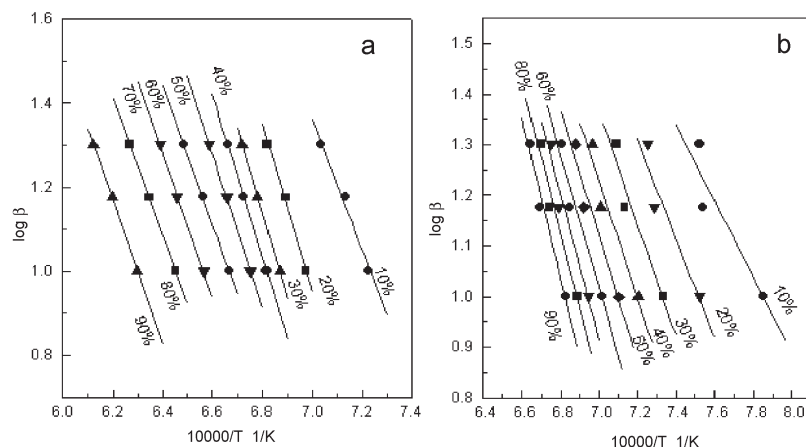
Fig. 4 Isoconversional plots for a – samples B and b – C

for sample B show a higher resistance to oxidation than sample A. The pre-exponential factors, calculated from DTG and DTA data, were $9.7\pm0.3\cdot10^{11}$ and $2.1\pm0.5\cdot10^{13}$ for sample B, $3.7\pm0.9\cdot10^{8}$ and $12.3\pm1.3\cdot10^{8}$ for sample A, and $12.8\pm0.2\cdot10^{8}$ and $1.4\pm0.4\cdot10^{9}$ for sample C, respectively.

Figures 4a and 4b show the plots obtained for samples B and C using the isoconversional method. The average values obtained for coated and uncoated samples are 323 ± 10 and 224 ± 7 kJ mol^{-1}, respectively. This method is more representative of what occurs as reaction proceeds. Table 1 presents all the values estimated for different oxidation degrees.

Table 1 Estimation of the activation energy for oxidation by isoconversional method for AlN samples

Conversion/% (oxidation degree)	E_a/kJ mol^{-1} Coated sample B	E_a/kJ mol^{-1} Uncoated sample C
10	274±8	137±4
20	361±10	178±5
30	370±11	200±6
40	353±10	208±6
50	334±10	224±7
60	301±9	241±7
70	309±9	262±8
80	295±9	273±8
90	310±9	289±9

Conclusions

The oxidation behavior of coated and uncoated AlN samples are different. The protective coating, besides avoiding the action of the humidity, increases the resistance to oxidation. The activation energy for oxidation of the uncoated AlN samples seems to be independent of their hydration degree.

*   *   *

References

1 P. Garrou, A. Knudsen and T. Guiton, Proc. 42nd Electr. Comp.& Techn. Conf., 1992, B29.
2 T. J. Mroz, Amer. Ceram. Soc. Bul., 71 (1992) 782.

 3 H. E. Kissinger, Anal. Chem., 29 (1957) 1702.
 4 J. Llópiz, M. M. Romero, A. Jerez and Y. Laureiro, Thermochim. Acta, 256 (1995) 205.
 5 J. H. Flynn and L. A. Wall, J. Polym. Sci. Part B, 4 (1966) 323.
 6 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.
 7 T. Ozawa, Thermochim. Acta, 203 (1992) 159.
 8 V. J. Fernandes, Jr. and A. S. Araujo, Thermochim. Acta, 255 (1995) 273.
 9 S. Vyazovkin, Thermochim. Acta, 340/341 (1999) 53.
10 I. V. Nicolaescu, G. Tardos and R. E. Riman, J. Am. Ceram. Soc., 77 (1994) 2265.