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The course of the hydrolysis and the reaction kinetics of AlN powder in diluted aqueous suspensions

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Abstract

The reactivity of AlN powder in diluted aqueous suspensions in the temperature range 22–90 °C was investigated in order to better understand and control the process of hydrolysis. The hydrolysis exhibits three interdependent stages: during the induction period (first stage) amorphous aluminum hydroxide gel is formed, followed by the crystallization of boehmite (second stage) and bayerite (third stage). The hydrolysis rate significantly increased with higher starting temperatures of the suspension, but was independent of the starting pH value; however, the pH value of 10 caused the disappearance of the induction period. The kinetics was described using un-reacted-core model, and the chemical reaction at the product-layer/un-reacted-core interface was the rate-controlling step for the second stage of the hydrolysis in the temperature range 22–70 °C, for which the calculated activation energy is 101 kJ/mol; whereas at 90 °C, the diffusion through the product layer became the rate-controlling step.

Keywords: Nitrides; Suspensions; Hydrolysis; Electron microscopy

1. Introduction

Aluminum nitride (AlN) powder was synthetically produced for the first time in the 19th century, by heating aluminum turnings in an atmosphere of nitrogen at around 700 °C.[1] AlN, like aluminum,[2] is water sensitive[3] and in the presence of water it slowly degrades, forming aluminum hydroxides and ammonia by the following general reaction:[4]

$$\mathrm{AlN} + 3\mathrm{H_2O} \rightarrow \mathrm{Al(OH)_3} + \mathrm{NH_3} \qquad (1)$$

The hydrolysis of AlN powder was exploited for the production of ammonia in at the beginning of the 20th century, prior to the invention of the Haber–Bosch process.[5] Afterwards, AlN was almost forgotten, until the discovery of its unique set of material properties, which are useful in electronic, structural and refractory applications. Owing to its high thermal conductivity, high electrical resistivity, low dielectric constant, low thermal expansion coefficient, high strength and high temperature stability, sintered AlN ceramics are used as a substrate material for power circuits and as a packaging material for integrated circuits.[6] AlN powder is also used as a minor constituent in the formation of SiAlON ceramics[7,8] and as a sintering additive for SiC-based ceramics.[9] In the production of the above-mentioned ceramics, the reactivity of the AlN powder with water became a major drawback, because of the formation of $\mathrm{Al(OH)_3}$ (Eq. (1)), which during the sintering of the AlN ceramic transforms to $\mathrm{Al_2O_3}$; this then, lowers the thermal conductivity of these ceramics.[10] The water sensitivity of AlN powder was avoided by the use of non-aqueous powder processing, or alternatively, by employing a water-resistant AlN powder.[11–13]

More recently, the exploitation of AlN powder hydrolysis has been revived. As shown by Kosmač et al.[14,15] AlN can be used as a reactant in the hydrolysis-assisted solidification (HAS) forming process, where the hydrolysis at elevated temperatures is exploited in the solidification of an aqueous ceramic suspension in an impermeable mould. Furthermore, AlN powder hydrolysis at elevated temperatures can be exploited in the preparation of nanostructured aluminate coatings onto ceramic substrate immersed into a diluted AlN suspension.[16] The heat-treated coatings can be applied in dentistry as a non-invasive, pre-treatment method for yttria-stabilized tetragonal zirconia

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(Y-TZP) ceramics[17,18] and as a template in the preparation of superhydrophobic surfaces.[19]

In spite of the emergence of many applicable procedures that exploit the hydrolysis of AlN powder, its chemistry has not yet been investigated in detail. Only a handful of studies were focused on the reaction kinetics of AlN powder with water and on the formation of hydrolysis reaction products (aluminum hydroxides). The majority of these studies were focused on the prevention of the hydrolysis.[20–23] Some researches noticed an incubation time prior to the start of the hydrolysis reactions,[24–26] which was attributed to a thin, hydrated aluminum oxide layer on the surface of the AlN particles that, has to be dissolved or penetrated by the water molecules in order that the hydrolysis can begin. The presence of a 5–10-nm thick aluminum oxide layer on the surface of the AlN particles was first confirmed by Slack and McNelly.[27] Later, Saito and Ishizaki[28] performed auger electron spectroscopy (AES) on AlN powder surfaces and reported that the chemical states of the powder surfaces depend on the manufacturing processes for the preparation of the powders. The AES analysis indicated the presence of an oxide-like θ-Al_2O_3 containing an AlON phase on the surface of AlN powder prepared by the carbothermal-nitridation process, while those prepared by chemical vapor deposition (CVD) and the direct-nitridation method are covered by an oxide-like γ-Al_2O_3 with an oxygen diffusion layer and do not contain the AlON phase. Other researchers[22] did not observe a layer of any kind on the surface of the AlN particles.

Bowen et al. were amongst the first authors who extensively studied AlN powder hydrolysis at room temperature (RT) and did the pioneering work on the kinetics and mechanisms of AlN powder degradation in water.[29] They proposed the following reactions:

$$AlN + 2H_2O \rightarrow AlOOH_{(amorph)} + NH_3 \qquad (2)$$

$$NH_3 + H_2O \leftrightarrow NH^{4+} + OH^- \qquad (3)$$

$$AlOOH_{(amorph)} + H_2O \rightarrow Al(OH)_{3(xstal)} \qquad (4)$$

According to these authors, the AlN powder first reacts with water to form an X-ray amorphous aluminum mono-hydroxide, with a stoichiometry close to boehmite (γ-AlOOH), which later dissolves and recrystallizes to form bayerite (α-$Al(OH)_3$). The kinetics of the AlN hydrolysis was described by an un-reacted-core model,[30] based on the oxygen weight gain of the hydrolyzed powder. The chemical reaction at the product-layer/un-reacted-core interface was proposed to be the rate-controlling step during the initial stage of the reaction.[29] This was later confirmed by Krnel et al.,[25] who evaluated the kinetics of the hydrolysis from the data collected from pH measurements, since the change in pH is directly related to the formation of ammonia (Eq. (2)). Mobley,[31] on the other hand, performed solution calorimetry tests and calculations of the heats of formation for the AlN powder hydrolysis at RT. The formation of the amorphous mono-hydroxide (AlOOH) is exothermic, *i.e.*, $\Delta H = -105.4$ kJ/mol; and so is the formation of bayerite (α-$Al(OH)_3$), *i.e.*, $\Delta H = -81.2$ kJ/mol. However, the dissolution of mono-hydroxide is endothermic, *i.e.*, $\Delta H = 133$ kJ/mol. The sum of the reaction enthalpies is negative, indicating that overall the hydrolysis is an exothermic process.

During the hydrolysis of AlN powder ammonia is released (Eq. (1)); this leads to an increase in the pH value of the suspension, so shifting it into the alkaline region. Reetz et al.[32] anticipated that the hydrolysis is a basic-catalyzed reaction, because of the impact of hydroxyl ions (OH^-) on the aluminum–nitrogen (Al–N) bond. The strongly electronegative OH^- apparently combines with the aluminum and displaces the nitrogen. The hydrolysis of the AlN powder is also a temperature-dependent process, since it proceeds faster with higher starting temperatures of the suspension.[24,25] Regardless of the exothermic nature of the hydrolysis, the literature data lack a kinetic analysis of the hydrolysis at elevated temperatures.

In the present paper, the course of the AlN powder hydrolysis and the reaction kinetics for the hydrolysis were systematically studied in the temperature range between RT (22 °C) and 90 °C, giving a unique perspective on the hydrolysis in a form that has not been presented in the literature so far. The influence of the starting temperature and the pH on the hydrolysis behavior was monitored by measuring the pH and the temperature change of the diluted suspensions containing 3 wt.% of AlN powder in deionized water. The temperature-dependent conversion of the AlN powder in water was recorded using a thermogravimetric (TG) analysis by calculating the mass ratio between the aluminum hydroxide and the AlN in the hydrolyzed powders. On the basis of the results of the conversion and using transmission electron microscopy (TEM) the course of the hydrolysis was studied in detail. The reaction kinetics was then described using an un-reacted-core model and the activation energy for the hydrolysis of the AlN powder in water in the temperature range 22–70 °C was determined.

2. Experimental

2.1. Hydrolysis tests

The AlN powder used in this study was AlN grade C powder (H.C. Starck, Berlin, Germany) with a nominal particle size of 1.2 µm, a specific surface area of 3.2 m^2/g, and an oxygen content of 2.2 wt%. For the hydrolysis tests, water suspensions of 3 wt% AlN powder were prepared. Prior to the addition of the powder the water was blown through with nitrogen in order to minimize the dissolution of CO_2. For the hydrolysis tests at elevated temperatures the water was preheated to 50 °C and 90 °C. The time-dependent pH and temperature profiles of the AlN powder suspensions were recorded using a Metrohm 713 pH-meter and a combined pH-glass electrode linked to PC. The data were collected with Vesuv™ software (Metrohm AG, Herisau, Switzerland).

2.2. Characterization of powders

The powders for the characterization were prepared as follows. AlN powder aqueous suspensions were filtered and thoroughly washed with 2-propanol to remove excess water and to exclude any possible further hydrolysis. The cakes were dried at 80 °C for 24 h and then stored in plastic, airtight containers for subsequent analysis. Powder X-ray diffraction (XRD) data were collected on a PANanalytical X'Pert PRO diffractometer using Co Kα radiation. TEM images and selected-area electron diffraction (SAED) patterns were obtained using a Jeol 2100 microscope operating at 200 kV. The samples for the TEM and SAED analyses were prepared by re-dispersing the (un)hydrolyzed AlN powders in acetone, *i.e.*, applying two drops of as-prepared suspension onto a carbon-coated grid.

2.3. Conversion of AlN, i.e., X_{AlN}

The degradation of the AlN powder in water was monitored with the TG analysis. These TG analyses of the as-received AlN powder and the hydrolyzed AlN powders were performed at a heating rate of 10 °C/min up to 1300 °C in flowing air/argon using a Jupiter 449 (Netzsch, Selb, Germany) instrument for the evaluation of the mass ratio between the aluminum hydroxide and AlN in the hydrolyzed powders, which was expressed as the conversion of the AlN powder in water (X_{AlN}). At 800 °C, the hydrolysis solid reaction products, *i.e.*, aluminum hydroxides, were already dehydrated in to alumina, since the mass of the sample was constant, whereas the remaining AlN in the powder started to oxidize at higher temperatures by the following reaction:[33]

$$4\mathrm{AlN} + 3\mathrm{O_2} \rightarrow 2\mathrm{Al_2O_3} + 2\mathrm{N_2} \qquad (5)$$

which resulted in a mass increment of the powder, due to the formation of alumina. The TG analysis of the as-received AlN powder (Appendix A; Fig. A1) gave a 23.48% mass increase. The hydrolyzed AlN powders exhibited lower mass increases (Fig. A1), since in accordance with the aluminum hydroxides formed during the hydrolysis, there was a smaller amount of the AlN phase in these powders. The weight fraction of AlN in the hydrolyzed powders, *i.e.*, X_{AlN}, was evaluated using the following equation:

$$X_{\mathrm{AlN}} = 1 - \frac{(m_{\mathrm{Al_2O_3+AlN}})/m_{\mathrm{f}}}{m_{\mathrm{AlN}}/m_{\mathrm{f,AlN}}} \qquad (6)$$

where $m_{\mathrm{Al_2O_3+AlN}}$ is the mass of oxidized hydrolyzed sample at 800 °C containing alumina ($\mathrm{Al_2O_3}$) and AlN, m_{f} is the final mass of the analyzed sample at 1300 °C, m_{AlN} is the mass of the as-received AlN sample and $m_{\mathrm{f,AlN}}$ is the mass of the oxidized as-received AlN sample after the TG analysis.

3. Results

3.1. Hydrolysis tests

Since the reaction of AlN with water (Eq. (2)) is an exothermic process and the formation of ammonia gives rise to an $\mathrm{OH^-}$ concentration (Eq. (3)), the hydrolysis at RT, *i.e.*, 22 °C, was monitored by measuring the pH and the temperature of the 3 wt% suspension. The chosen solids loading proved to be the most suitable for the pH/temperature measurements, because of its moderate impact on the time-dependent temperature change of the suspension for different starting temperatures. The initial pH of the suspension at the onset of the hydrolysis was about 5.2, as can be seen in Fig. 1. Then, immediately after the addition of the AlN powder, the reaction was initiated, based on the fact that the pH and the temperature started to increase. The maximum pH value of the AlN powder suspension at 22 °C was reached after 1680 min (28 h) of the hydrolysis. The time-dependent temperature profile of the suspension during the hydrolysis exhibited two maxima: after 510 min (8.5 h), the temperature of the suspension reaches its first peak at 25.6 °C, while the second temperature maximum at 28.2 °C was reached after 1620 min (27 h) of hydrolysis. In Fig. 2, the results of the pH and the temperature changes for the AlN powder suspensions at three different starting temperatures, *i.e.*, 22 °C, 50 °C and 90 °C, are compared. A higher starting temperature evidently accelerates the hydrolysis of the AlN powder. Compared to the hydrolysis at 22 °C, the maximum pH values of the suspensions at 50 °C and 90 °C (Fig. 2(a)) were lower; furthermore, they were obtained more quickly, *i.e.*, 9.93 after 220 min and 9.25 after 110 min, respectively. The maximum pH value of the suspension was lower at the higher starting temperatures, presumably due to the decreasing solubility of the ammonia with the increasing temperature.[34] An initially slower rate of the hydrolysis reaction can be observed in the AlN powder suspensions at 22 °C and heated to 50 °C (Fig. 2(a)). The temperature-dependent rate of the hydrolysis was confirmed by the temperature measurements of the suspension, as shown in Fig. 2(b). Compared to 22 °C, the AlN powder suspension at 50 °C exhibits only one temperature peak, after 57 min ($\Delta T = 17.9$ °C). The same, *i.e.*, only one temperature increment, was observed during the AlN powder hydrolysis at the initial 90 °C, but the single temperature increment was interrupted by the boiling of the suspension after only 2 min of hydrolysis. This is manifested as a plateau ($\Delta T = 7.7$ °C), which lasted for approximately 10 min.

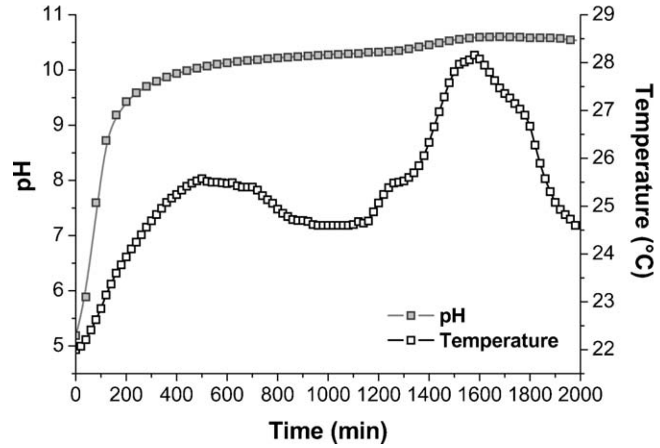

Fig. 1. pH and temperature versus time for a 3 wt% AlN powder suspension in water at 22 °C.

3.2. Kinetic measurements

The kinetic measurements of the degradation rate of the AlN powder in water at 22 °C, 50 °C and 90 °C, were performed by

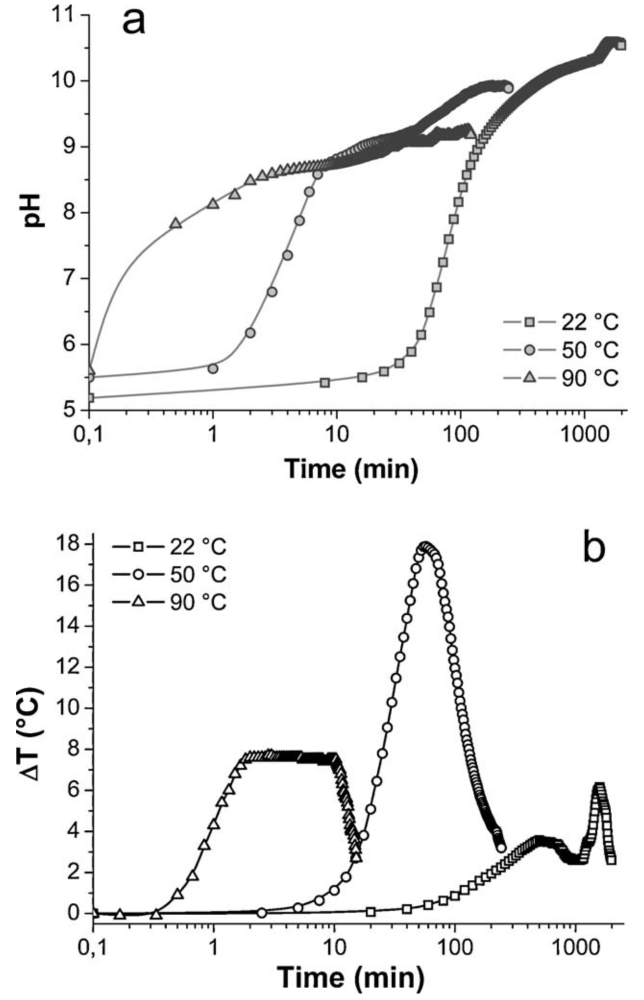

Fig. 2. Time-dependent (a) pH and (b) temperature change for a 3 wt% AlN powder suspension in water at 22 °C, 50 °C and 90 °C.

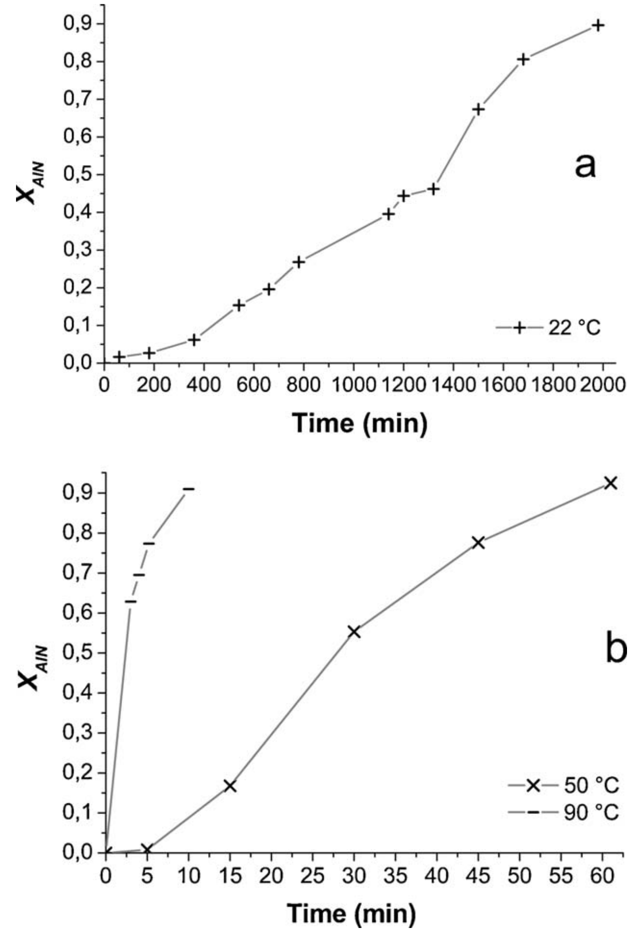

Fig. 3. Time-dependent conversion (X_{AlN}) for a 3 wt% AlN powder suspension in water at (a) 22 °C, (b) 50 °C and 90 °C.

following the mass ratio between the aluminum hydroxides and the AlN in the hydrolyzed powders, which increased with the time of hydrolysis, and was expressed in terms of the conversion of AlN powder in water (X_{AlN}). The calculated X_{AlN} values were plotted versus time for the hydrolysis at 22 °C, 50 °C and 90 °C, as shown in Fig. 3. After the addition of the AlN powder in to the water at 22 °C (Fig. 3(a)), the initial slow rate of hydrolysis took place for about 180 min (3 h), after which it accelerated. The corresponding time-dependent X_{AlN} curve exhibited a slightly parabolic character. The reaction rate was accelerated again after 1320 min (22 h), which is in line with the secondary temperature increment of the suspension (Fig. 1). The hydrolysis of AlN powder at 22 °C was completed after 1980 min (33 h) of the reaction, where the X_{AlN} was about 90%. Higher starting temperatures (Fig. 3(b)) dramatically accelerated the rate of the hydrolysis: while a 50% conversion of the AlN powder in water at 22 °C was achieved after 1350 min, at 50 °C only 29 min were needed, and even less was needed at 90 °C, *i.e.*, 2.5 min. Compared to 22 °C the rate of hydrolysis at 90 °C was accelerated by more than 500 times. An initial slow rate of reaction can also be observed at 50 °C, where the hydrolysis was accelerated after 5–10 min of contact with the water. However, at 90 °C, after the addition of the AlN powder to the water the reaction was instantaneous and the initial slow rate of the reaction was not detected.

4. Discussion

4.1. Course of the hydrolysis

The results of the hydrolysis tests at 22 °C (Fig. 2) and the TG analyses of the hydrolyzed powders expressed as the conversion of AlN powder in water, *i.e.*, X_{AlN} (Fig. 3), implied that the hydrolysis was partitioned by a series of inter-dependent steps that were additionally elucidated by subsequent TEM analyses of the hydrolyzed powders at various times and temperatures. Based on these observations a schematic conversion diagram representing three stages of the hydrolysis was constructed, as shown in Fig. 4. Also shown are the corresponding TEM micrographs of the characteristic powder morphologies of the three stages. These stages are: the first stage of the hydrolysis, *i.e.*, the induction period (initial slow rate of hydrolysis), the second stage of the hydrolysis, *i.e.*, the growth of boehmite and the third stage of the hydrolysis, *i.e.*, the growth of bayerite. The hydrolyses at the initial temperatures of 22 °C and 50 °C exhibit all three stages, while the hydrolysis at 90 °C exhibited only one stage,

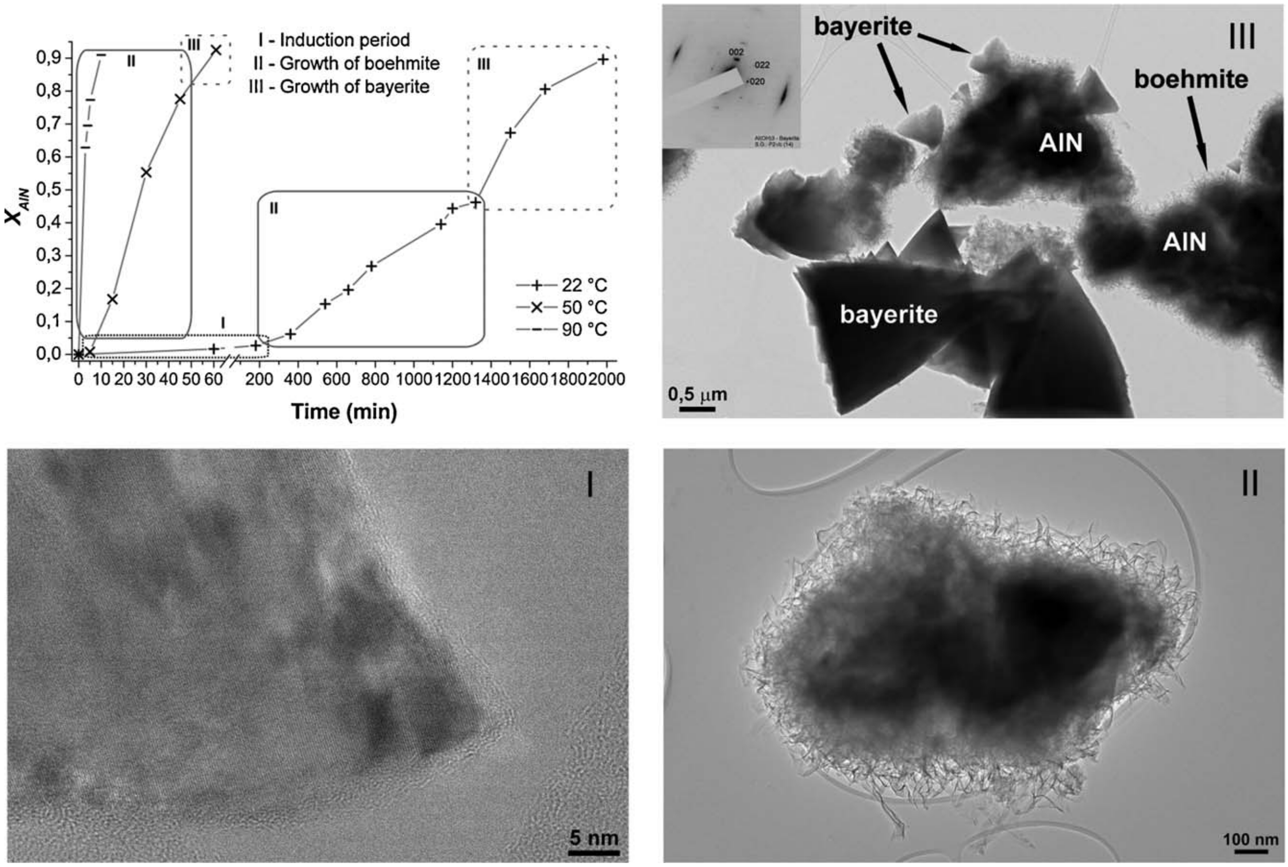

Fig. 4. A schematic conversion diagram representing the three characteristic stages of the hydrolysis with the corresponding TEM micrographs. I – induction period, II – growth of boehmite, III – growth of bayerite with corresponding SAED pattern.

i.e., no induction period and no third stage of the hydrolysis were observed.

4.1.1. First stage of the hydrolysis, i.e., induction period

While the incubation time or a delay prior to the hydrolysis was noticed in some studies and its existence was supported by the presence of a thin hydrated oxide layer on the surface of the AlN particles,[24,25] in our study with H.C. Starck AlN powder, no incubation time was detected. As shown with the hydrolysis tests (Fig. 1), the pH of the suspension started to rise immediately after the AlN powder was added to the water, indicating an immediate start to the reaction. To verify the presence (or absence) of a thin (hydr)oxide layer on the surface of the as-received AlN particles, the as-received powder was examined by TEM. As shown in Fig. 5, atoms comprising a crystal lattice on the edge of a single AlN crystal are clearly visible and the SAED pattern from the edge of the crystal matches to pattern of the AlN. The absence of a continuous thin (hydr)oxide or amorphous layer on the surface of the AlN particles still could not exclude the possible existence of a small amount of hydrolysis products in the powder caused by moisture. Since the as-received powder had the smell of ammonia, it is assumed that individual AlN particles that reacted with moisture were randomly distributed in the powder mixture, whereas the vast majority of the particles remained intact.

In spite of the absence of an incubation time, the initially slower rate of the hydrolysis, *i.e.*, an induction period was observed for the AlN powder suspensions at 22 °C and 50 °C, as shown in Fig. 3. It lasted about 180 min (3 h) at 22 °C and approximately 5–10 min at 50 °C (Fig. 3). The powder surface morphology hydrolyzed for 2 h at 22 °C was analyzed with TEM. As shown in Fig. 4(I), a thin about 3-nm thick layer of amorphous aluminum hydroxide gel was formed during the induction period. A very similar surface morphology, *i.e.*, a 3-nm thick

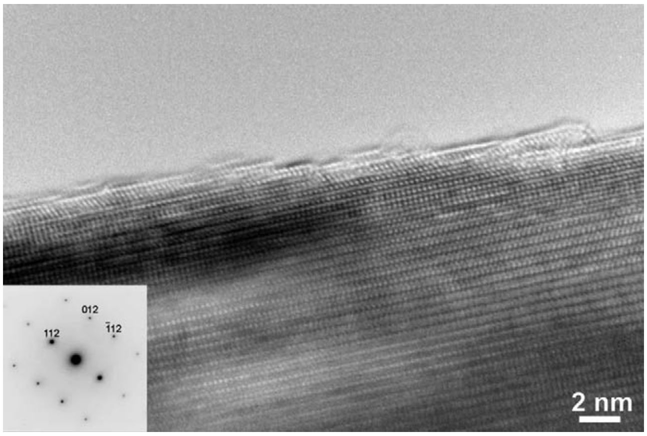

Fig. 5. TEM micrograph of as-received AlN particle surface with corresponding SAED pattern.

layer of amorphous aluminum hydroxide gel, was observed on powder particles hydrolyzed for 5 min at 50 °C. It is assumed that during the induction period, the OH^- ion, as a reactant, arrives at the AlN surface and attacks the Al–N bond, which then decomposes.[32] In this way the Al^{3+} ion is released and ammonia is formed. The latter then dissolves, resulting in an increase in the pH of the suspension. On the other hand, the Al^{3+} in an acidic solution at RT forms a hexahydrated complex $[Al(OH_2)_6]^{3+}$.[35] This complex behaves as an acid, giving rapidly and reversibly a series of pH-dependent, soluble, mononuclear, hydroxylated species according to the following equation:[35,36]

$$[Al(H_2O)_6]^{3+} \overset{pH\,4-6.5}{\longleftrightarrow} [Al(H_2O)_5(OH)]^{2+} \overset{pH\,4.5-8}{\longleftrightarrow} [Al(H_2O)_4(OH)_2]^{+} \overset{pH\,5-10}{\longleftrightarrow} Al(H_2O)(OH)_3 \overset{pH>7}{\longleftrightarrow} [Al(OH)_4]^{-} \quad (7)$$

With increasing pH values, the $[Al(OH_2)_6]^{3+}$ progressively hydrolyzes to $[Al(H_2O)_5(OH)]^{2+}$ and $[Al(H_2O)_4(OH)_2]^{+}$. Neutral species $Al(H_2O)(OH)_3$ start to form at around pH 5–6 and are stable up to a pH value of 9.5. The $Al(H_2O)(OH)_3$ species may condense forming an amorphous aluminum hydroxide gel that is in equilibrium with $[Al(H_2O)_4(OH)_2]^{+}$ and/or $[Al(OH)_4]^{-}$ in the solution. Since the starting pH of the AlN powder suspension is greater than 5, the released Al^{3+} ion immediately forms an amorphous aluminum hydroxide gel on the surface of the AlN particle. When formed, the OH^- ion arrives at the AlN surface bond by the diffusion through this layer. It was observed that the thickness of this layer did not alter significantly throughout the induction period. When the pH of the suspension is in the range 7–10, an equilibrium between the formation and dissolution of the amorphous gel layer, *i.e.*, $Al(H_2O)(OH)_3$, was obtained. However, maximum pH value of the AlN powder suspension at a starting 90 °C was only 9.25 (Fig. 2(a)). The absence of the induction period during the course of the hydrolysis at 90 °C can be related to the instability of the amorphous aluminum hydroxide gel, since it is unstable at this temperature.[37] The so-called induction period was already observed in the corrosion of aluminum surfaces immersed in water, during which the formation of an amorphous aluminum oxide layer by an electro-chemical reaction, prior to the boehmite and bayerite formation, takes place.[38,39]

4.1.2. *Second stage of the hydrolysis, i.e., growth of boehmite*

The induction period ended and the hydrolysis was accelerated after 180 min at 22 °C and after 5–10 min at 50 °C (Fig. 3). This segment of the hydrolysis was referred to as the second stage of hydrolysis or the growth of boehmite. It is the predominant step at elevated temperatures and the only step in the hydrolysis at 90 °C (Fig. 4). The second stage of the hydrolysis presumably starts when the critical concentration of $[Al(OH)_4]^{-}$ in the suspension (at the expense of the dissolution of the aluminum amorphous hydroxide gel) is achieved, which results in the nucleation and growth of porous lamellar-like particles comprising a product shell on the surface of the AlN particles. However, when the AlN powder suspension reaches higher pH values ($pH \geq 10$) the amorphous aluminum hydroxide gel is not stable anymore and, therefore, it completely dissolves. Then, the $[Al(OH)_4]^{-}$ species needed for the boehmite growth are formed at the expense of the decomposition of Al–N bonds on the surface of the AlN particles. A product shell layer surrounding an AlN particle cluster, hydrolyzed for 19 h at 22 °C, is shown the TEM micrograph presented in Fig. 4(II). Three AlN particles are encircled with a 100-nm thick layer of lamellar-like particles. However, this layer was too thin for a successful SAED analysis. It was anticipated by Bowen et al.[29] this layer is composed of amorphous, porous, mono-hydroxide particles, with a stoichiometry close to boehmite, according to an X-ray photoelectron spectroscopy (XPS) analysis. On the other hand, Svedberg et al.[40] reported on the presence of crystalline boehmite in the AlN powder after just rinsing it with water at RT. Therefore, the possible crystallinity of this layer was additionally checked by analyzing the powder with XRD at a 10-times longer radiation time compared to a routine radiation time. The result is shown in Fig. A2 (Appendix A), where broad peaks of boehmite (γ-AlOOH) along with peaks of AlN are visible. The broadness of the peaks representing the (0 2 0) and (0 2 1) planes indicates that this layer consists of poorly crystalline boehmite nanoparticles. Crystalline boehmite with a similar morphology (Fig. 4(II)) was observed amongst the AlN powders hydrolyzed at elevated temperatures, representing the second stage of the hydrolysis.

4.1.3. *Third stage of the hydrolysis, i.e., growth of bayerite*

At 22 °C, the third stage of the hydrolysis is accompanied by the second acceleration of the rate of hydrolysis (Fig. 4), also corresponding to the second pH/temperature increment of the AlN powder suspension (Fig. 1). During this last step of the hydrolysis the bayerite phase was formed, according to the SAED pattern demonstrated in Fig. 4(III). The bayerite phase was present in the hydrolyzed powders in the form of conical-like particles known as somatoids.[2] Their nucleation began within the boehmite shell product layer, but the growth of the particles tended to be outwards from the layer. It is known that during the evolution of polymorphic hydroxides, such as aluminum hydroxides, the hydroxide formed second (in this case bayerite), which is thermodynamically more stable, nucleates within a kinetically favorable initially formed phase (in this case boehmite).[36] The third stage of the hydrolysis was observed at both 22 °C and 50 °C, whereas at 90 °C, the hydrolysis exhibited only one stage (Fig. 4), since bayerite particles were not detected. However, the third stage of hydrolysis at 50 °C could not be distinguished solely on the basis of the hydrolysis tests (Fig. 2) and from the conversion of AlN powder in water (Fig. 3(b)), but was additionally confirmed by TEM analyses. At 50 °C it begins after more than 45 min.

4.2. *Effect of the initial pH*

Several authors observed the strong pH-dependency of the hydrolysis. It was claimed that the hydrolysis rate is higher with higher starting pH values of the AlN powder suspension, presumably due to the impact of the OH^- on the Al–N bond.[25,32]

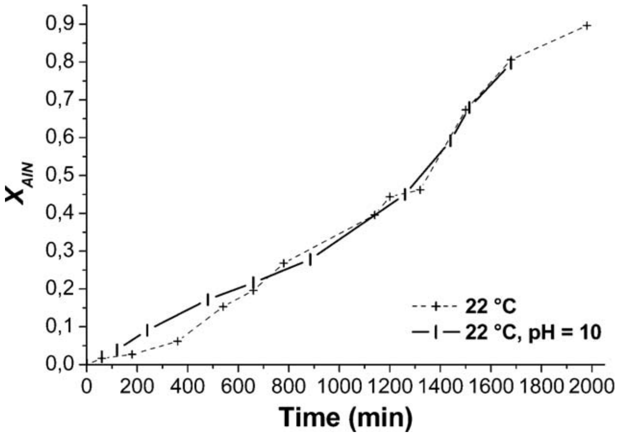

Fig. 6. Time-dependent conversion (X_{AlN}) for a 3 wt% AlN powder suspension in water and in a TMAH solution.

On the other hand, the hydrolysis is retarded or even prevented at lower pH values (pH = 1), due to the low concentration of OH^-.[25,32] In order to verify the effect of the initially higher pH value of the suspension, the AlN powder hydrolysis at a pH value of 10 at 22 °C was monitored. Prior to the addition of the AlN powder the pH value of the water was adjusted to 10 with tetramethylammonium hydroxide (TMAH). The results of the conversion of the AlN powder in TMAH solutions (X_{AlN}) are presented in Fig. 6, and are also compared to those from Fig. 3(a). As is clear from Fig. 6, the higher initial pH value does not speed up the reaction rate of the hydrolysis, since the conversions of the AlN powder in the water and in the TMAH solution at 22 °C are similar. The slopes during the second stage of the hydrolysis are practically the same. The only difference is in the duration of the induction period. The X_{AlN} curve of the AlN in the TMAH solution does not seem to exhibit an induction period, *i.e.*, an initial slow hydrolysis rate, and it started immediately. To further investigate the reason for the observed diminution of the induction period in the hydrolysis of AlN powder at elevated pH values, TEM analyses of the hydrolyzed powder were performed. Fig. 7 shows a TEM micrograph of an AlN particle surface of a powder hydrolyzed for 2 h in the TMAH solution at 22 °C.

Fig. 7. TEM micrograph of AlN particle surface hydrolyzed in a TMAH solution for 2 h.

In contrast to the 2-h hydrolyzed powder in the water (Fig. 4(I)), the thin amorphous aluminum hydroxide gel was not present on the surface of the AlN particles. Instead, discrete vermicular-like particles on the surface of the AlN were observed, which could be a sign of the possible growth of boehmite particles. The absence of the induction period at high pH values during which an amorphous aluminum hydroxide gel layer was formed, can be explained in terms of the formation of soluble aluminum mononuclear species (Eq. (7)). During the degradation of the AlN powder in the TMAH solution (pH = 10) the only stable species formed was $[\mathrm{Al(OH)_4}]^-$, and therefore the amorphous aluminum hydroxide gel, *i.e.*, $\mathrm{Al(H_2O)(OH)_3}$, cannot form, as already mentioned. When the suspension became supersaturated with $[\mathrm{Al(OH)_4}]^-$, the nucleation of boehmite lamellas occurs. On the other hand, when the hydrolysis was initiated at a pH value of 5.3 (Fig. 1), which is the pH value of deionized water, the $[\mathrm{Al(H_2O)_4(OH)_2}]^+$ is the most stable species. With increasing pH, the $\mathrm{Al(H_2O)(OH)_3}$ phase was being formed (Eq. (7)), which was later, with higher pH values, also dissolved on account of the $[\mathrm{Al(OH)_4}]^-$ formation.

4.3. Reaction kinetics

The degradation of AlN powder in water is a heterogeneous reaction of a solid particle in a fluid. The un-reacted-core model, as a kinetic model for an irreversible fluid-particle reaction carried out by Levenspiel,[30] was chosen for the kinetic interpretation of the hydrolysis. In this model, the reaction starts at the outer surface of the solid particle and moves inward, leaving behind a product layer with increasing thickness. There are three possible regimes of rate control: (I) mass transfer of the reactant through the film surrounding the particle to the surface of the solid, (II) diffusion of the reactant through the product layer to the surface of the un-reacted core, and (III) chemical reaction of the reactant and the solid at the core surface, where the slowest step will be the rate limiting one. For a spherical particle:

$$\text{(I)} \qquad t = \tau X_{\mathrm{B}} \tag{8}$$

$$\text{(II)} \qquad t = \tau[1 - 3(1 - X_{\mathrm{B}})^{2/3} + 2(1 - X_{\mathrm{B}})] \tag{9}$$

$$\text{(III)} \qquad t = \tau[1 - (1 - X_{\mathrm{B}})^{1/3}] \tag{10}$$

where t is the time, τ is the time for the complete reaction of a particle, and X_{B} is the volume fraction of the un-reacted core with respect to the total particle volume. The model is suitable for a representation of the degradation of AlN powder in water, since, during the hydrolysis, the AlN particle, as a reactant, is shrinking, while a porous layer of boehmite, as a product, forms and grows on the surface of the AlN. However, according to the results of the conversion of AlN in water (Fig. 4) and TEM micrographs of the hydrolyzed powders (Fig. 4(III)), it is inappropriate to fit the hydrolysis at 22 °C and 50 °C with this model throughout the whole conversion of the AlN powder in water. The exception is the hydrolysis at 90 °C. During the induction period, a thin amorphous layer of aluminum hydroxide gel exhibits a constant thickness. Therefore, the model cannot be applied during this stage of hydrolysis. Furthermore, as it can be

Table 1
Estimated rate-controlling steps with corresponding rate constants, *k*, and regression coefficients, R^2, for the second stage of the hydrolysis of a 3 wt% AlN powder in water in a temperature range 22–90 °C.

Temperature (°C)	Rate-controlling step	$k = 1/\tau$ [s−1]	R^2
22	Reaction	2.87E−06	0.999
50	Reaction	1.84E−04	0.999
60	Reaction	3.34E−04	0.997
70	Reaction	8.99E−04	0.996
90	Diffusion	1.048E−03	0.998

seen from Fig. 4(III), bayerite is not a part of the uniform product shell layer on the surface of the core AlN particles and the model cannot be applied there either. For this reason, the equations from the model were rewritten so that they can be applied to the desired time interval between t_1 and t_2 of the hydrolysis (the evolution of the equations is presented in Appendix A). If the mathematical equations (Eqs. (15)–(17); BI*–BIII*), with the respect to experimental data (X_{AlN}), are plotted versus time, then the model that best describes the reaction being studied should give a straight line. The best fit, as expressed by the regression coefficient (R^2), revealed the possible regime of control for the hydrolysis and the results are presented in Table 1. From the slope of the linearized lines, the rate constants for the hydrolysis for the various starting temperatures were calculated and are listed in Table 1. According to the un-reacted-core model the hydrolysis in the temperature range between RT (22 °C) and 70 °C in its second stage is likely to be a reaction-controlled process (III; Eq. (10)), because this regime gave the best fits. On the other hand, the hydrolysis at 90 °C becomes a diffusion-controlled process (Eq. (9); II). The reason for the shift in regime at 90 °C could be the boiling of the suspension. Since the reaction on the surface of the AlN particle is exothermic, water near the particle surface could be in its gaseous state, due to the hot AlN surface. Water vapor, in turn, could hinder the diffusion of the reactant (OH^-) to the AlN surface, as well as the diffusion of the products (ammonia and Al-species) through the porous boehmite layer that is formed. We believe that diffusion becomes the rate-limiting step for hydrolysis of AlN powder at 90 °C or when the suspension is boiling.

The calculated rate constants for the hydrolysis in the temperature range between 22 °C and 70 °C enabled us to calculate the activation energy (E_a) for the second stage of the hydrolysis. The Arrhenius equation in its logarithmic form gives the relationship between the rate constant and the inverse temperature for the chemical reaction:

$$\ln(k) = \frac{-E_{\mathrm{a}}}{R}\frac{1}{T} + \ln(A) \tag{11}$$

where *R* is the ideal gas constant, *A* is a pre-exponential factor. The Arrhenius plot was designed as shown in Fig. 8. The diagram exhibits a fairly good linearity. From the slope of the straight line the activation energy for the second stage of the hydrolysis in the temperature range was estimated to be 101 kJ/mol.

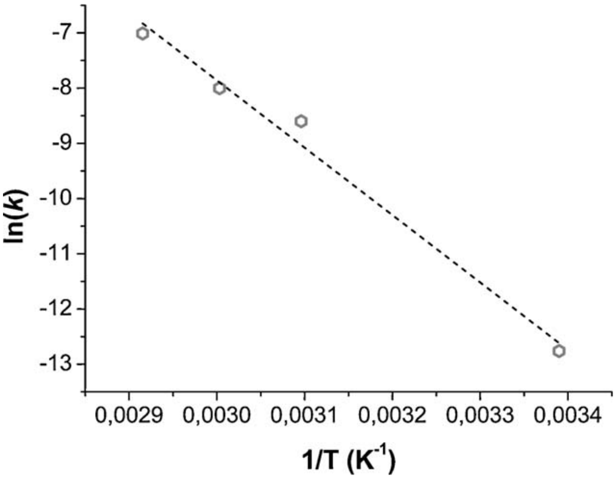

Fig. 8. Arrhenius plot for the second stage of the hydrolysis for a 3 wt% AlN powder suspension in water in the temperature range 22–70 °C.

5. Conclusion

The influence of the temperature and the pH on the course of hydrolysis and the reaction kinetics during the hydrolysis of the AlN powder in diluted aqueous suspensions in the temperature range 22–90 °C were studied systematically. After the addition of the AlN powder to the water the reaction starts immediately, *i.e.*, no incubation time was detected prior the hydrolysis. Ammonia, as a by-product, increases the pH value of the suspension, while because of the exothermic nature of the hydrolysis reaction the temperature of the suspension increases with time. The hydrolysis of the AlN powder was divided in to three stages. The first one is the induction period, *i.e.*, the initial slow rate of the reaction, during which an about 3-nm thick layer of amorphous aluminum hydroxide gel is formed on the surface of the AlN particles. This layer grows on the AlN surface/gel-layer interface, while it is being dissolved on its outer surface in contact with water. In the second stage of the hydrolysis the rate was accelerated, during which the porous layer composed of poorly crystalline boehmite particles was formed. The nucleation of the boehmite lamellar-like particles occurred after the supersaturation of $[Al(OH)_4]^-$ was reached on account of the dissolution of the amorphous aluminum hydroxide gel layer, formed within the induction period. During the last stage, *i.e.*, the third stage of hydrolysis, which takes places at temperatures lower than 90 °C, bayerite in the shape of large conical somatoids was formed. While the initial pH value of 10 does not accelerate the rate of hydrolysis, it does cancel the induction period, because the aluminum-hydroxide-gel-forming species $Al(H_2O)(OH)_3$ is not stable at this pH. Due to the exothermic nature of the hydrolysis, the initial temperature of the suspension has a great impact on the rate of hydrolysis. According to the un-reacted-core model for heterogeneous reactions, the hydrolysis in its second stage is a reaction-controlled process in the temperature range between 22 °C and 70 °C, whereas at 90 °C the diffusion of the reactants (OH^-) through the product layer of boehmite controls the second stage of the hydrolysis. The rate constants, *k*, were calculated and an Arrhenius plot was drawn. The calculated activation energy for the hydrolysis in the temperature range 22–70 °C was 101 kJ/mol.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jeurceramsoc.2010.12.009.

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