

The influence of temperature and time on the AlN powder hydrolysis reaction products

Andraž Kocjan*, Kristoffer Krnel, Tomaž Kosmač

Jožef Stefan Institute, Jamova 39, Ljubljana, Slovenia

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Abstract

The influence of hydration temperature and ageing time on the formation of crystalline phases found after the AlN powder hydrolysis was investigated. The AlN hydrolysis behavior was observed by measuring the pH of the suspension, whereas for the characterization of the reaction products XRD, SEM and TEM analyses were employed. The starting temperature, from RT up to 90 °C and the ageing time, from 10 min to 24 h, have an impact on the reaction products and their morphology. After prolonged time of the AlN reaction with water, the only crystalline product is bayerite at RT. At elevated temperatures the very first solid reaction product is pseudoboehmite, transforming to crystalline boehmite and part of it dissolving and recrystallizing to bayerite with ageing time. At temperatures above 80 °C, boehmite is the predominant crystalline phase, nevertheless, after long time of ageing in the mother liquor, even at these temperatures the boehmite → bayerite conversion was observed.

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1. Introduction

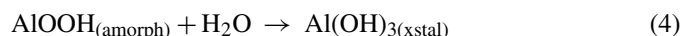
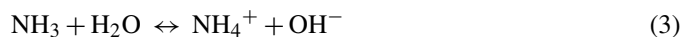
The reaction of aluminum nitride (AlN) powder with water has been known for a long time. In the presence of water AlN will decompose, forming aluminum hydroxide and ammonia:



About a century ago this reaction was exploited for the production of ammonia. However, with the introduction of the Haber–Bosch process, AlN was almost forgotten until the discovery of its unique set of material properties, which are useful in many electronic, structural and refractory applications. Due to its high thermal conductivity, high electrical resistivity, low dielectric constant, low thermal expansion coefficient, high strength and high temperature stability, AlN is very attractive as a substrate material for power circuits and as a packaging material for integrated circuits.¹ AlN is also used as a minor constituent in the formation of SiAlONs and as a sintering additive for SiC-based ceramics.^{2,3} The important issue in the processing of AlN powder is controlling the hydrolysis reactions. For example, in the production of ceramics containing AlN as a major or minor constituent (AlN, SiAlONs, SiC, etc.) it is necessary to prevent

hydrolysis. For this reason, non-aqueous powder processing is required, or, alternatively, water-resistant AlN powder must be used.^{4,5} On the other hand, AlN powder can be used as a setting agent, e.g., in the hydrolysis-assisted solidification (HAS) forming process, where the hydrolysis is exploited in the solidification of aqueous ceramic suspensions in an impermeable mould. In this process the reaction is thermally activated and later proceeds at elevated temperatures, typically 60–80 °C.^{6–8} Although the reactivity of AlN powder with water at room temperature (RT) was extensively studied, there are few literature data on AlN hydrolysis at elevated temperatures, especially for the later stages of the reaction, i.e., after the equilibrium pH value is reached.

For the reaction of AlN powder with water at RT Bowen et al.⁹ proposed the following reaction scheme:



According to these authors, AlN powder first reacts with water to form amorphous aluminum hydroxide (pseudoboehmite, AlOOH), which later recrystallizes to bayerite (Al(OH)₃). The kinetics of AlN hydrolysis was described using an unreacted-core model, described by Levenspiel,¹⁰ and the chemical

* Corresponding author. Tel.: +386 1 477 37 84; fax: +386 1 477 31 71.
E-mail address: a.kocjan@ijs.si (A. Kocjan).

reaction at the product-layer/unreacted-core interface was proposed to be the rate-controlling step. In this model it is anticipated that the dissolution–recrystallization process during AlN hydrolysis is very similar to that of the crystallization of aluminum hydroxide gels, where pseudoboehmite forms from fresh, highly hydrated, amorphous hydroxide.^{9,11} The mechanism of the transformation from amorphous boehmite to crystalline bayerite has been explained in terms of the dissolution of the pseudoboehmite and its subsequent crystallization as bayerite.¹² This ageing sequence was later confirmed by Yoldas,¹³ who studied the hydrolysis of alkoxides and bayerite conversion at two different temperatures. At RT the conversion of alumina gel followed the ageing sequence proposed by Bye and Robinson,¹² whereas at elevated temperature (above 80 °C) no bayerite conversion was observed.

In contrast to the crystallization of aluminum hydroxide gels, the evolution of hydrated aluminum oxides during AlN powder hydrolysis does not occur under constant conditions, i.e., temperature and pH, which in turn may influence the reaction kinetics and the morphology of the reaction products. During hydrolysis, ammonia is formed, resulting in an increase of the pH of the suspension until an equilibrium value is reached. Furthermore, the overall reaction is highly exothermic, such that the process is initially accompanied by a substantial increase in the temperature of the suspension.^{14–18}

Svedberg et al.¹⁴ studied the corrosion of AlN in aqueous solutions at various constant pH values (5, 8, 11, 14) heated to 85 °C for 1 h. In all pH regimes the pseudoboehmite and bayerite/gibbsite phases in various proportions were detected with XRD. According to these authors, the corrosion rate of AlN is at a minimum in the pH range 5.5–8, where the reaction product is not very soluble and remains on the surface of the AlN, acting as a barrier layer. At pH 9.5 and 12, where the solubility of the reaction product increases, the corrosion rate increases and is at a maximum when the aluminum trihydroxide reaction product is very soluble in the aqueous buffer solution.

Fukumoto et al.¹⁵ investigated the hydrolysis behavior of spherical aluminum nitride powder in various diluted solutions at RT and elevated temperatures up to 100 °C. They were mainly interested in the initial stage of the hydrolysis reactions, i.e., up to the point where the maximum pH value is reached. According to these authors the hydrolysis behavior changes at 78 °C: below this temperature crystalline bayerite will be the predominant phase, while above 78 °C crystalline boehmite will be formed. This phenomenon was tentatively ascribed to the change in the reaction kinetics, which, however, was not studied in detail. A similar observation, i.e., the presence of crystalline bayerite and boehmite, was also made by Krnel et al.¹⁶ They studied the degradation of AlN powders in various aqueous environments in the temperature range 40–70 °C, but the effect of ageing time on the crystalline products was not investigated.

In the present paper we report on the role of ageing time and hydration temperature on the formation and morphology of crystalline phases found after the hydrolysis of the AlN powder.

2. Experimental

The AlN powder used in this study was AlN Grade C (H.C. Starck, Berlin, Germany) with a median particle size of 1.2 μm, a surface area of ≈6 m²/g, and an oxygen content of ≈2.5 wt% O₂, based on information from the supplier.

The hydrolysis tests were carried out in dilute suspensions containing 3 wt% of AlN in deionized water. In these tests, water was preheated with an electric heater under constant stirring to the desired temperature (RT: 40 °C, 50 °C, 60 °C, 70 °C, 80 °C and 90 °C) and then the AlN powder was added to the water. The pH was measured versus time using a combined glass-electrode/Pt 1000 thermometer pH meter (Metrohm 827). For comparison, the hydrolysis tests were also performed without stirring, resulting in a higher starting pH of the suspension.

The crystalline phases of the hydrolysis products were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses. The powder samples were prepared as follows: samples were taken out from the suspensions at various times (15 min, 8 h and 24 h), filtered, and washed with 2-propanol to remove the excess water. Cakes were dried at 80 °C for 1 h and then stored in plastic, airtight containers. All further analyses (XRD, SEM and TEM) were performed within a short period of time (2 days) after the tests to exclude any possible further hydrolysis of the AlN powder due to moisture in the air.

3. Results and discussion

A typical SEM micrograph of the as-received AlN powder is shown in Fig. 1. The particles, up to several micrometers in size, have irregular shapes in the form of rods, spheres and hexagonal particles, and they are also partly agglomerated.

The results of the hydrolysis tests of this powder at various temperatures are shown in Fig. 2. The starting pH of the deionized water ranged from 4 to 5 because of the CO₂ adsorption from the air during stirring. When the AlN powder was added to the water the starting pH value initially decreased even more, presumably due to the uptake of additional CO₂ during the

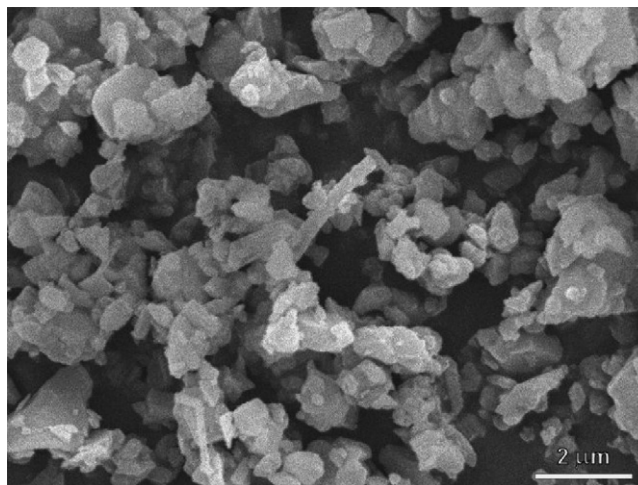


Fig. 1. SEM micrograph of the parent AlN powder.

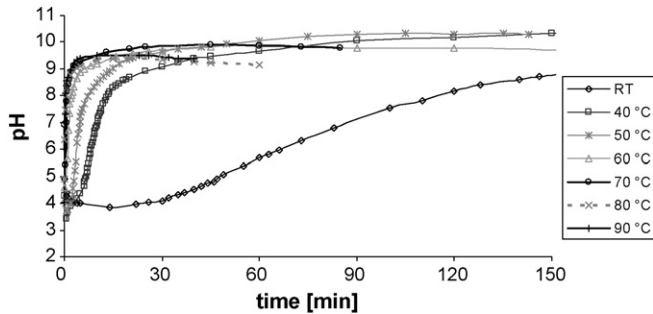


Fig. 2. pH vs. time for a 3 wt% AlN powder in water at RT; 40 °C, 50 °C, 60 °C, 70 °C, 80 °C and 90 °C.

vigorous stirring needed to homogenize the suspension. After a certain period of time (the incubation time) the pH of the suspension started to increase and reached an equilibrium pH value within a few minutes to several hours, depending on the process temperature. This is in line with previously published results.^{15–17,19} Since the solubility of ammonia decreases with increasing temperature, the equilibrium pH value is higher at lower temperatures and decreases with increasing temperature.

The results of the X-ray powder-diffraction analyses together with the estimated incubation times for the AlN powders hydrolyzed at various temperatures are summarized in Table 1. The term incubation time is used here to describe the time period up to the point when measurable changes in the pH and temperature could be detected. The suggested reason for the incubation time is the presence of a thin, hydrated oxide layer on the surface of the AlN particles, which has to be dissolved before the hydrolysis can start.^{13–15} As already shown, the incubation time is temperature-dependent, presumably because of the temperature- and pH-dependent solubility of the aluminum hydroxides in water. Furthermore, the more oxidized the powder surface, the longer it takes for the reaction to start.

According to the results of the XRD analyses in Table 1, the only crystalline reaction product found during ageing in water at RT was bayerite (T). However, a noticeable amount of bayerite was detected only after 24 h of hydrolysis; for shorter times only signals of unreacted AlN were detected and boehmite (M) could not be detected with the X-ray powder-diffraction technique at any time. This observation is in line with the results of Bowen et al.⁹ In their work, bayerite was first detected after 16 h and was the predominant phase after 24 h; the minor phase being

unreacted AlN, and no boehmite was detected at RT, except that their powder was more reactive, such that after 24 h the hydrolysis was nearly completed. For AlN powders hydrolyzed for 15 min at 40 °C and 50 °C weak but clearly distinguished peaks of boehmite and bayerite are observed in the XRD pattern. With a prolonged ageing time at these temperatures the relative intensity of the bayerite peaks increased and after a few hours the bayerite became the predominant crystalline phase. At still higher temperatures (60–90 °C) in contrast, the only crystalline reaction product detected after 15 min was boehmite, and no bayerite peaks could be found in the XRD pattern, in agreement with Yoldas¹³ and Fukumoto et al.,¹⁵ who stated that above 80 °C the conversion of bayerite is not likely to occur. However, as shown in Table 1, after 8 h of ageing at 90 °C we detected some bayerite using XRD analysis. Furthermore, as shown in Fig. 3, with even longer ageing times the peak intensity of the bayerite phase increased, but after 24 h of ageing boehmite remained the predominant crystalline reaction product. For the AlN powder used in the present work the observed tendency was that at higher ageing temperatures a longer time will be needed for the bayerite to form. It should be emphasized, however, that even after prolonged ageing times at high temperatures there were still peaks of unreacted AlN in the XRD pattern, indicating that the hydrolysis was not completed. This, in turn, may further influence the formation of the reaction products and their crystallization.

SEM analyses of the hydrolyzed powders at RT revealed that there is no significant difference in the powder morphology between the parent powder (see Fig. 1) and the powder hydrolyzed for up to 8 h (Fig. 4a), in agreement with the results in Table 1. However, as shown in Fig. 4b, after ageing for 24 h, characteristic bayerite somatoids were readily observed, while most of the AlN powder was still unreacted, giving support to the results of the XRD analysis. In addition to some unreacted AlN and bayerite somatoids a few discrete areas consisting of nanostructured agglomerates resembling the pseudoboehmite particles already described by Bowen et al.⁹ were also detected by SEM. After ageing for 64 h this nanostructured boehmite phase, also exhibiting a high specific surface area, began to dominate, although it remained undetectable with the XRD analysis. Since Bowen et al.⁹ obtained a similar microstructure with a much shorter hydration time, we assume that the “fresh” AlN powder used in their work was less oxidized on the surface than

Table 1
Crystalline phases observed by XRD after AlN hydrolysis at various hydration temperatures and ageing times (N, AlN; T, bayerite; M, boehmite)

| Temperature (°C) | Incubation time (min) | Phases [XRD] | | |
|------------------|-----------------------|--------------|---------|---------|
| | | 15 min | 8 h | 24 h |
| RT | 17 | N | N | N, T |
| 40 | 4 | N | T, M, N | T, M, N |
| 50 | 2 | N | T, M, N | T, M, N |
| 60 | 0.9 | N, M | M, T, N | T, M, N |
| 70 | 0.27 | N, M | M, T, N | T, M, N |
| 80 | 0 | N, M | M, T, N | M, T, N |
| 90 | 0 | N, M | M, N, T | M, T, N |

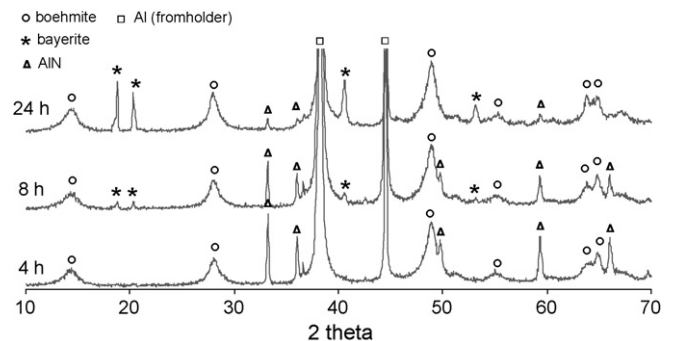


Fig. 3. XRD powder diffraction of AlN powder hydrolyzed at 90 °C for 4 h, 8 h and 24 h.

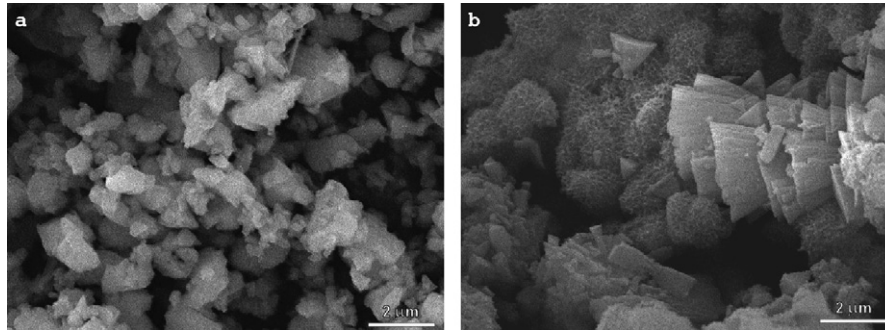


Fig. 4. SEM micrographs of the AlN powder hydrolyzed at RT for: (a) 8 h and (b) 24 h.

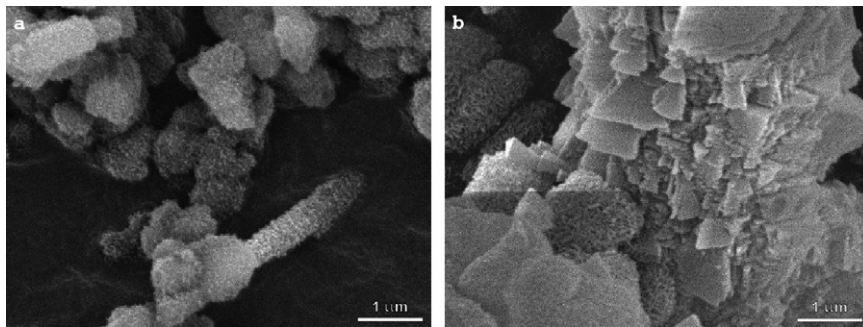


Fig. 5. SEM micrograph of the AlN powder hydrolyzed at 50 °C for: (a) 15 min and (b) 24 h.

our powder, which was stored for months in a closed container before being used in this work.

An SEM micrograph of AlN powder hydrolyzed at 50 °C for 15 min is shown in Fig. 5a. The surfaces of the parent AlN particles are entirely coated with a thin, hydrolyzed layer with a morphology characteristic of amorphous or poorly crystalline boehmite, undetectable with the XRD analysis. An almost identical powder morphology was obtained with any other powder after the initial stage of hydrolysis, i.e., close to or shortly after the saturation pH value was reached. However, with reference to the results in Table 1, the higher the hydration temperature, the shorter the hydration time needed for crystalline boehmite to be detected with XRD analysis. The thickness of the hydrated layer was estimated to be in the range 10–20 nm, in reasonable agreement with the values reported by Mobley.¹⁸

The morphology of the AlN powder aged at 50 °C for 24 h shown in Fig. 5b revealed the presence of two reaction products, i.e., agglomerated nanometer-sized boehmite particles and large bayerite somatoids. These two phases, with clearly distinct morphologies, were observed with all the powders subjected to ageing, though with different proportion(s) and particle size(s), depending on the ageing temperature and the time. Notice that with prolonged (24 h) ageing at 90 °C very large polycrystalline bayerite somatoids were formed (Fig. 6), giving additional support to the results obtained with the XRD analysis. It seems that for the bayerite conversion during the AlN hydrolysis at higher temperatures two competing parameters that exhibit a counteracting effect on the formation of aluminum hydroxide reaction products should be considered. At higher temperatures and moderate pH values boehmite is thermodynamically more stable than bayerite, whereas at lower temperatures and higher pH values

(i.e., with an increased concentration of OH⁻ ions in the suspension) conversion to bayerite is favored, as the OH⁻/Al³⁺ molar ratio is high enough to foster the formation of bayerite.

The above results imply that the applicability of Bowen et al.'s⁹ model, proposed for the behavior of AlN hydrolysis at RT, could be extended to elevated temperatures (up to the boiling point of water), by dividing Eq. (4) into two concurrently occurring reactions:

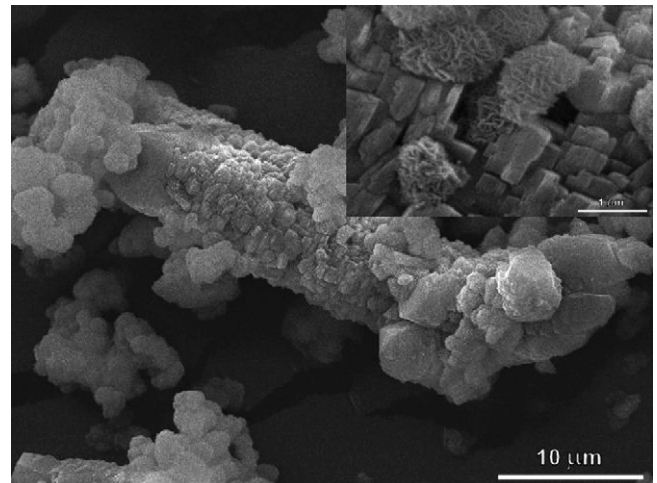
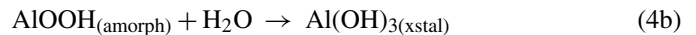
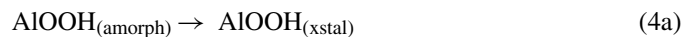


Fig. 6. SEM micrograph of AlN powder hydrolyzed at 90 °C for 24 h.

It is anticipated here that at any temperature the very first solid reaction product formed on the surface of the AlN particles would be pseudoboehmite (although at this point we still lack any solid experimental evidence for this). Once formed, part of the pseudoboehmite would be transformed to crystalline boehmite, while the other part would further react with water to form bayerite. The mechanism of reaction (4a) is the dissolution of smaller AlOOH particles and the reprecipitation and growth of larger boehmite crystals, while reaction (4b) proceeds by a dissolution/recrystallization process. Nevertheless, the formation of bayerite from crystallized boehmite cannot be excluded. One of the possible sequences of the formation of bayerite somatoids is from spherical amorphous particles that transform to fibres, to boehmite somatoids and finally to bayerite or other trihydroxide somatoids.²⁰

In order to obtain further information on the reaction products formed on the AlN particle's surface during the initial stage of hydrolysis, TEM analysis of a powder hydrolyzed for 10 min at 90 °C was performed. The TEM micrograph and the corresponding selected-area electron-diffraction pattern are presented in Fig. 7. The electron-diffraction pattern of the nanocrystalline particle, consisting of broadened circles, could not easily be analyzed, thus simulated electron-diffraction patterns of possible candidates were calculated and compared to the experimental-diffraction patterns. Based on these calculations we concluded that the nanocrystals have the structure of boehmite. In the simulation, the crystallite size was set to 5 nm; however, the experimental patterns have broader diffraction lines, indicating that the crystallite size is even less than 5 nm. These very small

and poorly crystallized boehmite particles result in very diffuse and poorly, or not visible diffraction lines, which is also the reason why a few inner rings are not present in the experimental electron-diffraction pattern.

4. Summary

The evolution of aluminum hydroxides during the AlN powder hydrolysis was monitored. After a short incubation time (<0.27–17 min), which was found to be temperature-dependent, the hydrolysis reaction started accompanied with the increase in pH and temperature. Higher starting temperatures also increase the reaction rate. The starting temperature and especially the ageing time (time of hydrolysis) strongly influence the reaction products and their morphology. It was confirmed that at RT the main crystalline reaction product is bayerite (Al(OH)₃), regardless on ageing time in the mother liquor. At elevated temperatures the first crystalline product is boehmite (AlOOH). With prolonged ageing the bayerite conversion takes place with dissolution of pseudoboehmite and recrystallization of bayerite. After 24 h of ageing in the temperature range from 40 °C to 70 °C bayerite became the predominant phase. At higher temperatures, e.g., at 80 °C and at 90 °C, both phases are present, but after 24 h of ageing boehmite remains the predominant phase. Based on these results, an extension of Bowen et al's model, for the AlN powder hydrolysis at RT to elevated temperatures is proposed. It is anticipated that at any temperature the very first solid reaction product formed on the surface of the AlN particles is pseudoboehmite. Once formed, part of the pseudoboehmite will be transformed to crystalline boehmite, while the other part will further react with water to form bayerite.

Acknowledgment

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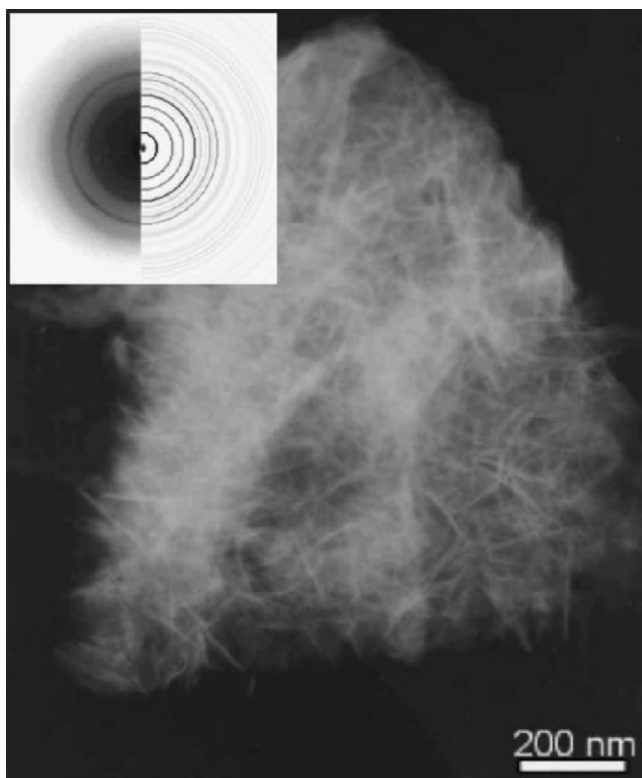


Fig. 7. TEM micrograph of AlN powder hydrolyzed at 90 °C for 15 min.

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