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Stereometric analysis of nanostructured boehmite coatings synthesized by aluminum nitride powder hydrolysis

Andraž Kocjan [a,*], Milan Ambrožič [b], Tomaž Kosmač [a,c]

[a] Engineering Ceramics Department, Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia
[b] Faculty of Natural Sciences and Mathematics, University of Maribor, SI-2000 Maribor, Slovenia
[c] Center of Excellence Namaste, Jamova 39, SI-1000 Ljubljana, Slovenia

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Abstract

We studied the morphological properties of precipitated, nanostructured, boehmite coatings on a polished alumina surface by exploiting the aluminum nitride (AlN) powder hydrolysis at elevated temperatures. The hydrolysis tests of the 3 wt% AlN powder suspensions in the temperature range 50–90 °C were performed in order to estimate the time needed for the synthesis of the coatings. They consisted of interlocked boehmite lamellas, positioned perpendicularly to the ceramic surface, and they exhibited a strong temperature-dependent size and surface density. The aim of this research was a quantitative assessment of the as-formed boehmite coatings. Based on electron microscopy micrographs, a stereometric analysis of the as-prepared coatings was performed in order to estimate the relevant geometric parameters of the lamellas. In spite of the temperature-dependent lamellas' size and surface density, the specific volume of the coatings was similar for all the synthesis temperatures.

Keywords: Aluminum nitride; Hydrolysis; Boehmite; Nanostructured coating; Stereometric analysis

1. Introduction

The tendency of AlN powder to hydrolyze when in contact with water has been known for a long time. At the beginning of the 20th century, prior to the invention of the Haber–Bosch process [1], the hydrolysis reaction was exploited in the production of ammonia. After the discovery of AlN's unique set of material properties, which are useful in electronic, structural and refractory applications [2], the reactivity of the AlN powder with water became a major drawback, because of the formation of aluminum hydroxides during the aqueous powder processing of AlN-based, non-oxide ceramics [3]. The un-desirable water sensitivity of the AlN powder was avoided by the use of non-aqueous powder processing or by employing a water-resistant AlN powder [4,5].

Recently, the exploitation of AlN powder hydrolysis reactions has been revived. It was shown that 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 mold. In this way, fully dense alumina and Y-TZP [6] or porous alumina ceramics can be prepared [7].

Furthermore, AlN powder hydrolysis at elevated temperatures can be exploited in the preparation of nanostructured boehmite coatings on a ceramic substrate immersed into a diluted AlN suspension. The coatings can be transformed into transient aluminas, with a subsequent thermal treatment up to 900 °C without any substantial change in the morphology [8]. The as-prepared alumina coatings can be applied in dentistry as a non-invasive, pre-treatment method for yttria-stabilized tetragonal zirconia (Y-TZP) ceramics [9,10] and as a template in the preparation of super-hydrophobic surfaces [11].

The heterogeneous precipitation of the boehmite phase on the ceramic surfaces occurs because during the hydrolysis of the AlN powder in water a sufficient amount of aluminum mononuclear and polynuclear species is formed. The latter are good structural nuclei for the initiation of the boehmite's precipitation [12]. The precipitated boehmite coatings consist

* Corresponding author.
E-mail addresses: a.kocjan@ijs.si (A. Kocjan), milan.ambrozic@uni-mb.si (M. Ambrožič), tomaz.kosmac@ijs.si (T. Kosmač).

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of lamellar particles that are typical for the boehmite phase [13], positioned almost perpendicularly to the ceramic surface and are extensively intercalated, forming a relatively complex morphology [8], very similar to that of the desert-rose crystal (gypsum and barite).

The complex geometry of the as-formed, boehmite, nanostructured coatings is reflected in the lamellas' surface density, their height, thickness, degree of skewness (if they are not exactly perpendicular to the ceramic surface), etc., which prevented us from using the standard techniques for surface evaluation, such as atomic force microscopy (AFM), and optical and/or contact profilometry. Unfortunately, the complexity of the coatings made these surface-evaluation techniques highly unreliable and ineffective. Therefore, the main goal of this study was to employ stereometric analyses [14] for the morphological characterization of the precipitated, nanostructured, boehmite coatings on the ceramic surface during the AlN powder hydrolysis at elevated temperatures.

Stereological analysis is a multidisciplinary technique enabling a quantitative estimation of the 3D inner structure of a complex body, based on the 2D intersections and/or topographical images obtained with an optical or electron microscope [14]. By employing this technique a constituent integrity characteristic for the entire nanostructured coating can be predicted. A scanning electron micrograph (SEM) of the coating is taken at an appropriate magnification, and on the basis of a 3D perspective of the porous nanostructured coating one can evaluate its respective particle density per unit area, the specific surface area and surface-area ratio parameter versus the various coating morphologies.

In the present study, the hydrolysis tests of the 3 wt% AlN powder suspensions in the temperature range 50–90 °C were performed by measuring the temperature increase of the suspensions in order to estimate the time needed for the synthesis of the boehmite coatings on the polished alumina ceramic surfaces. Using stereometric analyses the surface density of the lamellas in the coating, the lamellas' width, height, and thickness were estimated and the effective thickness (h_{eff}), i.e., the normalized volume of boehmite per unit area (V/S), the specific surface area (S_{spec}), and the surface area ratio parameter (S_{dr}) of the coatings were calculated.

2. Materials and methods

The substrates used in this work were fabricated in the form of discs (diameter Φ = 15.5 mm, height h = 2 mm) from commercially available ready-to-press Ceralox alumina APA 0.5 (Sasol, USA), sintered at 1550 °C for 4 h in air. One side of each disc was ground and polished using a standard metallographic procedure. Prior to the coating synthesis, the as-prepared alumina disks were ultrasonically cleaned using acetone, ethanol, and deionized water, and then stored in deionized water.

The substrates were then inserted into the deionized water that was preheated to 50 °C, 60 °C, 70 °C, 80 °C and 90 °C. After 30 s of tempering the AlN Grade C powder (H.C. Starck, Berlin, Germany) was added to the water so that a diluted suspension containing 3 wt% of AlN in the deionized water was obtained. After a certain period of time needed for the hydrolysis reaction to complete the substrates were removed from the suspension, rinsed with deionized water, dried and then stored for subsequent analyses.

The coated substrates were analyzed using a FE-SEM (Supra 35LV; Carl Zeiss, Oberkochen, Germany) at an operating voltage of 1 kV. The micrographs were taken at a magnification of 300 000. The cross-sectional coating micrographs were taken by tilting the stage by 30°. The lamellas' thickness was evaluated using a transmission electron microscope (TEM; JEM-2100, JEOL, Tokyo, Japan) at an operating voltage of 200 kV by measuring the thickness of the lamellas formed in the AlN powder after hydrolysis.

3. Results and discussion

3.1. AlN powder hydrolysis

The exothermic nature of the AlN powder hydrolysis reactions enabled us to monitor the temperature change versus time for the 3 wt% AlN powder suspensions preheated in the temperature range 50–90 °C. The results are presented in Fig. 1. The ΔT values for the suspensions preheated to 50 °C, 60 °C and 70 °C were 17.8 °C, 16.6 °C and 17.2 °C, respectively. The heat evolved during the exothermic hydrolysis reaction resulted in the boiling of the suspensions that were initially preheated to 80 °C and 90 °C. Consequently, the ΔT value for these two starting temperatures was apparently lower, i.e., 15.7 °C and 8.2 °C, respectively. The hydrolysis rate was progressively higher, with higher starting temperatures, which can be concluded from the ever shorter time needed for the start of the decrease of the suspension temperature after obtaining the maximum ΔT value (t_M; labeled with asterisks in Fig. 1). The times t_M for the starting temperatures of 50 °C, 60 °C and 70 °C were 50 min, 27 min and 12.5 min, respectively. For the 80 °C and 90 °C curves, the t_M values were estimated to be 8.5 min and 4 min,

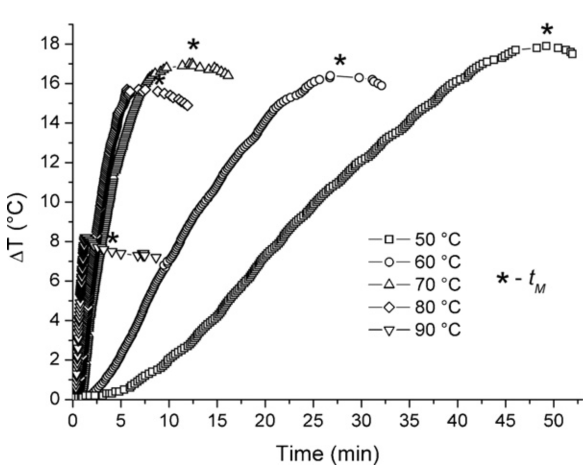

Fig. 1. ΔT versus time for a 3 wt% AlN powder suspension in deionized water at 50 °C, 60 °C, 70 °C, 80 °C and 90 °C.

respectively. It has been shown that when the t_M is reached, the conversion of AlN in water exceeds 90%, and the extensive growth of boehmite is terminated [15].

With regard to Fig. 1 we were mostly interested in the question of whether or not roughly the same volume of coating material per unit area of substrate is precipitated for different temperatures when the corresponding times t_M are used for the nucleation and growth of boehmite lamellas.

3.2. Coating synthesis

Based on the results of the hydrolysis tests of the 3 wt% AlN powder suspensions in Section 3.1, the soaking times of the polished alumina samples (in the form of disks) were set at t_M values, since during this period the extensive growth of the boehmite phase takes place [15]. Thus, the nanostructured boehmite coatings were successfully deposited onto the polished surfaces by exploiting the hydrolysis reaction, as presented in the SEM micrographs in Fig. 2. The lamellas that form the nanostructured boehmite coatings fully cover the alumina substrates. They are also interconnected and positioned more or less perpendicularly to the ceramic surface. From comparing Fig. 2a–e, it is evident that higher hydrolysis temperatures resulted in a coating consisting of fewer lamellas, which are also larger, better defined and exhibit a lower interconnectivity. This assumption was additionally checked by analyzing the onset of the boehmite lamellas' nucleation on the alumina surfaces, which were immersed in the AlN powder suspensions at 50 and 90 °C, for only 10 and 0.5 min, respectively. The corresponding SEM micrographs are shown in Fig. 3a. It is clear that immersing the substrate into the AlN powder suspension at 50 °C resulted in numerous particles, which were, compared to 90 °C, more abundant and smaller, having a less-pronounced lamellar shape. A similar tendency was observed when prolonging the time of the synthesis at 50 and 90 °C to 25 and 1.5 min, respectively (Fig. 3b). More particles, that were already interconnected, comprised the coating after immersing the substrate in the suspension at 50 °C, while larger, and fewer, were found on the alumina surface immersed in the suspension at 90 °C. However, at that stage, both coatings were made up of lamellar particles that were similar to those found in the coatings (Fig. 2a and e) after the required synthesis time, t_M (Fig. 1).

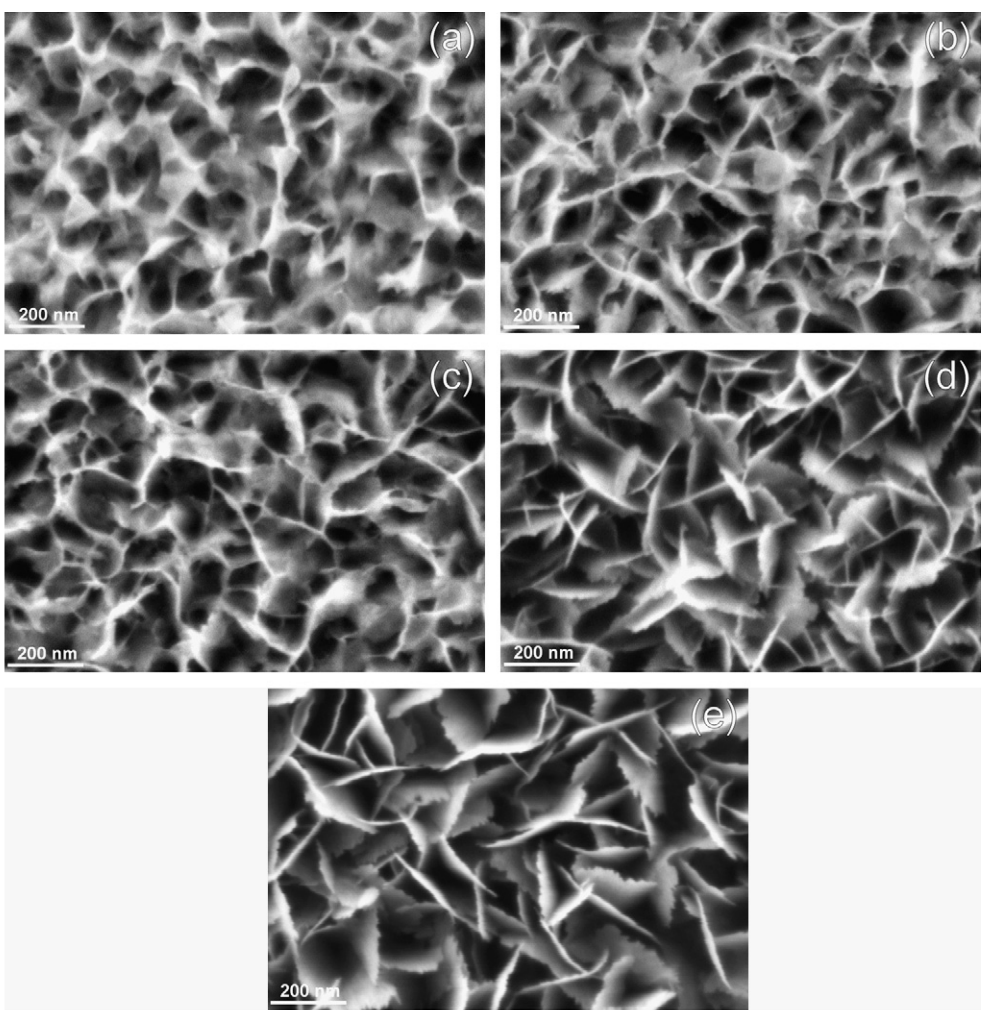

Fig. 2. SEM micrographs of the synthesized nanostructured boehmite coatings on the alumina surface by exploiting AlN powder hydrolysis at (a) 50 °C, (b) 60 °C, (c) 70 °C, (d) 80 °C and (e) 90 °C.

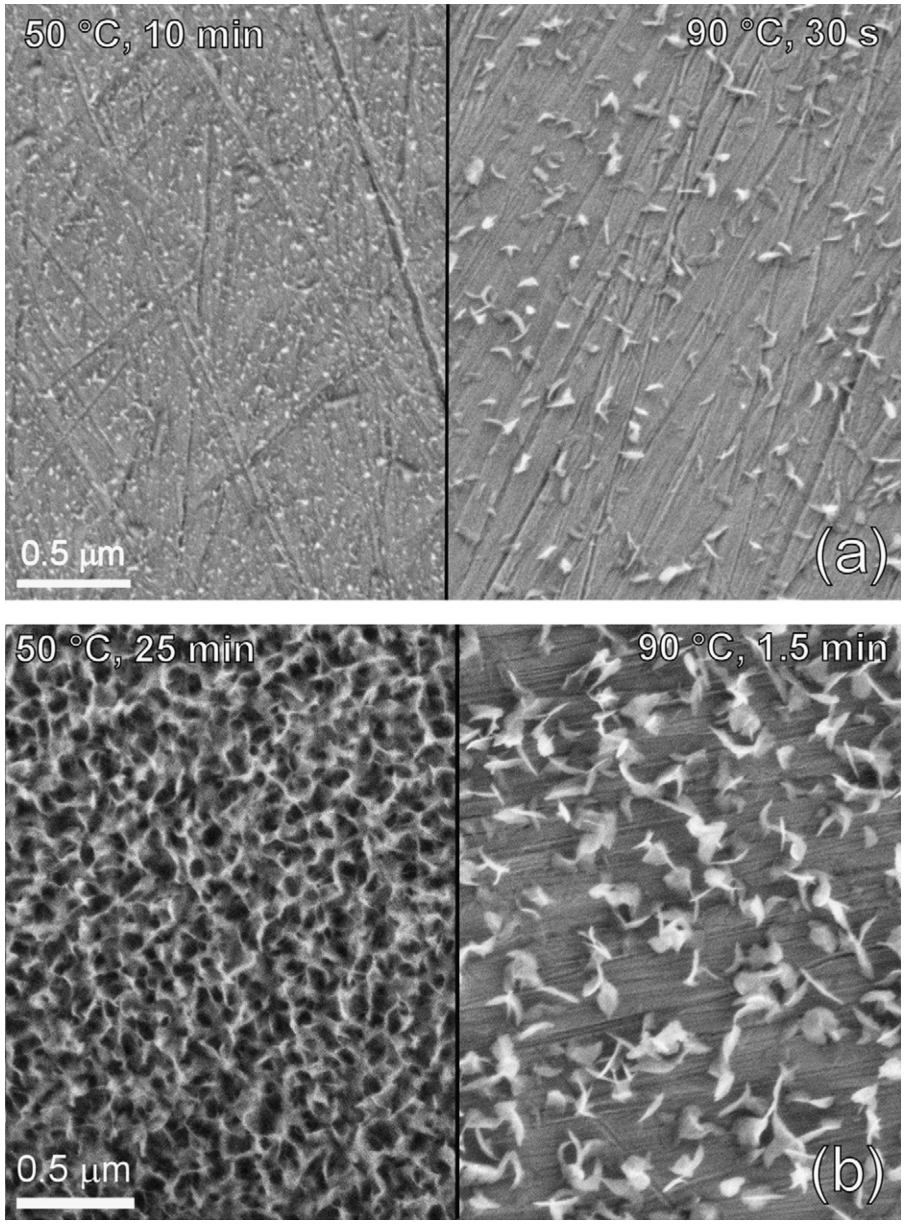

Fig. 3. SEM micrographs of the synthesized nanostructured boehmite coatings on the alumina surface by exploiting AlN powder hydrolysis at 50 °C and 90 °C for (a) 10 and 0.5 min; (b) 25 and 1.5 min, respectively.

3.3. Stereometric analysis

On the basis of the SEM micrographs the stereometric analyses of the coatings, synthesized by exploiting the AlN powder hydrolysis in the temperature range 50–90 °C, was performed. Thus, a quantitative evaluation of the 3D structure of the coatings can be obtained based on the 2D SEM micrographs. First, the surface density of the lamellas (*N*/*S*) making up the coatings was evaluated using the linear-interception method and the results are summarized in Table 1. The obtained *N*/*S* values for each hydrolysis temperature confirm the initial assumption with regards to the SEM micrographs, i.e., that the number of lamellas per unit area decreases with higher hydrolysis temperatures. It turned out that the decrease in *N*/*S* between 50 °C and 90 °C was 3-fold

Table 1
Extracted data based on a stereometric analysis of the nanostructured boehmite coatings on the polished alumina surface synthesized by exploiting AlN hydrolysis at different starting temperatures: surface density of lamellas (*N*/*S*), horizontal ellipse axis stands for the lamella's width ($2a_L$), vertical ellipse semi-axis stands for the lamella height (b_L), the effective coating thickness (h_{eff}), i.e., normalized volume of boehmite per unit area (*V*/*S*) and the surface-area ratio parameter (S_{dr}), i.e., the relative increase in the actual surface area of a flat surface.

T [°C]	50	60	70	80	90
N/S [μm^{-2}]	158 ± 12	125 ± 8	103 ± 4	72 ± 3	51 ± 4
$2a_L$ [nm]	135 ± 18	159 ± 23	188 ± 23	223 ± 23	259 ± 41
b_L [nm]	159 ± 34	176 ± 19	196 ± 24	222 ± 16	237 ± 16
h_{eff} [nm]	8.0	8.2	8.9	8.4	7.4
S_{dr} [%]	550	637	610	572	505

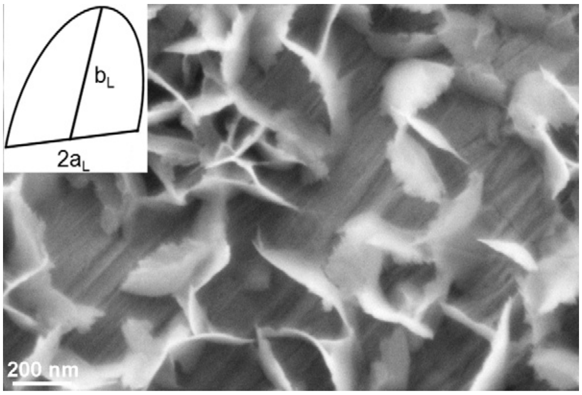

Fig. 4. SEM micrograph of the synthesized nanostructured boehmite lamellas on the polished alumina surface; $T = 90$ °C; geometrical half-elliptical parameters for the single lamella are delineated in the inset.

and approximately linear. Secondly, the geometry of a single lamella had to be assessed, but it was impossible to determine it from the present pictures, due to the high *N*/*S* value and the interlocking of the lamellas. An additional synthesis of the coating was conducted, where the weight percent of AlN in the suspension preheated to 90 °C was only 0.1 wt%. The amount of AlN in the suspension was sufficiently low, so that the polished alumina surface was not fully covered by the boehmite lamellas and then the geometry of the single lamella could be assessed. The SEM micrograph is shown in Fig. 4. As can be observed in the micrograph, a single boehmite lamella can be geometrically approximated with half-elliptical parameters, as delineated in the inset of Fig. 4. The elliptical parameter b_L (vertical ellipse semi-axis) stands for the lamella height, and $2a_L$ (horizontal axis) stands for the lamella's width; the third lamella's parameter is its thickness, d_L.

The average width of the lamella, $2a_L$, synthesized in the temperature range 50–90 °C was calculated by measuring 10 lamellas from SEM micrographs (Fig. 2a–e). The coating height, i.e., the parameter b_L, was evaluated on the basis of SEM micrographs, where the cross-sectional nanostructured coatings were captured by tilting the sample in the SEM chamber by 30°. In Fig. 5a, an example of such a cross-sectional view of the coating prepared by exploiting the AlN powder hydrolysis at 70 °C for 15 min is shown.

The measured $2a_L$ and b_L values are listed in Table 1. In contrast to the *N*/*S* value, the $2a_L$ and b_L parameters increase with the increased hydrolysis temperatures since more lamellas of smaller size are needed to cover the same area of the substrate. The lamellas' average thickness, d_L, as observed from the SEM micrographs, was of the order of nanometers. Therefore, for an accurate estimation, transmission electron microscopy was employed (TEM). Fig. 5b shows a typical bundle of lamellas found in the AlN powder after the hydrolysis at 70 °C for 12.5 min. By assuming their size is identical, compared to those in the coating, the thickness of 10 lamellas at each hydrolysis temperature was measured and an average d_L value of 3.3 ± 0.5 nm was obtained. Interestingly, irrespective of the starting hydrolysis temperature, the lamellas exhibited the same d_L value of about 3 nm. Therefore, d_L is the single temperature-independent parameter, even though the morphologies of the lamellas were quite different. Like with the lamellas' thickness, the crystallite sizes of the boehmite phase, i.e., the lamellas, found in the AlN powders after hydrolysis are also temperature independent. It was shown that they exhibited a crystallite size of about 6 nm, irrespective of the starting temperature of the AlN powder suspension [16]. This was ascribed to the temperature-dependent, oriented, aggregation mechanism of the metastable, poorly crystalline, hydrated nuclei [12,17], resulting in a variety of lamellar morphologies, as seen in the SEM micrographs (Fig. 2a–e). It is known that crystallites of boehmite tend to form a lamellar structure during their growth, having only two growth dimensions, which makes them 2D particles [13].

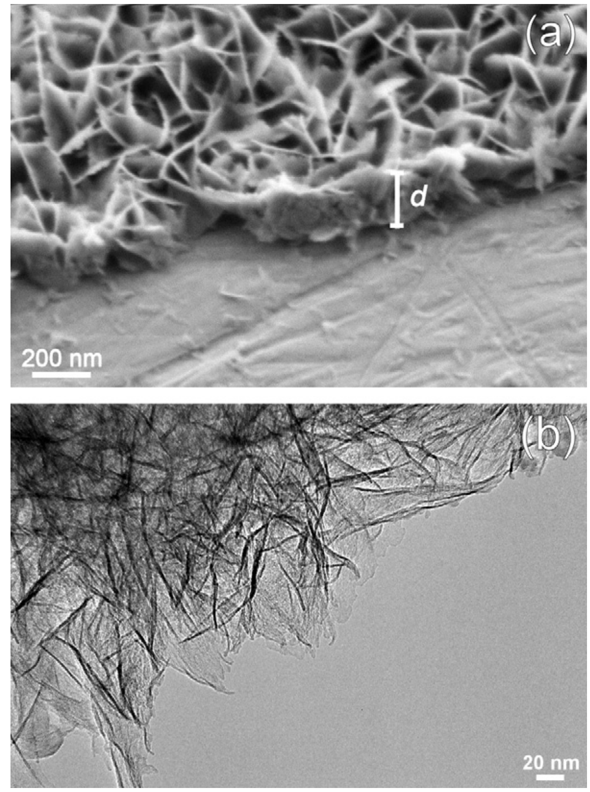

Fig. 5. (a) SEM micrograph of the cross-sectional nanostructured boehmite coating on a polished alumina surface synthesized by exploiting the AlN powder hydrolysis of a 3 wt% suspension at 70 °C for 12.5 min and (b) TEM micrograph of the respective hydrolyzed powder showing bundles of aggregated boehmite lamellas.

By considering the average parameters (*N*/*S*, $2a_L$, b_L and d_L) belonging to the boehmite lamellas comprising the nanostructured coatings prepared at different hydrolysis temperatures, the specific material volume, i.e., the normalized volume of boehmite per unit area (*V*/*S*), was calculated and expressed as an effective coating thickness, h_{eff}. Taking $d_L \approx 3$ nm, the h_{eff} can be calculated using the following equation:

$$h_{eff} = \frac{1}{2} \cdot \frac{N}{S} \cdot \pi a_L b_L d_L \tag{1}$$

The specific surface area (S_{spec}), i.e., the area of all half-ellipses per their unit mass, was calculated as follows:

$$S_{spec} = \frac{2}{\rho d_L} \quad (2)$$

where the boehmite density $\rho = 3.03$ g/cm^3 is assumed. Taking again $d_L \approx 3$ nm we obtain for all cases $S_{spec} = 222$ m^2/g. The contribution of the lamella's edge to the specific surface area was insignificant and was, therefore, neglected (since $d_L \ll a_L$, b_L). For comparison, the measured BET surface area of the bundles of agglomerated lamellas obtained after hydrolyzing the AlN powder for 4 h (the time needed to fully hydrolyze the AlN, which, when present, lowers the BET surface area of the powder) at 90 °C was 175 m^2/g [18]. The lamellas found in the powder cannot be directly correlated to those grown on the coating, but the comparable magnitude of the surface areas gives, nevertheless, additional support to the employed stereometric analysis.

From the calculated h_{eff} it can be seen that, irrespective of the starting hydrolysis temperature, an analogous amount of boehmite is precipitated onto the polished alumina surface at t_M, i.e., 7.4–8.9 nm, which is associated with the coating thickness of the non-porous, fully dense, boehmite film, containing the exact amount of boehmite, as in the nanostructured porous coating. This result is in agreement with the conversion of the AlN powder (X_{AlN}) at various starting temperatures, which is, irrespective of the starting hydrolysis temperature, slightly above 90% after a single temperature increment (after t_M) was obtained [15]. This result is also indicative of the high specific surface area of the nanostructured boehmite coating, synthesized by exploiting the AlN powder hydrolysis. Lastly, the calculation of the surface-area ratio parameter (S_{dr}), expressed as the relative increase in the actual surface area of a flat surface, was performed:

$$S_{dr} = \frac{N}{S}\pi a_L b_L \quad (3)$$

Again, the contribution of the lamella's edge to the S_{dr} value was neglected. The results are presented in Table 1. The calculated S_{dr} values are relatively high, between 505% and 610%. The S_{dr} value decreases with higher hydrolysis temperatures, except for the temperature 50 °C. This is because for the same specific volume of the precipitated material the total area of the constitutive particles decreases with their size.

The high values of S_{spec} and S_{dr} for the coated surfaces are one of the main reasons why the coating has numerous applicable potentials: such as in dentistry, where it significantly improves the adhesion bonding between the luting cement and the tetragonal zirconia (Y-TZP) surface [9,10], or as a template in the preparation of the superhydrophobic surfaces, where high surface-to-volume ratio surfaces are needed [11], which can be further employed for their self-cleaning properties. There could be another application of such coatings in dentistry: tetragonal zirconia is often sand-blasted before its use for dental prosthetics (one of the reasons for this is making its surface rough, in order to improve adhesion). However, sand particles also cause local damage in the surface region, leading to a loss of the material's strength [19]. These local damages could be reduced by the precipitation of the coatings before the sand-blasting.

4. Conclusions

The results of this study indicate that by using stereometric analyses it is possible to perform a genuine morphological characterization of complex structures, in our case nanostructured boehmite coatings, which were synthesized by exploiting AlN powder hydrolysis at elevated temperatures. The following conclusions can be drawn from the study. The number of lamellas per unit area was approximately linearly, and decreased with increased hydrolysis temperatures. A 3-folded decrease between the coatings prepared at 50 °C and 90 °C was observed. In contrast, the lamellae's length and height decreased with increased temperatures. The effective coating thickness, i.e., the normalized volume of boehmite per unit area, was between 7.4 and 8.9 nm, implying that irrespective of the starting hydrolysis temperature, an analogous amount of boehmite is precipitated onto the polished alumina surface. The calculated specific surface area of the nanostructured coating was 222 m^2/g, irrespective of the hydrolysis temperatures, due to the same thickness of the lamellas. The calculated surface-area ratio parameter, expressed as the relative increase in the actual surface area of a flat surface, was between 505% and 610%.

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