

Influence of dispersion state of initial AlN powder on the hydrolysis process in air environment

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Abstract. The research results of the hydrolysis processes of aluminum nitride powders received by the SVS method in dependence on humidity of the storage environment, and grain size distribution are presented in this work. Oxidation kinetics was estimated by means of X-ray Diffraction (XRD) and scanning electron microscopy (SEM). The induction period of the hydrolysis process for various powders, its dependence on powder dispersion and thickness of the oxide layer on surface of particles have been defined.

1. Introduction

Aluminum nitride (AlN) is advanced material for substrates of electron devices due to combination of electrical, physical, and dielectric properties [1,2] and high thermal conduction ($320 \text{ W} / (\text{m} \cdot \text{K})^{-1}$) [3]. Production of ceramics on the basis of aluminum nitride increases every year. Thermal conduction of sintered AlN depends on impurities in AlN grains, the largest action is performed by oxygen impurity because oxygen, replacing nitrogen, makes vacancies on aluminum which scatter phonon fluctuation of the lattice [3, 4-8]. Therefore, AlN powders with the low oxygen content are preferable for production of high-heat-conducting products. Change of oxygen content can happen in the course of production of powder, technological processing and at its storage.

The aim of this work is the study of the kinetics of interaction reaction of wet air with powdery aluminum nitride at storage in the conditions of real production.

2. Materials and methods of researches

Aluminum nitride powders produced by method of the self-propagating high-temperature synthesis (SHS) (Chernogolovka, Russia) of SHS-S, SHS-I and SHS-K grades were chosen for this research. The phase composition of the initial powders and products was determined with help of the Shimadzu XRD-7000 (Japan) x-ray diffractometer, we used the ICDD PDF-2 database (2013) for interpretation. According to the obtained data all initial powders are presented by the only phase – aluminum nitride (PDF 000-08-0262).

Definition of particle size distribution was performed with the help of the SALD 7101 laser diffraction particle size analyzer (Japan). Results are presented in (table 1).

The obtained data are in accord with the results of calculation of average diameter of particles (d_{av}) according to BET data obtained with the Nova 2200-e Quantachrome installation (USA). Oxygen content was determined with the LECO installation of the ONH836 grade, table 1. If to assume that all oxygen is in form of Al_2O_3 which is evenly distributed on the surface of particles, thickness of the oxide layer – l_{cal} , can be calculated according to method [9]. The thickest oxide layer (table 1) coated



aluminum nitride powder particles of SHS -K grade, the thinnest oxide layer was on the surface of SHS -S particles.

Table 1. Properties of initial powders of aluminum nitride

Grade of AlN powder	Particle size, μm			S_{spec} , m^2/g	d_{av} , μm	Content of O_2 , wt. %	thickness of the oxide layer l_{cat} , nm
	D_{10}	D_{50}	D_{90}				
SHS-S	0.23	2.11	5.05	7.04-8.01	2.20	1.60	0.12
SHS-I	1.64	3.10	5.12	1.55-2.50	7.40	1.14	0.32
SHS-K	1.92	12.29	29.71	0.50-0.70	26.30	0.92	0.88

Data of electron microscopy of aluminum nitride powders performed by the JEOL JSM 6000 scanning electron microscope are presented in figure 1. Powder of SHS-S grade (figure 1, a) is presented by particles of irregular shape with size from 1 to 5 μm . Aluminum nitride of SHS-S grade (figure 1, b) is formed by volume particles of rounded (spherical) form with size not more than 5 μm . One can see large volume particles of clastic form with shell-like fracture with sizes to 20 μm on microphotographs of aluminum nitride of SHS-K brand (figure 1, c). Fine particles with sizes from 2 to 5 μm and less are located between large particles. The received microphotographs confirm these definitions of particle size distribution of initial powders.

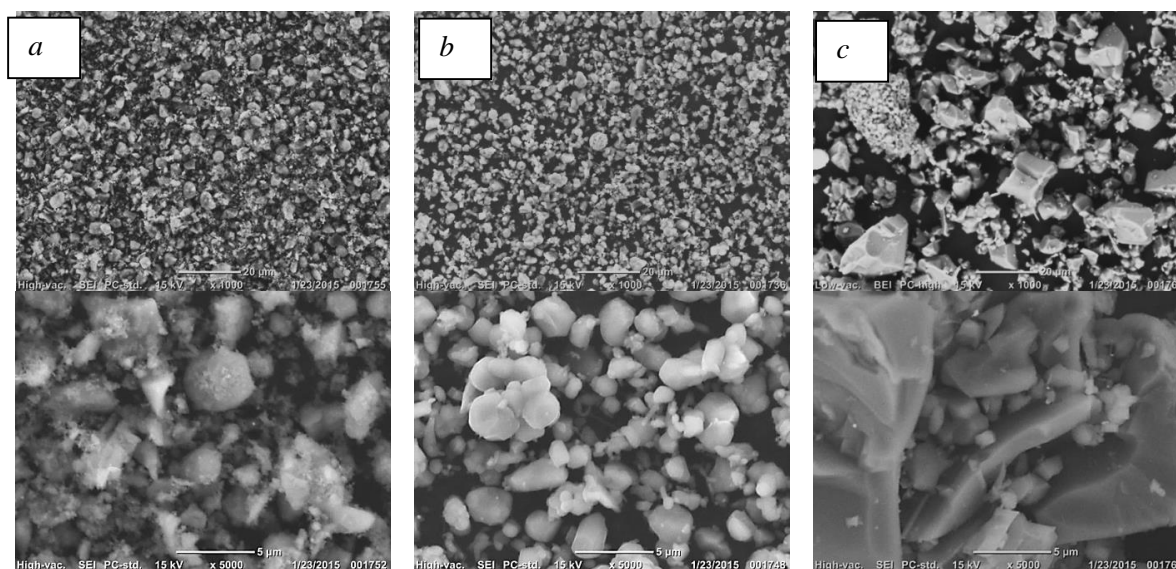


Figure 1. Microphotographs of aluminum nitride powders ($\times 1000$ and $\times 5000$) brands: a) SHS-S; b) SHS-I; and c) SHS-K

Difference in the granulometry of powders is defined by features of their behavior at heating. Data of synchronous thermal analysis, which has been performed using F3 Jupiter Netzsch STA 449 device (Germany), are given in table 2 and in figure 2. Conditions of analysis were: environment – air, T_{max} – 1500 $^{\circ}\text{C}$, the rate of heating 15 $^{\circ}/\text{min.}$, standard $\alpha\text{-Al}_2\text{O}_3$.

Table 2. Thermal analysis data

Aluminum nitride powder grade	Characteristic temperatures				ΔH , J/ $^{\circ}$
	$T_{\text{b.o.}}$	T_{p1}	T_{p2}	$T_{\text{e.o.}}$	
SHS-S	1045	1149	-	1349	15568
SHS-I	1116	1171	-	1300	21208
SHS-K	1120	1186	1361	1500	25946

Similarity of nature of oxidation of aluminum nitride powders of SHS-S and SHS-I grades is explained by similar particle size distribution. Powders are completely oxidized in one stage up to the temperature of 1500 °C in air. Two stages oxidation of SHS-K grade powder is connected with bimodal particle size distribution. Differences in temperature of the beginning of oxidation ($T_{b.o.}$) are connected with protective action of oxide film on particle surface, which thickness correlates with temperature of the beginning of oxidation.

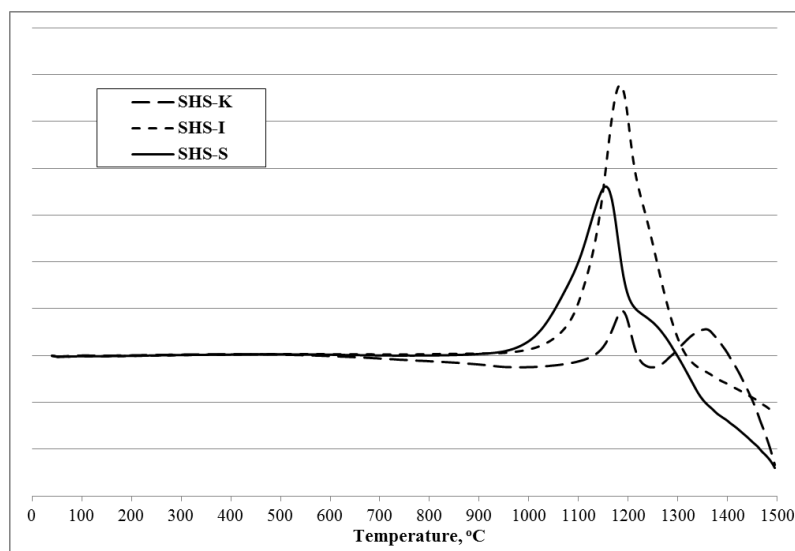
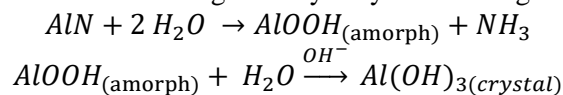


Figure 2. Thermograms of aluminum nitride powders

Method of carrying out experiment. Initial aluminum nitride powder was poured in the Petri dish with layer with thickness not more than 2 mm to increase area of interaction and was located in two exsiccators. One exsiccator contained air environment with high humidity (96-98%) created and maintained with the help of distilled water. Humidity of air environment in other exsiccator was not more than 15% (conditionally "dry" environment).

Aluminum nitride at interaction with water begins to hydrolyze according to following reactions [10]:



Assays were sampled with certain periodicity, then they were analyzed on content of oxygen, nitrogen, hydrogen, as well as X-ray phase analysis was performed.

3. Results and discussion

According to data of definition of phase structure of the assays stored in dry atmosphere, all powders irrespective of grade and duration are presented by the only phase of aluminum nitride (PDF 000-08-0262). Change of content of oxygen, nitrogen, hydrogen in them is in measurement error limit. Data of RFA of assays of aluminum nitride of SHS-S, SHS-I, and SHS-K grade after storage during 63 days in dry environment are presented in figure 3.

At storage of assays in the wet atmosphere change of phase composition for different grades of aluminum nitride begins at various terms of interaction. The powder of SHS-S grade with the minimum particle size and the thinnest layer of protective oxide film from all presented powders has the greatest reactivity. Emergence of $\text{Al}(\text{OH})_3$ peaks on XRD patterns is fixed for 9th day of experiment. With increase of storage periods intensity of aluminum hydroxide peaks increases that testifies intensification of interaction processes. At the same time intensity of aluminum nitride peaks naturally decreases.

SHS-K grade powder has the smallest activity that is connected with larger thickness of protective oxide layer on surface of AlN particles. Emergence of aluminum hydroxide peaks (figure 4) is fixed at the 32nd

day of storage in wet medium. Powder of the SHS-I grade has average activity, $\text{Al}(\text{OH})_3$ is revealed on XRD patterns on the 14th day of experiment.

Analysis of powders surface after 63-day interaction with moisture of air (figure 5) showed that powders of all grades have similar surface structure. There are loose formations on the powder particles, which have less clear sides in comparison with initial structure. Assays kept initial size distribution. Powders of the SHS-S (figure 5, a) and SHS-I (figure 5, b) grades are formed by particles with sizes from 2 to 5 μm . At the same time fine powders with more uniform sizes agglomerated in strength granula-like formations. Aluminum nitride of SHS-K grade (figure 5, c) is presented both by fine (2-5 μm), and by large particles (to 20 μm).

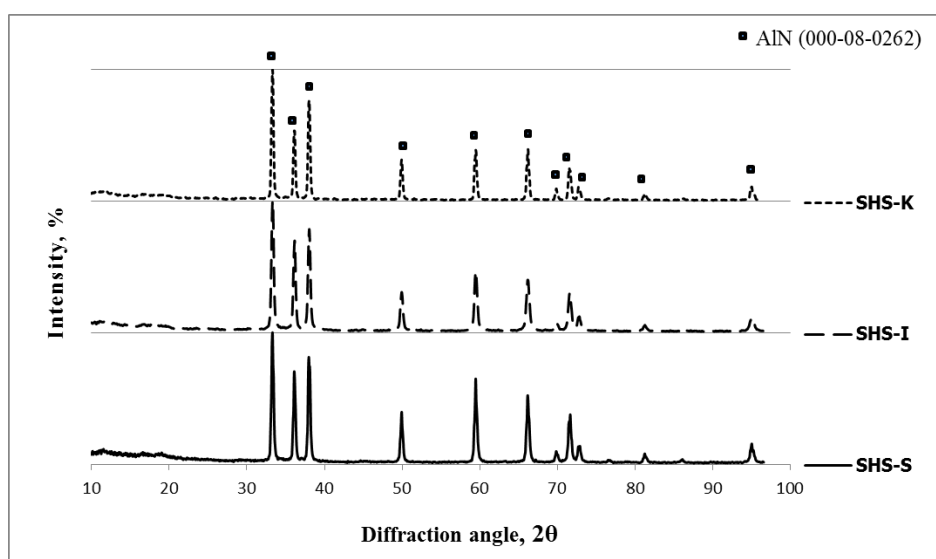


Figure 3. XRD pattern of aluminum nitride assays stored in the dry atmosphere during 63 days.

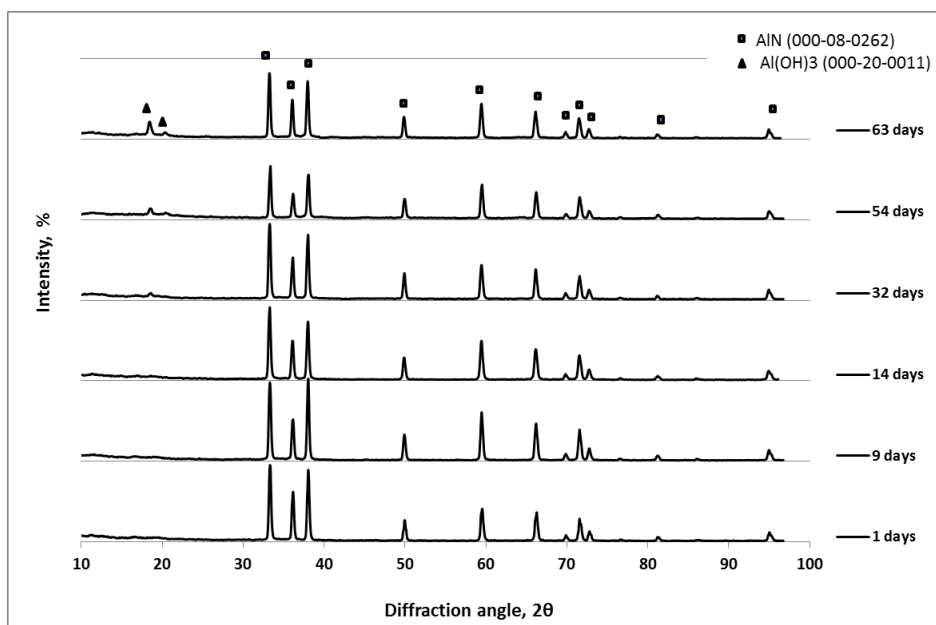


Figure 4. XRD patterns of aluminum nitride assays of SHS-K grade at different terms of interaction, stored in wet conditions

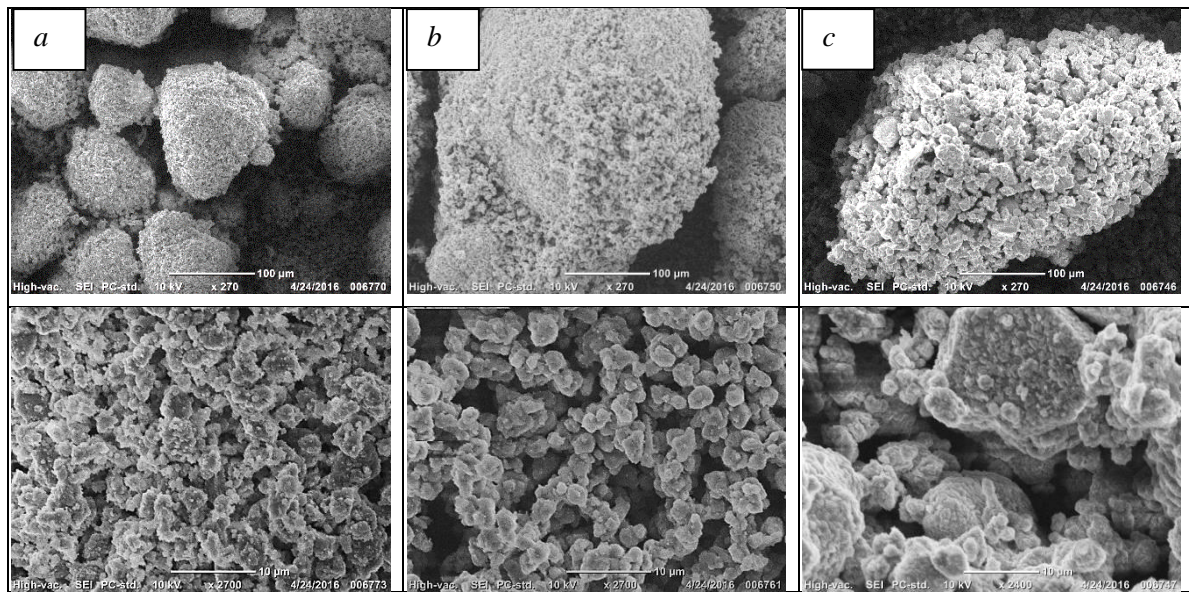


Figure 5. XRD patterns of aluminum nitride powders stored in the wet atmosphere during 65 days ($\times 1000$ and $\times 5000$): a) SHS-S; b) SHS-I; and c) SHS-K.

To describe mechanism of interaction of initial powders with moisture of air environment we calculated degree of transformation. According to obtained data (figure 6) one can see that all powders have the induction period which duration depends on thickness of surface oxide layer of particles. Large particle powder of aluminum nitride of SHS-K grade (20 days) has the longest induction period, since its surface aluminum oxide layer is larger by 2.5 times than one of other powders. With decrease of thickness of surface layer of Al_2O_3 on particles of initial powder, duration of induction period is reduced.

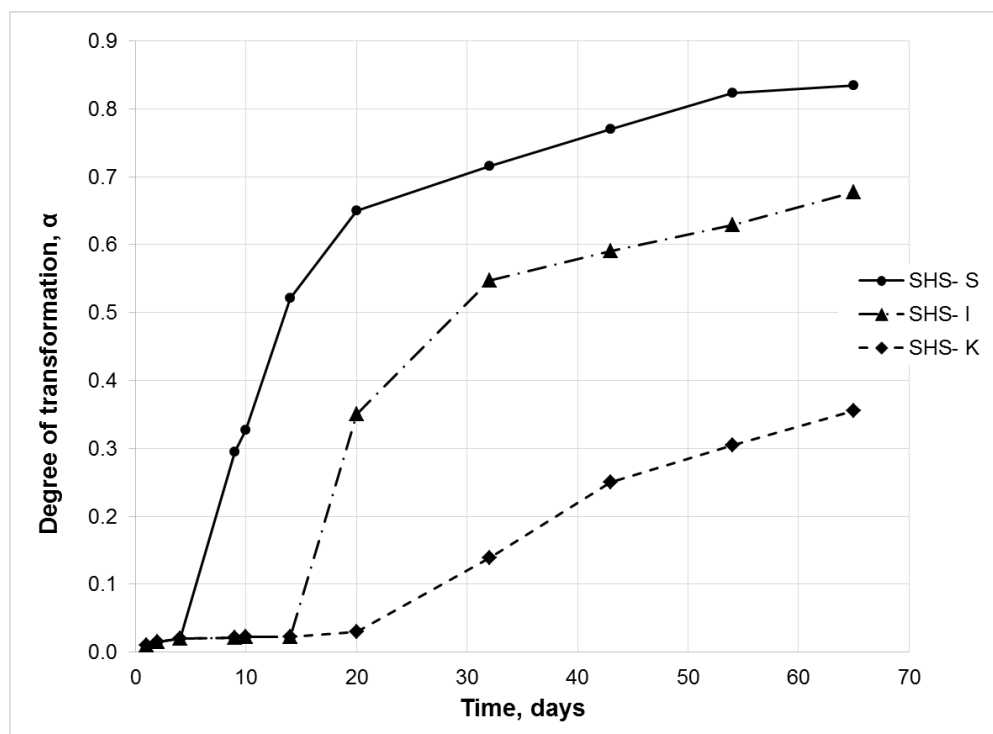


Figure 6. Degree of transformation of aluminum nitride of various grades at storage in wet conditions

4. Conclusion

Disturbance of storage procedure for aluminum nitride powders can lead to considerable changes of phase structure. Quantitatively these changes will depend on external environment, storage periods, dispersion state of initial assay, and thickness of the surface oxide film.

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