Obtaining high thermally conductive materials by pressing from the granulate

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Abstract. This work contains results of investigation of obtaining high thermally conductive ceramics from commercial powders of aluminum nitride and yttrium oxide by the method of monoaxial compaction of granulate. The principal scheme of preparation is proposed and technological properties of granulate are defined. Compaction conditions for simple items to use as heat removal in microelectronics and power electrical engineering have been established. Investigations of thermophysical properties of obtained ceramics and its structure by the XRD and SEM methods have been carried out. Ceramics with thermal conductivity from 172 to 174 W/m\(\cdot\)K has been obtained as result of this work.

1. Introduction
Growing demand for power semiconducting modules of high power, high reliability and affordable cost is caused by permanently developing power converter installations market: drives, energy management systems, uninterrupted power supplies, switched power supplies in electrical transport means. Ceramic substrate plays role of an electrically insulating and thermally conducting layer between semiconducting crystals and basis in power modules both brazed one with insulated basis and in modules of pressure construction (IGBT, FRD and so on). Increase of power increases heat generation which leads to increase of module temperature and deterioration of performance of semiconductive crystals and element of power electric engineering in whole, decreases its reliability and service life. Ceramics on the basis of Al\textsubscript{2}O\textsubscript{3}, that is used at the present, cannot ensure efficient heat removal (thermal conductivity of Al\textsubscript{2}O\textsubscript{3} is 24 W/m\(\cdot\)K), use of BeO is limited by its high cost, danger of production and toxicity for human (thermal conductivity of BeO is between 180 and 250 W/m\(\cdot\)K). Therefore problem of heat removal in power converter modules is very urgent and its solution is possible only using high thermal conducting ceramic materials. At the present there are no acting productions of high thermal conducting ceramic materials on the basis of aluminum nitride in Russia, all consumable volume of aluminum nitride items is import production.

2. Experimental procedure
Aluminum nitride industrial powders of the firm H.C. Starck grade B were used in this work. Yttrium oxide of firm H.C. Starck grade C was inserted to decrease sintering temperature and to purify aluminum nitride from oxygen admixture.
According to data of X-ray phase analysis performed with the Shimadzu XRD-7000 diffractometer, aluminum nitride powder is presented with single phase (000-25-1133). X-ray pattern of yttrium oxide powder contains only yttrium oxide reflexes (000-41-1105).

Results of laser granulometry of initial powders of aluminum nitride and yttrium oxide obtained on the SALD 7101 laser diffraction particle size analyzer are presented in Table 1.

| Initial powder | Particle size, μm |  |
|----------------|------------------|--|
|                | D$_{10}$ | D$_{50}$ | D$_{90}$ |
| AlN            | 0.200   | 1.200   | 5.100    |
| Y$_2$O$_3$     | 0.641   | 1.455   | 2.926    |

Obtained results of laser granulometry are confirmed by data of Scanning Electron Microscopy performed on the JSM 7500FA microscope for powders of aluminum nitride and yttrium oxide under investigation.

To calculate quantity of sintering addition (Y$_2$O$_3$) the oxygen content in aluminum nitride powder using the ONH836 device of the LEGO firm was defined; oxygen content was 1.153 wt. %.

To make compacts mixture of aluminum nitride and yttrium oxide powders was granulated because initial powders and their mixture had unsatisfactory properties (bulk density: 0.23 g/cm$^3$ and 0.63 g/cm$^3$, accordingly). Flowability of initial powders could not be measured. Granulation of powder mixture was performed with the “break of a briquette”.

According to proposed scheme powders of aluminum nitride and yttrium oxide were mixed in a ball mill during 24 hours. Obtained powder mixture was dried in a vacuum drying cabinet. Bond solution (PVB solution) was added to prepared powder mixture and a briquette was compacted from plasticized mass with specific pressure 1.0 t/cm$^2$. Obtained briquette was crushed and sieved on a vibration sieve to obtain granulate of specified fraction from 0.063 to 0.315 μm.

To remove excessive moisture obtained granulate was dried during day at room temperature. The samples were compacted in the form of discs with diameter 30 mm and height up to 5 mm, specific compaction pressure was changed from 1.0 up to 2.0 t/cm$^2$ with step 0.5. Compacted samples were sintered in the high temperature graphite furnace in nitrogen medium at sintering temperature of 1800 °C.

3. Results and discussion
At production of items with monoaxial compacting it is necessary to compact fine powder materials to improve important engineering properties, such as bulk density, flowability, and natural angle of slope. Use of fine powders in initial state is connected with many difficulties: spraying powders, increase of friction force between particles that leads to decrease of compacting force. All this does not allow obtaining compacts of good quality. The properties have been defined by standard methods on initial powders, on powder mixture and obtained granulate. Obtained data are given in Table 2.

Granulation allows to obtain granulate with bulk density being more than twice as one of initial powders and flowability of 25.0 g/s.

| Engineering properties | Material |
|------------------------|----------|
|                        | Initial powders | Powder mixture | Granulate |
|                        | AlN | Y$_2$O$_3$ |                 |           |
| Bulk density, g/cm$^3$ | 0.63 | 0.23 | 0.43 | 0.88 |
| Flowability, g/s      | 0   | 0   | 0   | 25.0 |

Granulation allows to obtain granulate with bulk density being more than twice as one of initial powders and flowability of 25.0 g/s.

Important moment at production of items is obtaining required compact form. It depends on number of factors: quantity of temporary organic bond, dispersity of granulate, specific pressure, and
mold construction. Granulate was prepared varying the main factors influencing compact properties: content of bond, specific pressing value, fraction composition, and granulate moisture.

All prepared granulates had similar granulometric composition, determined by sieving method, that is connected with the same method of granulate obtaining. Granulometry data of prepared granulates are presented in Figure 1.

All granulates have similar form of granules as volume particles of fragmentary form of various size, that is connected with the same method of making granulate, microphotographs of granules are presented in Figure 2.

Influence of various factors was estimated according to properties of compacts obtaining by monoaxial compaction in metallic molds, and according to relative density of compacts. Apparent density of compacts was determined by geometric way.

Solution of polyvinyl butyral was used as temporary bond, its content in granulates changed from 3 to 7 mass % (Table 3).

Results of compaction of obtained granulates are presented on the plot in Figure 3.
Figur e 3. Dependence of relative density of compacts on content of temporary bond.

It is established, that relative density of compacts growths with specific pressure at all contents of bond. Minimal content of bond being necessary to compact samples of specified form has been determined.

| Granulate component | Granulate Code |
|---------------------|----------------|
| PVB, wt.%           | B-97, B-95, B-93 |
| Powder mixture, wt.%| 3.0, 5.0, 7.0   |
| 97.0                | 95.0, 93.0      |

Necessary content is 5 wt.% , at smaller content one cannot obtain good compacted samples of the specified form (edges were spalled), and at greater content of bond relative density of compacts was less at all specific pressures. Compositions of granulate with combined bond (bond + plastificator) in quantity of 5 wt. % were studied on the next stage of works, prepared compositions are presented in Table 4. Addition of plasticizer to bond decreases strength of granules and at compaction its destruction will begin at less specific pressures. Diagram of dependence of relative density on plasticizer content is presented in Figure 4.

Relative density of compacts decreases with increasing of plasticizer content, in as much as density of granules is decreased and their destruction occurs on the initial stages of compaction process. In connection with this granulometric composition of granulate is sharply changed and density of its package is decreased. Force of friction between particles is increased and efficiency of compaction is decreased.
Table 4. Compositions of prepared granulates with combined bond.

| Granulate component | Granulate Code |
|---------------------|----------------|
|                     | C-50 | C-20 | C-10 | B-95 |
| PVB, wt.%           | 2.5  | 4.0  | 4.5  | 5.0  |
| DBP, wt.%           | 2.5  | 1.0  | 0.5  | 0    |
| Powder mixture, wt.%| 95.0 | 95.0 | 95.0 | 95.0 |

Influence of granulometric composition on relative density of compacts was estimated on obtained granulates with continuous granulometric composition and two fraction composition. Granulate B-95 has continuous granulometric composition and granulate A-95 contained two fractions: large one from 0.200 to 0.315 μm and small one less than 0.063, taken in ratio 70/30 in vol. %. Results of compaction are presented in Figure 5.

Relative density of compacts for model 2 fraction granulation is more than one for granulate with continuous granulometric composition inasmuch as package density for 2 fraction granulate is more.

![Figure 5. Influence of granulometric composition on relative density of compacts.](image)

![Figure 6. Influence of granulate moisture on relative density of compacts.](image)
Obtained dependence of relative density of compacts on granulate moisture is presented in Figure 6. If moisture increases relative density is decreased at all compaction pressures. It is connected with the fact that if moisture increases, pore volume after its evaporation is increased. Air permeability of material is decreased and more quantity of air is solved in moisture. Moisture quantity on the level of 0.04 wt. % (natural) in combination of bond in quantity of 5 wt. % is enough to decrease force of friction between particles, ensure slide and rotation of particles each against other on initial stages of compaction. It was impossible to obtain compactions at granulate moisture more than 2.5 wt. %.

Data of thermal analysis of made granulate is presented on Figure 7. Four effects are determined on thermogramm: the first one at temperature of 49 °C is endothermic and connected with removal of solvent; the second one at temperature of 175 °C is exothermic and connected with oxidation of organic bond; the third peak at temperature of 236 °C is connected with oxidation of surfactant and the last exothermic effect at temperature of 376 °C is connected with oxidation of carbon residue. Temperature chart of removal of bond has been proposed on the basis of results of thermal analysis. Removal of bond occurs on air at temperature 500 °C, and heating rate 5 °/min with 30 min. exposure at temperatures 170, 230, and 500 °C.

Sintering of aluminum nitride was performed in the high temperature furnace with graphite heaters in nitrogen medium at temperature of 1800 °C and isothermic exposure 4 hours.

To obtain high thermal conductivity it is required to ensure purification of aluminum nitride from oxygen admixture, direct contact between aluminum nitride grains, and continuity – absence of pores in sintered material. To ensure this requirement it is necessary to insert sintering addition – yttrium oxide - in aluminum nitride powder.

On the microphotographs presented in Figure 7 one can see that sintering addition is evenly distributed in sintered ceramics. At sintering formation of eutectic compound of yttrium aluminum garnet takes place as result of interaction of yttrium oxide and aluminum oxide, which is in the aluminum nitride powder.

Appearance of melt in the time of sintering ensures transport reaction, sintering by liquid phase mechanism that considerably accelerates process and ensures purification of aluminum nitride from oxygen admixture. After that the melt is forced in triple point ensuring direct contact between aluminum nitride grains where it crystallizes in yttrium aluminum garnet. According to data of electronic microscopy, size of aluminum nitride grain is from 2 to 7 μm, size of yttrium aluminum garnet is about 2 μm.

Apparent density, relative density, porosity and water absorption of sintered samples were determined by means of hydrostatic weighing. According to data of determination of relative density one can say that all samples are sintered, relative density growths with increasing of specific pressure of sample compaction for all granulates, the highest relative density is achieved for granulates C-10 and B-95 and is 99.96 % and 99.92 %, accordingly. Open porosity for majority of samples is close to zero value excepting B-95 with specific pressure 1.0 t/cm². Such high value of open porosity and low value of relative density is connected with low relative density of compact. Granules had high strength and at low pressure they are not destructed at compaction, and dense package of particles is not ensured.
Shrinkage of specimens at sintering is different in different planes and is in interval from 14.6 to 16.9%, when specific pressure increases, it decreases.

4. Conclusion
Principal scheme to obtain granulate from aluminum nitride and yttrium oxide is proposed in the work. Study of influence of various factors on properties of granulate, compacts and sintered ceramics has been carried out. Granulation improves engineering properties (bulk volume, flowability) and increases quality of compacts. Relative density of compacts is influenced in more degree by specific pressure of compaction and granulometric composition of granulates. The highest relative density of compacts being 62.0 % has been obtained at specific pressure 2.0 t/cm$^2$ for granulate with content of 5 wt. % of bond and consisting from two fractions. Sintered ceramics has high physical properties, relative density of all granulates exceeds 99 %, open porosity is close to zero. Important characteristic of ceramics is thermal conductivity that determines ability to use obtained materials as heat removal. Thermal conductivity of obtained ceramics is from 172 to 174 W/m·K, answers to requests of consumers, and corresponds to world level.

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