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Mechanically Stimulated Low-Temperature Synthesis of Aluminium Nitride*

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Abstract

Synthesis method is based on grinding coarse aluminium powder in the planetary centrifugal mill in the presence of a surface-active organic substance that promotes a decrease in the size of aluminium particles and covers the resulting products with a film that is impermeable for oxygen. The synthesis is carried out in the flow of high-purity nitrogen. At a temperature of 300–400 °C, the organic film is evaporated from the precursor particles, aluminium surface, active toward nitriding, shows up, and the reaction takes place at a temperature of about 750 °C. The yield of the product is about 100 %, its oxygen content is less than 0.6 mass % (the detection limit for the method used). Because of low temperatures, the resulting powder is weakly agglomerated; particle size varies within the range 350–500 nm.

Key words: aluminium nitride, synthesis, mechanical activation, sintering

INTRODUCTION

Aluminium nitride is a material with a unique combination of high thermal conductivity (200–240 W/(m · K) and good electric insulating properties (its resistivity exceeds 10^{12} Ohm · m). Due to these properties, the ability to sustain high temperature and work in aggressive environment, and the coefficient of thermal expansion close to that of silicon, ceramics made of aluminium nitride is widely relevant for the modern electronic industry [1, 2].

At present, many methods to synthesize aluminium nitride powders are known. Among them, the most efficient ones are considered to be direct nitriding of aluminium powder [3], carbothermal reduction [4, 5], SHS [6, 7] and plasmachemical method [8]. These methods have some disadvantages: a high synthesis temperature (up to 2100 °C), conditioned by the presence of a film of aluminium oxide on the par-

ticles of initial powder that is not destroyed up to high temperatures; contamination of the reaction product with carbon (carbothermal reduction); low product yield; complicated instrumentation (SHS). As a result of the reaction, the primary product of the synthesis is coarse powders. To improve their rheological properties, additional operations are to be carried out before subsequent moulding and sintering, which causes the contamination of the powder with the material of milling bodies and often leads to a higher content of impurity oxygen [9].

In the present work an attempt was made to reduce the temperature of AlN synthesis through direct nitriding by means of the preliminary removal of the oxide film from the particles of initial metal aluminium and to obtain a powder with characteristics that are more favourable for the subsequent ceramic production.

EXPERIMENTAL

PA-4 aluminium powder (State Standard GOST 6058–73), stearic acid (ch. reagent grade),

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paraffin, polyvinyl alcohol (PVA) were used in the work. The initial powder was activated in the AGO-2M centrifugal planetary mill with steel balls 10 and 11.5–12.5 mm in diameter, the ratio of ball mass to the charge mass in the cylinder was 40 : 1, the acceleration was within the range 6–40g, or in a jar roller mill (LE-101, Budapest). The synthesis of AlN from activated powders was carried out in a tubular furnace Carbolite STF 15/180 in the flow of high-purity nitrogen (TU 2114-003-05758954-2007) under heating at the rate of 5 °C/min before the start of the reaction, followed by exposure for 3–5 min; then the furnace was cooled. At the moment of the start of nitriding reaction, determined as a noticeable drop of gas flow rate at the outlet of the furnace; its gas input increased from 0.1 to 5–6 L/min per 100 g of the product. The X-ray phase analysis of initial, activated and synthesized powders was carried out with a DRON-4 diffractometer (CuK α radiation, graphite monochromator). The powder morphology, size and shape of particles were determined with a TM-1000 scanning electron microscope. The specific surface of the powders was determined using a “Sorbtoometr” set-up by means of the thermal desorption of nitrogen. The O, N, C content in the synthesized powder was determined by means of thermogravimetry with a STA 449 F₁ Jupiter instrument for synchronous thermal analysis. The sample was heated in platinum crucibles from room temperature to 1450 °C at a rate of 5 °C/min in the flow of the gas blowing at a rate of 10 mL/min (80 % He + 20 % O₂).

The synthesized powder was mixed in AGO-2M centrifugal planetary mill using steel balls 5 mm in diameter with 3 mass % Y₂O₃ and moulded by dry pressing at a pressure of 1.5–2 t/cm². Sintering was carried out in the atmosphere of nitrogen at a temperature of 1850°C in the SNVE – 1,7.3.1,7/20 furnace or Nabertherm. The density of the resulting ceramic material was determined using the hydrostatic method according to GOST 20018–74; its thermal diffusivity was measured by means of laser flash using the LFA-427 set-up at room temperature. The thermal conductivity was determined from the thermal diffusivity using equation $\lambda = a\rho C_p$, where a is thermal diffusivity, m²/s; ρ is density, kg/m³; C_p is specific heat of the material, equal to 0.74 kJ/(kg · K).

RESULTS AND DISCUSSION

The micrographs of aluminium powder activated with 3 mass % of the organic substance are shown in Fig. 1, while Fig. 2 shows the X-ray diffraction patterns of activated aluminium nitride powders after heating in nitrogen flow at 750 °C.

It was expected that during grinding the additive would form a film to cover the fresh formed metal surface and to separate particles formed as a result of mechanical action. As a result, it would be possible to prevent recrystallization which usually accompanies metal grinding, and to avoid the formation of conglomerates composed of small particles with the surface film protecting them from oxidation when in contact with the air.

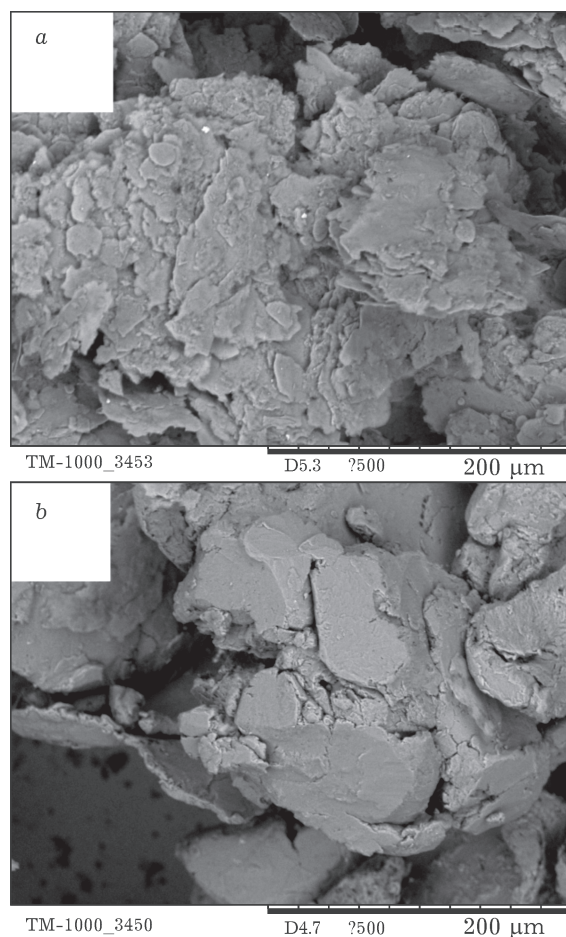


Fig. 1. Micrograph of mechanically activated PA-4 aluminium powder with stearic acid (a) and paraffin (b).

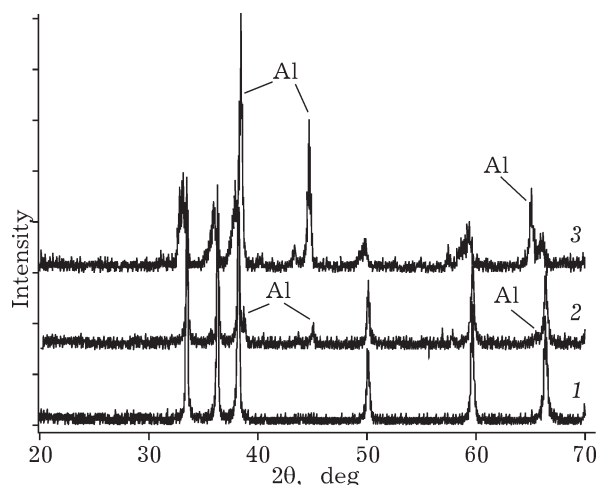


Fig. 2. X-ray diffraction patterns of aluminium nitride synthesized at 750 °C from activated metal powder with the organic additive: stearic acid (1), paraffin (2) and PVA (3).

In Fig. 1, one can clearly see coarse formations larger than 200 μm . In the case when paraffin is used, dense lumps are formed; stearic acid promotes the scaly structure of agglomerates. With PVA, results similar to activation with paraffin were obtained but the size of the formed agglomerates is about 1.5 times larger. The organic film is evaporated during heating, and oxide-free aluminium surface readily interacts with nitrogen.

The data shown in Fig. 2 unambiguously indicate that the synthesis of aluminium nitride proceeds at a low temperature. If PVA or paraffin is used as organic additives, the reflections of metal aluminium are clearly seen in the X-ray diffraction patterns; only in case of stearic acid a monophase product is observed. In our opinion, the latter fact is connected with a good wettability of powdered aluminium by stearic acid; due to its low melting point, it is possible to achieve the fluid state even at the temperature occurring in the mill. In the end, the resulting film protects well the activated metal from oxidation and prevents the adhesion of the comminuted metal particles.

In case of other organic additives, the negative effect of particle adhesion is likely to be expressed as a much lower porosity of agglomerates formed as a result of the mechanical action. Thus, the specific surface of activated metal is 3.5–5 or less than 1 m^2/g in the case

when stearic acid and paraffin are used, respectively. In this case, the specific surface of the metal activated in stearic acid after the removal of the organic film increased in more than three times, which explains its so high activity in the process of nitriding.

In case when the porosity of the metal activated with the acid was decreased artificially by pressing into briquettes, nitriding was not observed, only a thin nitride film was formed on unreacted metal surface at a temperature of 1300 °C. It is obvious that the presence of the precursor composed of fine aluminium particles, arranged in the manner providing the best access of nitrogen to the surface of particles, free from the oxide film, is necessary for the completeness of the reaction of nitridation.

It turned out that if stearic acid is added at the stage of aluminium activation not as the dry powder but as a solution in benzene (0.01 g/mL), only 1 mass % of the acid is sufficient to achieve a positive result: to form a monophase product as a result of nitriding (see Fig. 2, curve 1). In addition, it is not necessary to change the gas atmosphere of the activator cylinder for the inert one. A positive result was obtained for the mechanical treatment of aluminium at the acceleration of 6g and higher. The necessary time of treatment with the minimal acceleration 6g was 15 min. For the case of roller mill, the necessary time is 5 h; however, the mass of the substance under treatment is substantially larger.

The furnace temperature, at which nitriding of activated aluminium starts, varies within the range 750–900 °C depending on the charge

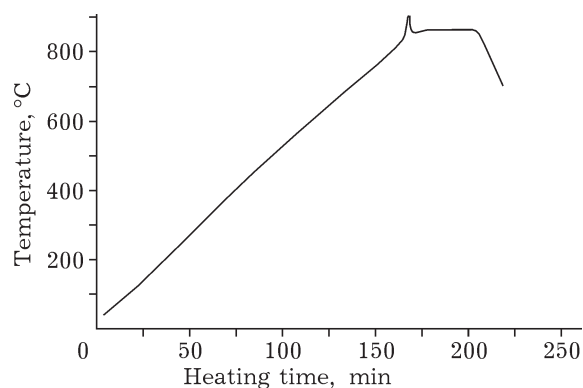


Fig. 3. Dependence of the temperature of powder charge on heating time.

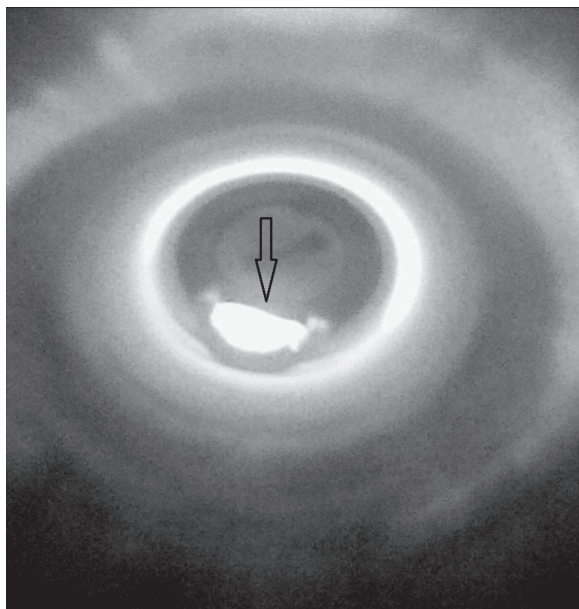


Fig. 4. Sample image in corundum trough at the moment of reaction progress (reactor temperature 750 °C).

mass, method of its arrangement in the reactor and other parameters of the experiment. For example, with an increase in the gas input rate at the stage of heating by a factor of 3–4, the temperature of the process start increases, and the concentration of the unreacted metal in the product is substantial. At a temperature below 750 °C, the initial powder does not undergo visible changes. The absence of alloying of metal particles between each other in this case probably indicates the formation of a thin aluminium nitride film on the surface after the removal of the protective layer of stearic acid.

Figure 3 shows the dependence of the temperature of a small powdered charge (2–3 g) on time under the conditions when thermocouple was inserted directly into powder volume. One can see that heat liberation, which can be logically attributed to the start of exothermal nitriding reaction, starts rather sharply and is over within a short time interval. Reagent temperature increases substantially during this time. It is evident that actual temperature at which nitriding proceeds is higher than furnace temperature and depends on the ratio of the rates of heat liberation and removal, that is, on the charge mass, geometric features of its arrangement (thin or thick layer), crucible material, flow rate *etc.*

Reagent temperature may exceed the furnace temperature in some cases by a substantial value. For example, intense glow of powder at the moment of reaction presented in Fig. 4 is the evidence of process temperature above 1100 °C, while furnace temperature is only 750 °C. Too high temperatures developed in the reaction mixture are undesirable because a very strong cake of the product is formed. In addition, the interaction of the reagent with the crucible material is possible (Fig. 5). On the other hand, insufficiently intense heat evolution does not provide necessary heating of the whole charge. As a consequence, the product contains metal aluminium.

In case of the optimal conditions of nitriding process, the product appears as grey porous fragile cakes easily destroyed in an agate mortar. The powder is composed of agglomerated spherical particles (Fig. 6) with the average size of 0.2–0.5 μm, which is comparable with the size determined on the basis of specific surface (3.6–5.2 m²/g). Nitrogen content is (34.48±0.68) mass %, oxygen less than 0.65 mass %, while carbon was not detected. Agglomeration of moulded tablets gave ceramic material with the density more than 97 % and thermal conductivity 195–220 W/(m · K).

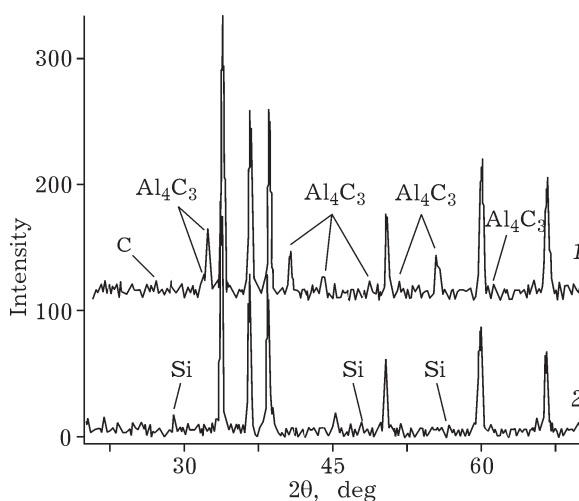


Fig. 5. X-ray diffraction patterns of aluminium nitride powder synthesized at the furnace temperature of 800 °C in graphite (1) and quartz (2) troughs.

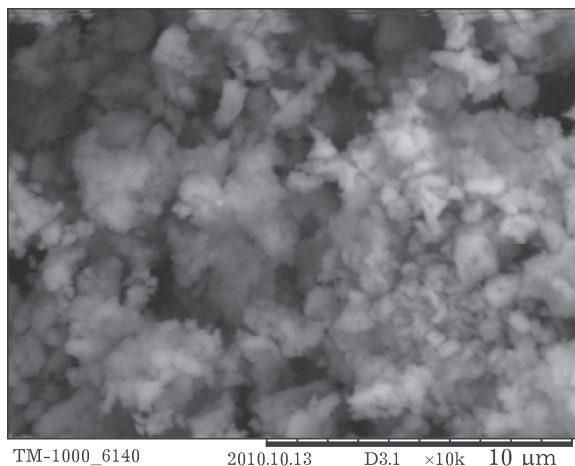


Fig. 6. Photomicrograph of the synthesized aluminium nitride powder.

CONCLUSION

Porous agglomerates are formed during the mechanochemical treatment of metal aluminium in the presence of a small amount of stearic acid. They are composed of ground metal particles coated with an organic film protecting them from oxidation. Under heating this precursor in nitrogen flow, the organic film evaporates, and the particles liberated from the oxide layer interact with nitrogen forming AlN at

much lower temperatures than usually. The furnace temperature, at which the interaction takes place, differs from the temperature developed within the charge and it is determined by the ratio of the intensities of heat evolution as a result of the reaction and heat removal. Under optimal conditions of the experiment, single-phase nitride is an easily destroyable cake even at 750 °C. After the addition of 3 mass % Y_2O_3 , the resulting powder is moulded by dry pressing and sintered at 1850 °C into a dense ceramic material with the thermal conductivity more than 195 W/(m · K).

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