

REPLACED SHEETS		SG
☒	Description : paged ...1... to paged ...14...	
☒	Claim(s) : paged ...15... to paged	
☒	Drawing(s) : paged ...14... to paged	
☒	Abstract : paged ...14... to paged	
DATE OF RECEIPT		

1

The subject of the invention is a continuous process for making aluminium nitride by the carbonitriding of alumina.

5 Processes are known for making aluminium nitride by the carbonitriding of alumina which employ a fluidized-bed reactor (see for example European Patent Application 0,266,927, the Japanese Application 63.297205 and the British Patent Application 87.00208).

10 It has also been proposed to carry out the reaction in a rotary kiln (see for example the Japanese Patent Applications 62.278109, 62.20030 and 61.74635).

It has also been proposed to make aluminium nitride in a shaft kiln having a stack of travelling
15 buckets (see for example the European Patent Application 0,272,377) or fixed (Japanese Patent 1,290,562).

These various technologies have a certain number of drawbacks. On the one hand, they have in
20 common a capability of only a single limited production and limited productivity since the working volume of the reactors is always low.

On the other hand, the products obtained are generally characterized by their heterogeneity due to a
25 wide distribution in the residence time of the reactants in the kiln. This is particularly so for the

This Sheet Has Been Replaced



rotary kiln and for the fluidized-bed reactor operating continuously.

It has been further proposed to carry out the reaction in a continuously operating methodical or moving-bed reactor (see the European Patent Application 0,519,806 and the Application WO 92/16467). These processes make it possible to achieve a production close to one kilogram, or indeed several kilograms of aluminium nitride per hour. However, the productivity of these reactors remains low.

It goes without saying that these deficiencies are unacceptable and that there is always a need to increase the productivity of the plant while at the same time maintaining both a high level of production and a high homogeneity of the product.

The invention therefore provides a novel process for continuously making aluminium nitride by the carbonitriding of alumina, this process being characterized in that the reaction is carried out in a reactor whose reaction zone, consisting of at least one conduit, has an exchange surface area/volume ratio of between 5 m^{-1} and 150 m^{-1} . Preferably, this ratio is between 10 m^{-1} and 50 m^{-1} .

By reaction zone is meant here that zone of the reactor having a temperature compatibility with the carbonitriding reaction of alumina, this temperature generally being between 1350 and 2000°C .

By exchange surface area is meant here the



surface area of the internal wall(s) of the conduit(s) of the reaction zone.

According to a first method of implementing this process, the reaction between alumina, carbon and
5 nitrogen is carried out in a reactor operating continuously by successive charges.

According to another preferred method, the reaction between alumina, carbon and nitrogen is carried out in a moving-bed reactor.

10 In the first implementation method, a reactor operating by successive charges is used, consisting of at least one straight conduit, generally made of graphite, intended to operate in a substantially vertical manner. The reactor is fed by means of
15 granules obtained by shaping a paste constituted by a mixture of alumina and of carbon and advantageously, especially in order to facilitate the compounding of this paste, of a binder capable possibly of acting as a complementary raw-material(s) carrier.

20 By binder is meant here any product which imparts to the granules a mechanical strength compatible with the process according to the invention. Generally, this mechanical strength is determined by measuring the crushing strength and the attrition loss.

25 When the binder is constituted by a thermosetting resin capable of generating carbon during its pyrolysis, the amounts of carbon and thermosetting resin are adjusted so as to impart to the granules at



the same time sufficient porosity and sufficient mechanical strength.

Carbon black provides the pore volume favourable to the rate of carbonitriding and the resin binds the granules.

The thermosetting resin may be advantageously chosen from phenol-formaldehyde resins in aqueous solution, but it goes without saying that other resins may be used, such as epoxy, polyester or polyimide resins.

The black may be chosen from a wide range of carbon blacks, as long as the average diameter of the particles of black lies within the range of from 0.5 to 10 μm and preferably from 1 to 5 μm and as long as their pore volume is at least equal to 0.3 cm^3/g . Purely by way of indication, acetylene black, whose pore volume may reach 10 cm^3/g may especially be mentioned.

As regards the alumina, a high-purity alumina should be chosen and a grain size of the same order of magnitude as those of the black is recommended. For the compounding of the paste (and of the granules) and for reasons of homogeneity, it may be advantageous to make use of a dispersant, for example of the type comprising an ammonium salt of a polyacrylic acid.

In the compounding of the granules, a total-carbon quantity is generally employed, that is to say carbon as it is and carbon generated by the thermosetting resin equal to or greater than the



stoichiometry of the carbonitriding reaction (C/Al_2O_3 ratio = 3): this excess may reach 100% and is preferably between 0 and 50%.

These feed granules have a crushing strength generally of between 0.2 and 3 MPa (measured according to the "Bulk Crushing Strength" - Shell method) and an attrition loss generally less than 15%. This attrition loss is measured according to the method which consists in introducing 25 g of granules into a closed cylindrical metal tube (internal diameter 36 mm, length 305 mm), in fixing the said tube to a rotating support in such a way that the rotation axis of the support passes through the middle of the length of the tube. After 1 hour of treatment at a speed of 25 rpm, the solids obtained are screened (425 μ m screen), and the fines are recovered and weighed.

The attrition loss is expressed by the relationship:

$$A \% = (P2/P1) \times 100$$

in which:

- A % represents the attrition loss;
- P1 represents the initial weight of the granules;
- P2 represents the weight of fines obtained.

Percolation of the charge by nitrogen is advantageously achieved by continuous inlet of the gas at the bottom part of the conduit(s) of the reactor.

The top part of the conduit(s) of the reactor



is connected to a manifold for the outlet gases, the said gases essentially consisting of CO and N₂ in excess, it being possible for these to be directed towards the base of an incineration furnace.

5 After a sufficient reaction time for the carbonitriding reaction to be complete, granules, which may contain an excess of carbon (AlN + C), are recovered after cooling, the said granules having a residual α -Al₂O₃ content generally less than 0.5% with
10 respect to AlN (measurement carried out by X-ray diffraction). Purely by way of indication, this reaction time can vary from 0.5 to 25 hours.

 The excess carbon may be removed by combustion in a gas containing oxygen, preferably at a
15 temperature not exceeding 700°C.

 The pure aluminium nitride is finally deagglomerated, for example in an air-jet mill advantageously equipped with a grinding chamber coated with elastomer, so as to prevent any contamination.

20 The aluminium nitride powder obtained by virtue of the implementation of the process described hereinabove is in the form of particles of average size of between 0.5 and 5 μ m, consisting of AlN with a residual α -Al₂O₃ content not exceeding 0.5% (by weight
25 with respect to AlN) and a BET specific surface area generally at least equal to 2 m²/g and possibly reaching 5 m²/g.

 According to the second, preferably used,



method, the process in accordance with the invention is implemented in a moving-bed reactor.

The expression "moving bed" is used here in its conventional sense, that is to say that it
5 designates a reactor of the plug-flow type.

More precisely, the reaction between alumina, carbon and nitrogen is carried out in a moving-bed reactor operating at a constant filling rate, with a homogeneous and constant residence time of the
10 reactants and with percolation of the charge under conditions ensuring homogeneous composition of the gas phase around each particle at a given level and intense mass transfer and heat exchange.

In this process, the constant filling rate
15 may be obtained by continuous extraction, for example by a weight-metering or volume-metering device located at the base of the moving bed, and a plug-type flow of the charge in a shell of constant cross-section.

In the process in accordance with the
20 invention, and whatever the type of reactor chosen, the latter provides at least the functions:

- of heating the starting granules (shaped raw materials), by the hot outlet gases, that is to say of a heat exchanger,
- 25 - of a carbonitriding reactor,
- of heating the nitrogen entering the reactor by contact with the granules leaving the hot zone of the kiln.



The reactor generally comprises a single conduit, all or part of which constitutes the reaction zone.

The cross-section of the conduit in the
5 reaction zone may have a regular or arbitrary shape. By way of examples of a regular shape, circles, ellipses, annuli, right or curvilinear polygons, either regular or non-regular, and the geometrical shapes having an axis of symmetry may be mentioned. Preferentially, a
10 conduit having a cross-section of circular shape is used.

The reaction zone may also include a plurality of conduits, either identical or different, the cross-section of which may have a shape as defined
15 hereinabove.

When the reaction zone comprises several conduits, these conduits may be uniformly or non-uniformly arranged inside the reactor. Generally, the conduits are uniformly arranged such that, for example,
20 the centre of each conduit is located on a circle or several concentric circles whose origin is the centre of the reactor or by nesting when this involves annuli of various sizes (Figure 1). Preferentially, the conduits are arranged so that the centre of each
25 conduit is located on a circle whose origin is the centre of the reactor.

The space between the conduits generally consists of a heat-conducting material. By way of



examples, graphite, tungsten and molybdenum may be mentioned. Preferentially, the same material is used as that which forms the conduits, this generally consisting of graphite.

5 When the reaction zone is composed of several conduits, the nitrogen-heating zone, contiguous with the said reaction zone, may or may not also be constituted only by a single conduit or more generally by a different number of conduits and/or by one or more
10 conduits of different shape and/or size.

 Generally, the bottom part of the reactor is extended by a shell of frustoconical shape comprising a nitrogen feed and the bottom end of this shell possesses a sealed volume-metering device allowing
15 extraction of the granules with a view to their continuous weighing.

 The level of the fresh granules continuously feeding the reactor is kept constant by means of a sensor fixing the filling level, this sensor being
20 located in the top part of the reactor.

 The hot carbonitrided granules, by pursuing their movement towards the bottom part of the reactor, are progressively cooled by the continuously inlet nitrogen. The cold granules are extracted by virtue of
25 the volume-metering device defined hereinabove.

 Cold granules are thus extracted which can contain a carbon excess ($\text{AlN} + \text{C}$), the said granules having a residual $\alpha\text{-Al}_2\text{O}_3$ content of less than 0.5% with



respect to AlN (measurement carried out by X-ray diffraction).

The excess carbon may be removed by combustion in a gas containing oxygen, preferably at a temperature not exceeding 700°C.

The pure aluminium nitride is finally deagglomerated, for example in an air-jet mill advantageously equipped with a grinding chamber coated with elastomer, so as to prevent any contamination.

The aluminium nitride powder obtained by virtue of the implementation of the process described hereinabove is in the form of particles of average size of between 0.5 and 5 μm , consisting of AlN with a residual $\alpha\text{-Al}_2\text{O}_3$ content not exceeding 0.5% (by weight with respect to AlN) and a BET specific surface area at least equal to 2 m^2/g and possibly reaching 5 m^2/g .

The invention is illustrated by the following examples.

Example 1

1 - 550 parts by weight of high-purity alumina, finely ground (average grain size: 1 μm - ASTM C678 Standard: pore volume: 0.76 cm^3/g) is mixed with 182 parts by weight of acetylene black (average particle size: 2 to 3 μm : pore volume: 7.0 cm^3/g), 257 parts by weight of phenol-formaldehyde resin in aqueous solution (approximately 60% concentration) and 11 parts by weight of an ammonium polyacrylate dispersant.

The mixture is processed in an alumina-coated



mixer until disappearance of the white particles of alumina.

The resulting paste is used to feed an extruding press whose extrusion orifices have a diameter of 3 mm. At the exit from these orifices, a cutter cuts up the rods to a length of 6 mm.

The granules thus obtained, dried in a ventilated oven at 150°C, (10.8% weight loss), have the following weight composition:

10	- alumina	: 61.6%
	- carbon	: 20.4%
	- resin	: 17.5%
	- dispersant	: 0.5%.

The crushing strength of the granules is 2.8 MPa and the attrition loss is equal to 2.2%.

2 - The granules are used to feed a continuously operating flowing-bed graphite reactor. The reactor is constituted by a cylindrical conduit, the reaction zone of which has an internal diameter of 300 mm, this corresponding to an exchange surface area/volume ratio equal to 13 m⁻¹.

The feed rate of the granules is 4.2 kg/h.

The reactor is fed at its bottom part with nitrogen at a flow rate of 16 kg/h.

The temperature of the external wall of the reaction zone is 1450-1700°C, the residence time in this zone being approximately 12 hours.

Upon exiting the reaction zone, the cold



carbonitrided granules are removed at a rate of 2.40 kg/h (this corresponding to 2.04 kg/h of 100% aluminium nitride).

Under these conditions, the productivity of the reactor is equal to 0.0412 kg of 100% aluminium nitride per hour and per litre of reaction zone.

3 - The granules are taken up and spread out on Inconel trays in a layer of approximately 1 cm in thickness and are then loaded into an electrically heated discontinuous kiln, the temperature being maintained uniform at $650^{\circ}\text{C} \pm 5^{\circ}\text{C}$ by circulation of air. This temperature is maintained for 8 hours. The weight loss is approximately 12.5%.

After this treatment, the residual free carbon content is less than 700 ppm, the oxygen content not exceeding 1%.

The aluminium nitride thus obtained is deagglomerated in an air-jet mill with walls coated with elastomer.

The average size of the particles of the final aluminium nitride is $1\text{ }\mu\text{m}$ and the BET specific surface area of this aluminium nitride is $4\text{ m}^2/\text{g}$.

Example 2

The conditions of Example 1 are carried out in the presence of a reactor whose reaction zone consists of four conduits of circular cross-section, inscribed in a 300 mm diameter circle. Each conduit has a diameter of 110 mm, defining an exchange surface



area/volume ratio equal to 36 m^{-1} .

The feed rate of the granules is 4.05 kg/h .

The reactor is fed at its bottom part with nitrogen having a flow rate of 24 kg/h .

5 The residence time in the reaction zone is approximately 7 hours.

 Upon exiting the reaction zone, the cooled carbonitrided granules are removed at a rate of 2.3 kg/h (this corresponding to 2.0 kg/h of 100% aluminium nitride).

10

 Under these conditions, the productivity of the reactor is equal to 0.075 kg of 100% aluminium nitride per hour and per litre of reaction zone.

Example 3 (Comparative Example)

15 The conditions of Example 1 are carried out in the presence of a graphite reactor whose reaction zone consists of a conduit of circular cross-section having a diameter of 800 mm , this corresponding to an exchange surface area/volume ratio equal to 5 m^{-1} .

20 The nitrogen feed rate is 20 kg/h .

 The feed rate of granules is 5 kg/h , this corresponding to 2.5 kg/h of 100% aluminium nitride.

 The residence time in the reaction zone is approximately 90 hours.

25 Under these conditions, the productivity of the reactor is equal to 0.007 kg of 100% aluminium nitride per hour and per litre of reaction zone.

This Sheet Has Been Replaced



Example 4

The conditions of Example 1 are carried out, the alumina carbonitriding taking place in the reaction zone of the reactor operating continuously by successive charges.

45 kg of granules are introduced into the reaction zone of the reactor per sequence.

The temperature of the external wall of the reaction zone is 1500°C.

The residence time in the reaction zone is approximately 23 hours.

When the carbonitriding reaction is finished, the granules are removed and the reaction zone is filled once again with fresh granules.

During this removal-filling operation, which lasts approximately one hour, the temperature of the external wall of the reaction zone is kept constant, at approximately 1500°C.

Under these conditions, the productivity of the reactor is equal to 0.023 kg of 100% aluminium nitride per hour and per litre of reaction zone.

This Sheet Has Been Replaced





15 .

CLAIMS

1. Process for continuously making aluminium nitride by a carbonitriding reaction starting from alumina, carbon and nitrogen, characterized in
5 that the reaction is carried out in a reactor whose reaction zone, consisting of at least one conduit, has an exchange surface area/volume ratio of between 5 and 150 m⁻¹.
2. Process according to Claim 1,
10 characterized in that the exchange surface area/volume ratio varies from 10 to 50 m⁻¹.
3. Process according to one of Claims 1 and 2, characterized in that the conduit has a cross-section of a shape chosen from circles, ellipses,
15 annuli, right or curvilinear polygons, either regular or non-regular, and geometrical shapes having an axis of symmetry.
4. Process according to one of Claims 1 and 2, characterized in that the alumina and carbon,
20 combined with a binder, are employed in the form of granules having a crushing strength of between 0.2 and 3 MPa and an attrition loss less than 15%.
5. Process according to one of Claims 1 and 2, characterized in that a reactor operating by
25 successive charges is used.
6. Process according to one of Claims 1 and 2, characterized in that a moving-bed reactor is used.

This Sheet Has Been Replaced

