Corundum-zirconia abrasive grains containing more than 50 wt % of an alumina-zirconia eutectic mixture. The grains contain 0.3 to 3% nitrogen, and more than 75% of the zirconia crystals are cubic in shape. The abrasive grains are of particular use for making grinding wheels, abrasive fabrics and papers, polishing compounds and sprayed abrasives.
ALUMINUM AND ZIRCONIUM OXYNITRIDE ABRASIVE GRAINS

BACKGROUND OF THE INVENTION

[0001] The invention relates to the domain of abrasive grains, and particularly agglomerated grains intended for grinding wheels, grains applied to fabric and paper type supports, and grains used for spraying or contained in a polishing paste.

[0002] Description of Related Art

[0003] Alumina-zirconia based electromelton abrasives have been known for more than forty years and in particular have been described in several patents by the Norton company. Patent U.S. Pat. No. 3,181,939, filed in 1962, describes aluminum-zirconia type electromelton abrasives with ZrO₂ content between 10 and 60%, and a microstructure comprising an alumina-zirconia eutectic and zirconia and α alumina crystals. Patent U.S. Pat. No. 3,891,406 filed in 1971 relates to alumina-zirconia type electromelton abrasives with ZrO₂ content of between 35 and 50%. Patent U.S. Pat. No. 3,993,119 published in 1976 describes a molten abrasive oxides casting machine capable of vigorously quenching the molten mass. Patent U.S. Pat. No. 4,457,767, 1984, protects alumina-zirconia type electromelton abrasives with a content of yttrium oxide Y₂O₃ between 0.1 and 2%.

[0004] More recently, the 3M Innovative Properties Company has deposited patent applications:

[0005] WO 02/08143 that claims an electromolten abrasive grain characterised by a fraction of at least 20% by volume, composed of a eutectic mixture formed between firstly ZrO₂ and secondly at least two other constituents, including Al₂O₃ and/or defined compounds of the Al₂O₃—Y₂O₃ type.

[0006] WO 02/08146 that claims an electromolten abrasive grain with eutectic composition in which eutectic is formed between firstly ZrO₂ and secondly at least two constituents including Al₂O₃ and/or defined compounds of the Al₂O₃—Y₂O₃— rare earth oxides type.

[0007] The common point between these patent applications is that the abrasive grains always contain either yttrium oxide or at least one rare earth oxide, in one manner or another.

[0008] The Inorganic Chemistry Treatise by Paul Pascal, Massou, 1962, already described that ZrO₂ had three allotopic varieties. The monoclinic form stable at low temperature is transformed into quadratric zirconia at about 1100⁰ C, and then into cubic zirconia. The cubic form is the most stable at high temperature and it can be obtained by quenching; some elements, without any further precision, stabilise the cubic form.

[0009] The patents mentioned above always indicate that the product is prepared by casting the molten product followed by vigorous quenching, a process that tends to stabilise the metastable cubic form; however, experience shows that the efficiency of this quenching is fairly limited, which is the reason for the interest in patent U.S. Pat. No. 4,457,767 that divulges that yttrium oxide stabilises the cubic phase of ZrO₂. Patent application WO 02/08146 suggests that other stabilising elements exist in the group of rare earth metals.

[0010] Furthermore, patent EP 0 509 940 issued by the applicant describes a wide range of electromelton products for abrasive or refractory applications, composed of one or several oxynitrides of metallic elements in the list containing aluminum and zirconium; but there is no example of the case that mentions aluminum and zirconium oxynitrides nor double aluminum and zirconium oxynitrides.

SUMMARY OF THE INVENTION

[0011] The purpose of the invention is to provide abrasive grains to be applied onto fabric or paper supports or agglomerated in grinding wheels, or sprayed or contained in a polishing paste, and that have a better tenacity and machining performances than corundum—zirconia abrasives according to prior art with an equivalent content of zirconia.

[0012] The subject of the invention is corundum—zirconia abrasive grains containing more than 50% of a eutectic alumina—zirconia mixture, characterised in that they contain more than 0.3% of nitrogen, preferably from 0.3% to 3% of nitrogen, and more preferably from 0.3 to 1% of nitrogen, and in that less than 25% of the zirconia crystals are in monoclinic form. According to the invention, more than 75% of the zirconia crystals are in tetragonal or cubic form. Preferably, more than 75% of the zirconia crystals are in cubic form.

[0013] The content of metallic aluminum is less than 0.1% and preferably 0.01%, and the content of aluminum nitride is less than 0.1% and preferably less than 0.01%.

[0014] Another purpose of the invention is a process for manufacturing this type of abrasive grains by melting in an electric arc furnace with a load composed of alumina and babedelite, by adding a nitride material to this load composed of aluminum nitride and/or one or several aluminum oxynitrides.

[0015] Another purpose is a process for preparation of abrasive grains including the preparation of a mixture of aluminum nitride and/or oxynitride Al₉O₁₇N₂, alumina and zirconia powders, the reactive sintering of this mixture at a temperature between 1500⁰ C. and 1600⁰ C, and fast cooling of the sintered grains between 1100⁰ C. and ambient temperature.

DETAILED DESCRIPTION OF THE INVENTION

[0016] Within the very wide range of abrasive compositions described in patent EP 0509940, the applicant has demonstrated that products based on aluminum and zirconium oxynitrides have better performances than products according to prior art of the corundum—zirconia type or the aluminum oxynitride type such as AlON.

[0017] Products according to the invention contain oxides, nitrates and oxynitrides of aluminum and zirconium, and it is not always easy to measure the content of each of these compounds. However, it is easy to measure the elementary contents of aluminum, zirconium and nitrogen. This is why the “equivalent content” concept is used by arbitrarily considering the product as a being a mixture of Al₂O₃, ZrO₂, and AlN. The equivalent content of Al₂O₃ is the content for which all the nitrogen would be in AlN form, the equivalent content of ZrO₂ is the content for which all the zirconium would be in ZrO₂ form, and the equivalent content of Al₂O₃ is the content for which aluminum would be in Al₂O₃ form, except aluminum corresponding to the equivalent content of AlN. Another advantage of this concept of equivalent con-
tent is that the product can be compared with corundum—
zirconia abrasives according to prior art.

Products according to the invention are of the corundum—zirconia type with an equivalent content of ZrO₂ between 21 and 44%, an equivalent content of Al₂O₃ between 57 and 80% and a nitrogen content between 0.3 and 3%, and preferably between 0.3 and 1%. For more than 50% of their weight, their structure consists of a eutectic mixture of α alumina and zirconia crystals. More than 75% of the zirconia crystals are in cubic form, the remainder being in monoclinical form. Nitrogen is present essentially in the form of zirconium nitride, more than 90% of the remainder being in the form of aluminum oxynitride.

It has been experimentally observed that the presence of zirconium nitride in the product is accompanied by a large increase in the relative proportion of the cubic form in the zirconia contained. Zirconium nitride is a perfectly stable product in contact with the water and acids, which is not the case for aluminum nitride, which makes it an excellent stabilising agent.

These products may be obtained by melting in an electric arc furnace with a load composed of alumina, zirconia, for example in the form of baddleyite, and a nitride compound based on aluminum nitride and/or oxynitride. The aluminum nitride and/or oxynitride react with the zirconia during melting to form zirconium nitride.

The molten mass is cast and solidified quickly by any means known to those skilled in the art to cause efficient quenching; during these tests, the applicant used the technique described in patent U.S. Pat. No. 3,993,119, but using fixed casting equipment considering the size of the test. Casting is done on a cold support, with a mass equal to at least twice the mass of the molten mass, and at a temperature of between 500° C. and 350° C. before casting.

If a product produced by direct nitriding according to patent EP 0491219 issued by the applicant and containing aluminum nitride and oxynitride is used as the nitride compound, a product is obtained in which the content of free aluminum nitride is small, and typically less than 0.1%. Furthermore, this content can be reduced to less than 0.01% by slight acid etching, with final washing of the grains by a solution with a pH between 2 and 7, without reducing the mechanical strength of the material. The same is true for metallic aluminum.

Abrasive grains according to the invention can also be prepared by reactive sintering starting from a mixture of alumina, zirconia, and aluminum nitride and/or oxynitride powders.

Sintering is done at a temperature between 1500 and 1600° C., followed by fast cooling of the grains starting from 1100° C.

Exceptional mechanical properties are obtained using abrasive grains according to the invention, and particularly a Knoop hardness greater than or equal to 19 GPa, or even 20 GPa, and between 19 and 21 GPa, a tenacity of at least 2.3 MPa.m², very often more than 2.7 MPa.m², and performances in the machining test equal to 70% more than is obtained with a conventional corundum—zirconia abrasive with the same content of zirconia.

EXAMPLES

Analysis and Test Methods

The nitrogen content was measured on 5 mg samples weighed to the nearest 0.1 mg, by combustion in a LECO TC 436 gas analyser, and analyses by thermal conductivity of the gas obtained. The result indicated on each sample is the average of five measurements.

Example 1

2500 kg of powder Bayer alumina with a size grading of less than 100 μm was mixed with 1000 kg of powder aluminum with a size grading of less than 1.2 mm. This mixture was placed in a scaled furnace, vacuum degassed and then heated under a nitrogen pressure of 1 atm.

Nitriding began at about 700° C., and the nitrogen pressure was maintained to facilitate the increase in the temperature of the load. The exothermal reaction resulted in a temperature of about 1750° C. at the end of the operation.

After cooling, and at the end of the operation, the mass of porous, homogenous and mechanically unsound aluminum oxynitride recovered was 4010 kg.

The operation was repeated three times and finally a batch of 16 100 kg of product was obtained and was ground to a size grading of less than 10 mm, and then sampled and analysed; the result of the analysis gave an equivalent AlN content equal to 35.6%.

Example 2

400 kg of a mixture composed of 30 kg of the product obtained in example No. 1, 100 kg of baddleyite with 95% of ZrO₂ and 270 kg of Bayer alumina, was prepared.

This load was melted in a 100 kW melting arc furnace; the molten mass was cast on an ingot mould composed of 12 vertical cast iron plates (0.8 m x 0.8 m x 0.05 m) separated by 0.025 m. The cast mass was 390 kg; the product analysis was:

<table>
<thead>
<tr>
<th>Equivalent AlN content: 2.3%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr content expressed in ZrO₂: 23.6%</td>
</tr>
<tr>
<td>Al content expressed in Al₂O₃: 73.7%</td>
</tr>
</tbody>
</table>

An examination of the product structure demonstrated the existence of two majority phases:

α alumina and cubic zirconia, and two minority phases: zirconium nitride and monoclinical zirconia. The chemical analysis also gave a free AlN content of 0.07% in the product.

The hardness and tenacity measurements are shown in Table 1, which also shows the results for similar product:

<table>
<thead>
<tr>
<th>Product</th>
<th>Knoop hardness</th>
<th>Vickers hardness</th>
<th>Tenacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 2</td>
<td>19.9 GPa</td>
<td>18.9 GPa</td>
<td>2.8 MPa · m²/²</td>
</tr>
<tr>
<td>Corundum</td>
<td>18.7 GPa</td>
<td>17.9 GPa</td>
<td>2.1 MPa · m²/²</td>
</tr>
<tr>
<td>Zirconia with 25% ZrO₂</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Example 3

A batch of FG abrasive grains containing more than 50% of a certain abrasive content fraction and having a grain size distribution corresponding to the following procedure:

1. The average particle size of the abrasive grains is 0.05 mm.
2. The average grain size distribution is 0.05 μm to 0.5 mm.
3. The abrasive grains are of the type used in conventional grinding processes.
4. The abrasive grains are wet or dry.

TABLE 1 — continued

<table>
<thead>
<tr>
<th>Product</th>
<th>Supplier</th>
<th>Grit Size</th>
<th>Abrasive Content</th>
<th>Abrasive Form</th>
<th>Abrasive Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>120</td>
<td>150</td>
<td>180</td>
<td>210</td>
<td>240</td>
</tr>
<tr>
<td>150</td>
<td>200</td>
<td>250</td>
<td>300</td>
<td>350</td>
<td>400</td>
</tr>
</tbody>
</table>

A batch of FG abrasive grains containing less than 50% of a certain abrasive content fraction and having a grain size distribution corresponding to the following procedure:

1. The average particle size of the abrasive grains is 0.05 mm.
2. The average grain size distribution is 0.05 μm to 0.5 mm.
3. The abrasive grains are of the type used in conventional grinding processes.
4. The abrasive grains are wet or dry.

Example 4

A batch of FG abrasive grains containing more than 50% of a certain abrasive content fraction and having a grain size distribution corresponding to the following procedure:

1. The average particle size of the abrasive grains is 0.05 mm.
2. The average grain size distribution is 0.05 μm to 0.5 mm.
3. The abrasive grains are of the type used in conventional grinding processes.
4. The abrasive grains are wet or dry.

TABLE 1 — continued

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<thead>
<tr>
<th>Product</th>
<th>Supplier</th>
<th>Grit Size</th>
<th>Abrasive Content</th>
<th>Abrasive Form</th>
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3. The abrasive grains are of the type used in conventional grinding processes.
4. The abrasive grains are wet or dry.

Example 5

A batch of FG abrasive grains containing more than 50% of a certain abrasive content fraction and having a grain size distribution corresponding to the following procedure:

1. The average particle size of the abrasive grains is 0.05 mm.
2. The average grain size distribution is 0.05 μm to 0.5 mm.
3. The abrasive grains are of the type used in conventional grinding processes.
4. The abrasive grains are wet or dry.

TABLE 1 — continued

<table>
<thead>
<tr>
<th>Product</th>
<th>Supplier</th>
<th>Grit Size</th>
<th>Abrasive Content</th>
<th>Abrasive Form</th>
<th>Abrasive Grade</th>
</tr>
</thead>
<tbody>
<tr>
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