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(54) Title: PROCESS FOR THE PREPARATION OF ALUMINIUM OXIDE CERAMICS HAVING INCREASED ABRASION RESISTANCE (57) Abstract The invention relates to a process for the preparation of alumina ceramics having an increased abrasion resistance which comprises adding before forming to 96-99.5 % by weight of aluminium oxide in an amount of 0.1-4 % by weight an eutectic sintering additive prepared from 38.5-71.5 % by weight of calcium fluoride and 28.5-61.5 % by weight of magnesium fluoride by thermal treatment either per se and/or in a form applied onto a carrier and, if necessary, 0.1-1.0 % by weight of a particle size growth inhibitor and 0.2-1.5 % by weight of a further useful additive, grinding the components, forming the mixture in a manner known per se, and sintering the shaped articles at a temperature above 1300° C, preferably at 1450-1600° C.		

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PROCESS FOR THE PREPARATION OF ALUMINIUM OXIDE CERAMICS
HAVING INCREASED ABRASION RESISTANCE

Technical field

This invention relates to a process for the preparation of aluminium oxide ceramics having increased abrasion resistance. The said ceramics are particularly useful in the production of cylinder liners of drilling slime and slurry pumps.

Background art

It is known that ceramics prepared from aluminium oxide powder by sintering are highly resistant to friction and abrasion in dry or wet medium. For this reason the said ceramics are highly suitable for the preparation of structural elements with high lifetime (e.g. sliding bearing of slime pump, sand blaster, metal pulverizator, etc.). Abrasion resistance is however dependent on numerous further factors, e.g. on the following conditions:

- chemically pure basic material being particularly alkali-free and comprising only useful additives;
- mode of formation;
- sintering conditions of the shaped article (time, temperature, etc.);
- fine crystalline structure of the shaped article;
- solid interim connection of the crystals;
- maximal body density;
- exclusion of material continuity deficiencies;
- unstressedness;
- smooth working surface.

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In practice the above conditions can be provided only with several technological difficulties which are discussed in details in prior art.

It is generally known that in the manufacture of aluminium oxide based ceramics suitable for various purposes (e.g. electrotechnical, thermal technical, optical, mechanical and chemical fields of application) several basic materials are used (aluminas and raw materials of high purity) to which additives decreasing the sintering temperature are admixed.

Thus transparent and abrasion resistant ceramics may be prepared by the process disclosed in UK patent No. 1,264,914 by introducing 1 % by weight of $MgO + CeO_2$ and carrying out sintering at a temperature of about $1700^\circ C$ in hydrogen or in vacuo. According to the most well-known method pure magnesium oxide is incorporated (Hungarian patent No. 184,381 and UK patent No. 1,256,966); however, the addition of magnesium oxide per se only results in the inhibition of particle-size growth at a temperature of above $1700^\circ C$ while the sintering temperature can not be decreased below the said value. Similar results are obtained by admixing yttrium oxide (Y_2O_3) per se. /Amer. Cer. Bull. 61, /2/, 221 (1982)/ Improved results can be achieved by using the said two metal oxides together (US patent No. 3,377,176 and UK patent No. 1,072,536); however, the sintering temperature can not be decreased under $1700^\circ C$ by this method either.

Similarly, sintering carried out at a high temperature of

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about 1750 °C is reported in a further article /Ceram. Metal. Inst. Vol. 20, Bukarest (1979)/ by adding to aluminium oxide in an amount of 0.1-0.3 % by weight magnesium oxide, titanium oxide, nickel oxide and also simultaneously manganous oxide and titanium oxide, however, only the last-mentioned binary system could achieve a more significant temperature decrease but at the same time the product became harder and the size of the crystals increased considerably.

Complex systems proved to be more favourable (e.g. addition of zirconium oxide stabilized by yttrium oxide) /J. Am. Ceram. Soc. 67, /3/, (1984), 164/ or the binary system having the formula $13\text{BeO} \cdot 7\text{Y}_2\text{O}_3$ disclosed in Hungarian patent No. 163,704. The preparation of the said systems is however complicated and circumstantial and the sintering temperature can be decreased only slightly below 1700 °C. It is evident that sintering can be accomplished at lower temperature by using silicates, but - in an analogous manner to the introduction of many extraneous metal oxides - the properties of alumina ceramics are shifted towards the characteristics of the additive and the product becomes devoid of the outstanding parameters being characteristic of pure aluminium oxide ceramics.

Thus e.g. guillotines of high quality can be manufactured from aluminium oxide by introducing 30 % by weight of titanium carbide /Amer. Ceram. Bull. 62, /12/, 1384 (1983)/ and carrying out hot isostatic pressing. A further process is disclosed in US patent No. 4,357,427 but the

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said method requires the use of an isostatic press. According to a further method a press operating in three dimensions and a special so-called "reactive" aluminium oxide (Reinolds RC-HP) are used simultaneously and cutting tools are prepared by sintering twice at a temperature of about 1510 °C /Amer. Ceram. Bull. 61, /12/, 1311 (1982)/.

Summarized it can be stated that according to prior art methods high quality aluminium oxide ceramics can only be prepared by sintering in the presence of special additives at high temperature and/or by using expensive starting materials and costly equipments.

Disclosure of the invention

It is the object of the present invention to provide a simple, readily feasible and unexpensive process for the preparation of aluminium oxide ceramics having increased abrasion resistance.

It has been found that the said object can be achieved by adding to 96-99.5 % by weight of aluminium oxide in an amount of 0.1-4 % by weight an eutectic sintering additive prepared from 38.5-71.5 % by weight of calcium fluoride and 28.5-61.5 % by weight of magnesium fluoride by thermal treatment and, if necessary, 0.1-1.0 % by weight of a particle-size growth inhibitor and 0.2-1.5 % by weight of a further useful additive; grinding the components; forming the mixture in a manner known per se; and sintering the shaped articles at a temperature above

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1300 °C, preferably at 1450-1600 °C.

The present invention is based on the recognition that eutectic mixtures of calcium fluoride (mp.: 1410 °C) formed with magnesium fluoride (mp.: 1252 °C) of various compositions - used either per se or in the presence of other additives - continuously promote from a temperature of 980-1150 °C the recrystallization of the crystalline particles of aluminium oxide, which becomes definite in temperature-range of 1450-1600 °C.

The main characteristic data of eutectics of calcium fluoride formed with magnesium fluoride of various compositions are summarized in table 1.

Table 1: CaF₂-MgF₂ eutectic system

Approximate formula	CaF ₂ .2MgF ₂	CaF ₂ .MgF ₂	2CaF ₂ .MgF ₂
Mole %	33.3 + 66.6	50 + 50	66.6 + 33.3
% by weight	38.5 + 61.5	55.6 + 44.4	71.5 + 28.5
mp. (°C)	1070	980	1150

The effect of the eutectic sintering additive of the present invention can be explained in a simplified manner as follows: the said sintering additive reacts with aluminium oxide in the melt phase and dissolves in the boundary surface of the aluminium oxide crystals under thermal effect. The thus activated aluminium oxide crystals - which closely contact - easily dissolve in each other under further thermal effect, whereby the crystal-particles grow, the inter-crystals pores get closed and

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consequently the system continuously sinters.

According to the present invention the process of sintering - contrary to the so-called solid-phase reaction of metal oxides having high melting point - takes place gradually and continuously from 980 °C to about 1600 °C. The fluoride system having the composition according to the present invention participates at the reaction not at once but as a function of the changes of state depending on the rising temperature. Thus sintering begins already at low temperature (small thermal expansion), takes place continuously and is finished at relatively low upper temperature. In addition to the main process other reactions take place as well; e.g. under the effect of the rising temperature the split hydrated part of magnesium fluoride is converted into magnesium oxide, about 10 mole% thereof is dissolved in magnesium fluoride and at the same time fluorine leaves the system. From the point of view of sintering both mechanisms are useful, because at an eventual sintering at higher temperature or during the subsequent use of the shaped article (e.g. in plasma technics) magnesium oxide inhibits the formation of coarse particles. The minimal amount of nascent fluorine promotes the formation of stable alpha-corundum already at a temperature below 1000 °C in a manner being characteristic of halogens.

According to the process of the present invention the major amount of the eutectic sintering additive is incorporated into the aluminium oxide ceramics partly because the boiling point of the components is highly above

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2250 °C and particularly since it forms a solid solution with aluminium oxide. A minor part of the said additive sublimates from the mixture, particularly from the boundary surface of the shaped article.

Taking into consideration that the eutectic sintering additive strongly increases the crystal size as a function of the temperature, in order to decrease this effect it is expedient but not necessary to use a particle-size growth inhibitor. From the said additives inhibiting the growth of the crystals magnesium spinel acting at lower temperature (MgAl_2O_4), magnesium oxide (MgO) and nickel oxide (NiO) proved to be the most active, namely in an amount of 0.1-1.0 % by weight.

The calcium-magnesium-fluoride sintering additive according to the present invention significantly increases the abrasion resistance of aluminium oxide ceramics (this can be simply determined either by grinding corundum powder with alumina grinding balls for 100 hours and weighing the said grinding balls before and after the test or by comparing the operating hours of various slime pumps).

The abrasion resistance and to a considerable extent also the thermal shock resistance (i.e. the lifetime) of aluminium oxide ceramics can be further increased by introducing additives which react with aluminium oxide either difficultly or only at higher temperature. The said additives are generally used in an amount of 0.2-1.5 % by weight, depending on the type thereof.

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Thus e.g. the following additives can be used: chrome oxide (Cr_2O_3) which forms a solid solution with aluminium oxide and further increases the abrasion resistance and improves the thermal shock resistance thereof; cerium oxide (CeO_2) being highly abrasion resistant per se (grinding material) and being incorporated into the crystal lattice of aluminium oxide also increases abrasion resistance - particularly in wet medium - and also shock resistance; zirconium silicate (ZrSiO_4) and calcium feldspar (Anortite, $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, mp.: 1555°C) which enter readily into reaction with fluorides and as such promote shrinkage of aluminium oxide during sintering under forming a glassy phase and enable the preparation of shaped articles having a greater wall-thickness without the risk of cracking and facilitate the subsequent working of the said shaped article as well; zirconium oxide (ZrO_2) which - e.g. in a form stabilized with ceric oxide - increases thermal shock resistance of aluminium oxide ceramics; alundum (Al_2O_3) used e.g. in an amount of 20 % by weight which decreases the rate of shrinkage and by embedding coarse crystal particles enables the preparation of ceramics having a specially big size and a rough surface (in the latter case alundum is actually not an additive but one part of the aluminium oxide used is applied in the form of alundum). It is evident that a mixture of the said additives can be used as well.

The additive magnesium spinel (MgAl_2O_4) used as particle-size growth inhibitor and the zirconium silicate optionally used as additive can be prepared by known methods by

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firing a stoichiometrical amount of a metal salt or metal oxide thereof and finely grinding the fired product.

The optional additives may modify the properties of aluminium oxide ceramics. Thus the dry or wet abrasion resistance can be increased or the resistance of abrasion combined with thermal effects can be raised etc.

The eutectic sintering additives used according to the process of the present invention can be introduced either per se or can be applied onto a carrier. It is preferred to use aluminium oxide as carrier. One may preferably apply the eutectic sintering additive onto the carrier by grinding calcium fluoride and magnesium fluoride with the aluminium oxide carrier and firing the mixture at a temperature above 940 °C.

The use of aluminium oxide as carrier achieves two objects: on the one hand the eutectic additive gets caked to a smaller extent during the preparation thereof, while on the other hand required quantity thereof can be weighed in more precisely and accurately in this "diluted" form.

The eutectic sintering additive used according to the process of the present invention can be particularly preferably prepared by using 55.6 % by weight of calcium fluoride and 44.4 % by weight of magnesium fluoride. It is preferred to add 0.8 % by weight of the eutectic sintering additive to the aluminium oxide starting material.

The process of the present invention can be carried out

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in conventional and known equipment generally used in the manufacture of sintered aluminium oxide ceramics and no special apparatus is required. All the starting materials used are readily available. The finely ground powder used can be worked up by any known forming procedure and the sintering process can be accomplished in any generally used gas or electrically fired chamber- or tunnel-furnace in oxidizing atmosphere.

Industrial applicability

The process of the present invention can be accomplished at a lower temperature than the known methods while at the same time the products thus obtained show increased abrasion resistance and are superior to ceramics of similar destination obtained by known methods.

Modes of carrying out the invention

Further details of the present invention are to be found in the following Examples without limiting the scope of protection to the said Examples.

Example 1

556 g of technical grade calcium fluoride and 444 g of technical grade magnesium fluoride are weighed in a grinding mill comprising alumina balls. The powder mixture is preferably subjected to dry homogenizing grinding; the average particle size amounts to 1-2 μ m (90 %). The ground powder is compacted in a manner known per se (e.g. by granulating and pressing), whereupon the shaped articles thus obtained are subjected to thermal treatment

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in a heating sheath (on the air) in an oxidizing atmosphere, at first at 1150-1170 °C for an hour and thereafter at 940-970 °C for 2 hours.

The cooled product - at least 90 % thereof being characterized by the formula $\text{CaF}_2 \cdot \text{MgF}_2$ - is powdered and ground again; about 80-90 % of the powder has a particle size below 10 μm . The eutectic sintering additive No. 1 thus obtained is used as follows:

988.5 g of ceramical alumina (type "G", total alkali content below 0.1 % by weight; manufacturer: Almásfüzitői Tímföldgyár) are weighed in whereupon 8 g of sintering additive No. 1 and 3.5 g of magnesium spinel (1 g MgO + 2.5 g of Al_2O_3) are added. The powder mixture is ground - preferably in a mill comprising at least 99 % by weight alumina balls - in the presence of 1 part by weight of elaine surfactant so that 95 % of the powder has an average particle size below 5 μm and 50% is below 1 μm .

From the powder mixture balls are formed by die-cast in a manner known per se by melting with 14 % by weight of paraffine, embedding into alumina, removing the paraffine and sintering. The said procedure is carried out at a heating rate of 120-150 °C/hour at 1300 °C for 4 hours, then increasing the temperature to 1550 °C, heating at this temperature for a further period of 8 hours in an oxidizing (air) atmosphere.

The nominal aluminium oxide content of the shaped articles

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thus prepared amounts to 99.1 % by weight (calculated on the basis of the weighing-in), the magnesium oxide content is 0.1 % by weight (in Spinel form) at a maximum $\text{CaF}_2 \cdot \text{MgF}_2$ content of 0.8 % by weight.

Apparent density: 3.90 g/cm^3 ; water absorption: 0.

Fuch sine test negative, surface roughness $R_a = 3 \mu\text{m}$; /C.L.A./ average particle size (according to electron microscopical exposure) $5.4 \mu\text{m}$; rate of linear shrinkage: 15.5 %.

Field of application: preparation of valves, rolling bearing, bearing balls etc.

Example 2

Into a mill containing alumina balls 986.5 g of aluminium oxide of high purity /calcinated at 1500°C , aluminium oxide content 99.99 % by weight, manufacturer: "Diakor" SZIKTI Budapest/, 8 g of sintering additive No. 1, 3.5 g of magnesium spinel and 2 g of technical or analytical grade chrome oxide are weighed in. The powder mixture is ground in the presence of an equal amount of distilled water to an average particle size of 95 % below $5 \mu\text{m}$ including 50 % below $2 \mu\text{m}$. The grinding balls are removed by filtration in a known manner and the ground mixture is casted into cylindrical plaster of Paris (gypsum) moulds. The mouldings are removed, dried and subjected to thermal treatment at 1300°C for 4 hours and at 1550°C for 8 hours heating rate = $80\text{-}100^\circ\text{C/hour}$.

The nominal aluminium oxide content of the shaped articles

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thus prepared by slip-casting forming (so-called "ruby" ceramic) amounts to 98.9 % by weight; magnesium oxide content: 0.1 % by weight; chrome oxide content: 0.2 % by weight; at a maximum CaF_2MgF_2 content of 0.8 % by weight.

Apparent density: 3.86 g/cm^3 ; water absorption: 0.1 % by weight; surface roughness $R_d = 2.2/\mu \text{ /C.L.A./}$; average particle size $3.8/\mu\text{m}$; linear shrinkage: 16 %.

Field of application: cylinder liner of drilling slime and slurry pump, etc.

Example 3

Into a ball mill 385 g of technical or analytical grade calcium fluoride and 615 g of technical or analytical grade magnesium fluoride are weighed in, whereupon the powder mixture is subjected to homogenizing grinding to yield an average particle size of $1-2/\mu\text{m}$ (90 %). After compacting the shaped articles are ignited by thermal treatment at first at $1180-1200^\circ\text{C}$ for an hour and subsequently at $960-1000^\circ\text{C}$ for 2 hours.

The cooled product - at least 95 % thereof being characterized by the formula $\text{CaF}_2.2\text{MgF}_2$ - is pulverized and finely ground to yield a particle size below $10/\mu\text{m}$ (80-90 %). The product thus obtained as eutectic sintering additive No. 2 is used as follows.

Into a grinding mill comprising alumina balls 991.5 g of

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aluminium oxide of high purity calcinated at 1500 °C are weighed in, whereupon 2 g of sintering additive No. 2, 3.5 g of magnesium spinel and 2 g of analytical grade ceric oxide are added. The powder mixture is ground preferably in dry medium to an average particle size of 5,um (95 %) including 50 % of a particle size below 1,um. The powder is formed in a known manner by isostatic pressing under a specific pressure of at least 0.2 MPa, whereupon it is sintered to a compact structure by heating in an oxidizing atmosphere at 1450 °C for 4 hours and subsequently at 1600 °C for 8 hours; rate of heating: 100-120 °C/hour.

The nominal aluminium oxide content of the shaped articles thus obtained by "three-dimension" pressing amounts to 99.4 % by weight, the magnesium oxide content is 0.1 % by weight, the ceric oxide content amounts to 0.2 % by weight, at a maximal $\text{CaF}_2 \cdot 2\text{MgF}_2$ content of 0.2 % by weight.

Apparent density 3.92 g/cm³; water adsorption: 0; Fuchsin test negative; surface roughness: $R_a = 1-2, \mu\text{m} / \text{C.L.A.} /$; average particle size: 3.8,um; linear shrinkage: 16.4 %.

Field of application: pistons for machines in food and chemical industry, core-pipe for production well in oil industry, etc.

Example 4

715 g of technical grade calcium fluoride, 285 g of technical grade magnesium fluoride and 1000 g of aluminium

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oxide calcinated at a temperature not exceeding 1300 °C /having a total alkali content below 0.1 %, specific surface more than 5 m²/g (BET)/ are weighed in. The powder mixture is ground at a rate that 90 % of the particles have an average particle size of 5 µm including 50 % below 2 µm. The powder is compacted into shaped articles, which are subjected to thermal treatment at first at 1200-1250 °C for an hour and thereafter at 1050-110 °C for 3 hours. The caked powder mixture thus obtained is finely ground at a rate that 80-90 % of the particles should be below 10 µm.

The eutectic sintering additive No. 3 thus obtained can be characterized by the formula $2\text{CaF}_2 \cdot \text{MgF}_2$ and is applied onto an aluminium oxide carrier at a "dilution" rate of 1:1. The product is used as follows:

Into a ball mill 720 g of calcinated technical grade "TO" type aluminium oxide (manufacturer: Ajkai Tinföldgyár) are weighed in, whereupon 80 g of sintering additive No. 3 and 200 g of alundum washed iron-free with hydro-chloric acid (90 % of particles have a diameter of 0.05-0.1 mm; manufacturer: Mosonnagytörvéri Tinföldgyár) are added.

The powder mixture is subjected to homogenizing stirring whereupon it is admixed with 3 % by weight of polyisobutylene pressing additive (described in Hungarian patent No. 165,357), granulated and formed to shaped articles under a pressure of at least 0.1 MPa.

Sintering is carried out in air at a heating rate of

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130-150 °C/hour, at 1300 °C for 2 hours, at 1550 °C for 8 hours.

The nominal total aluminium oxide content of the ceramics thus obtained amounts to 96 % by weight at a maximum $2\text{CaF}_2 \cdot \text{MgF}_2$ content of 4 % by weight. Apparent density: 3.80 g/cm³; water absorption: 0.5 % by weight; surface: rough. Average particle size: about 60-85 μm . Linear shrinkage: 12 %.

Field of application: cutting wheel of high abrasion resistance, polishing file etc.

Example 5

967 g of alumina (type "G") are weighed in a mill comprising alumina balls, whereupon 20 g of sintering additive No. 2, 10 g of technical grade zirconium silicate and 3 g of technical grade nickel oxide are added.

The powder mixture is subjected to grinding in aqueous medium in the presence of an antifoam agent at a rate that 90 % of the articles should have an average particle size below 5 μm and 50 % thereof being 1-2 μm . From the mass thus obtained thick-wall pipes are formed by centrifuging slip-casting or compact bars are casted.

The product is dried and sintered under oxidizing conditions. The heating rate of 80-100 °C/hour, at 1200 °C for an hour, at 1300 °C for 4 hours and finally at 1550 °C for 6 hours.

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The nominal aluminium oxide content of the shaped articles thus obtained amounts to 96.7 % by weight, the zirconium silicate content is 1 % by weight, the nickel oxide content amounts to 0.3 % by weight, at a maximal $\text{CaF}_2 \cdot 2\text{MgF}_2$ content of 2 % by weight.

Apparent density: 3.88 g/cm^3 ; water absorption: 0; Fuch-sine test: negative; surface roughness $R_a = 2.7/\mu\text{m}$; average particle size: $5/\mu\text{m}$.

Field of application: cylinder liners of pumps used in chemical industry or pistons (in bar form).

Example 6

781 g of alumina post-calcinated at 1500°C , type "G" (Hungarian patent No. 179,981) are weighed in a grinding mill, whereupon 200 g of alkali-free gamma-aluminium oxide calcinated at $900-1100^\circ\text{C}$, 5 g of sintering additive No.2, 10 g of technical grade zirconium oxide, 3 g of technical grade ceric oxide (for the stabilization of the previous component) and 1 g of magnesium oxide are added.

The powder mixture is ground to the particle size disclosed above and extruded in a known manner for bored tubes by using a polyvinyl alcohol binder and plasticizer. The tubes are dried and sintered - preferably in suspended form - in an oxidizing atmosphere, at a heating rate of $100-120^\circ\text{C}$, at 1350°C for 3 hours, at 1400°C for 5 hours and finally at 1550°C for 8 hours.

The nominal aluminium oxide content of the shaped articles

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thus prepared amounts to 98.1 % by weight, the zirconium oxide content is 1 % by weight, the ceric oxide content amounts to 0.3 % by weight, the magnesium oxide content is 0.1 % by weight, at a maximum $\text{CaF}_2 \cdot 2\text{MgF}_2$ content of 0.5 % by weight.

Linear shrinkage: 17 %.

Apparent density: 3.80 g/cm^3 ; water adsorption: 0; Fuch-sine test: negative; surface roughness: $R_a = 3 \mu\text{m}$; /C.L.A./ average particle size: $5.5 \mu\text{m}$.

Field of application: in the first place for pyrotechnical purposes, e.g. holding capillary tube of thermoelment sleeve pipe of pyrometers, conducting pipe for acids, alkali and slurry etc.

Example 7

Into a ball mill 963.5 g of industrial grade alumina post-calculated at 1650°C (type "TO") are weighed in, whereupon 16 g of sintering additive No. 3, 2 g of chrome oxide, 15 g of industrial grade calcium feldspar / $\text{CaO} = 20.1\%$ by weight; $\text{Al}_2\text{O}_3 = 36.6\%$ by weight; $\text{SiO}_2 = 43.3\%$ by weight/ and 3.5 g of magnesium spinel are added. The powder mixture is ground to die casting or in case of more simple shaped articles by dry pressing. The shaped articles are sintered in an oxidizing atmosphere at a heating rate of $120\text{-}130^\circ\text{C/hour}$, at first at 1300°C for 4 hours, and then at 1560°C for 8 hours.

The nominal aluminium oxide content of the sintered articles

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amounts to 97.4 % by weight, the chrome oxide content is 0.2 % by weight, the calcium feldspar content amounts to 1.5 % by weight (in the form of glass phase), the magnesium oxide content amounts to 0.1 % by weight, at a maximum $2\text{CaF}_2 \cdot \text{MgF}_2$ content of 0.8 % by weight.

Apparent density: 3.87 g/cm^3 ; water adsorption: 0.8 % by weight; surface roughness: $R_a = 3.3 \mu\text{m}$ /C.L.A./; average particle size: $6.4 \mu\text{m}$; linear shrinkage: 15.5 %.

Field of application: structural elements subjected to simultaneous thermal shocks and mechanical load, e.g. nozzles of metal sprayers, holder plates of furnaces, etc.

Example 8

Alumina hydrate (type K-33; made free of alkaline; manufacturer: Alnásfüzitői Tinföldgyár) calcinated at 1500°C for 3 hours, whereupon 973 g of the calcinated product are weighed in a grinding mill, 1 g of sintering additive No. 1, 10 g of chrome oxide, 6 g of zirconium silicate and 10 g of magnesium spinel are added.

The powder mixture is ground preferably in aqueous medium in an analogous manner to the particle size described in the previous Examples, whereupon it is formed to thick-wall tubes, rings and discs by slip-casting.

The shaped articles are dried and sintered in an oxidizing atmosphere, at a heating rate of $120\text{--}130^\circ\text{C}/\text{hour}$, at first at 1500°C for 6 hours and then at 1600°C for 8 hours.

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The shaped articles are allowed to cool in the furnace depending on the size, wall-thickness and weight of the shaped articles.

The nominal aluminium oxide content of the sintered aluminium oxide ceramics amounts to 98 % by weight, the chrome oxide content is 1 % by weight, the zirconium silicate content is 0.6 % by weight, the magnesium oxide content amounts to 0.3 % by weight, at a maximum $\text{CaF}_2 \cdot \text{MgF}_2$ content of 0.1 % by weight.

Apparent density: 3.87 g/cm^3 ; water adsorption: 0; Fuch-sine test: negative; surface roughness: $R_a = 2.6 \mu\text{m}$; (C.L.A.) average particle size $4.7 \mu\text{m}$; linear shrinkage: 16.4 %.

Field of application: after subsequent processing and equipped with a metallic socket as sliding bearing, filament guide in wire industry, drawing spindle, etc.

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What we claim is:

1. Process for the preparation of alumina ceramics having an increased abrasion resistance which comprises adding before forming to 96-99.5 % by weight of aluminium oxide in an amount of 0.1-4 % by weight an eutectic sintering additive prepared from 38.5-71.5 % by weight of calcium fluoride and 28.5-61.5 % by weight of magnesium fluoride by thermal treatment either per se and/or in a form applied onto a carrier and, if necessary, 0.1-1.0 % by weight of a particle size growth inhibitor and 0.2-1.5 % by weight of a further useful additive, grinding the components, forming the mixture in a manner known per se, and sintering the shaped articles at a temperature above 1300 °C, preferably at 1450-1600 °C.
2. Process according to claim 1, which comprises using as eutectic sintering additive an eutectic prepared by heating 55.6 % by weight of calcium fluoride and 44.4 % by weight of magnesium fluoride at a temperature not lower than 940 °C.
3. Process according to claim 1 or 2, which comprises using the eutectic sintering additive in a form applied onto an aluminium oxide carrier.
4. Process according to any of claims 1 to 3, which comprises using the eutectic sintering additive in an amount of 0.1-4 % by weight, preferably 0.8 % by weight.
5. Process according to claim 3, which comprises using

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as carrier aluminium oxide having a specific surface of at least $5 \text{ m}^2/\text{g}$ (BET).

6. Alumina ceramics characterized by that the nominal total aluminium oxide content of the sintered ceramics having a polycrystalline structure amounts to 96-99.5 % by weight, and the chemically bound calcium-magnesium-fluoride content is at least about 0.1 % by weight and not more than about 4 % by weight.

7. Aluminium oxide ceramics according to claim 1 to 6, characterized by that in addition to calcium-magnesium-fluoride the said ceramics may also contain in an amount of 0.1-1.0 % by weight magnesium spinel, magnesium oxide and/or nickel oxide and as further component in an amount of 0.2-1.5 % by weight chrome oxide, ceric oxide, zirconium silicate, zirconium oxide, calcium feldspar and/or in an amount of preferably 20 % by weight alundum or any suitable mixture thereof as further useful additive.

INTERNATIONAL SEARCH REPORT

International Application No PCT/HU87/00009

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) * According to International Patent Classification (IPC) or to both National Classification and IPC Int. Cl⁴ - C 04 B 35/10																				
II. FIELDS SEARCHED Minimum Documentation Searched ⁷ <table border="1" style="width: 100%; border-collapse: collapse; margin-top: 5px;"> <tr> <td style="width: 30%; padding: 5px;">Classification System</td> <td style="padding: 5px;">Classification Symbols</td> </tr> <tr> <td style="padding: 5px;">Int. Cl⁴</td> <td style="padding: 5px;">C 04 B 35/10</td> </tr> </table> Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸ CS - C 04 B 35/10			Classification System	Classification Symbols	Int. Cl ⁴	C 04 B 35/10														
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