

METHOD FOR PARTICLE SURFACE TREATMENT OF A
CERAMIC POWDER AND CERAMIC POWDER PARTICLES
OBTAINED BY SAID METHOD

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Field of the invention

The present invention concerns a method for the particle surface treatment of a ceramic material in powder form and ceramic powder particles obtained by implementation of such a method. The ceramic powder particles obtained by the method according to the invention are
10 intended for the manufacture of shaped products, i.e. parts delivered in their final form and realized by means of sintering methods such as sintering at atmospheric pressure, or hot isostatic pressing, known as HIP.

Background of the invention

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The mechanical and physical properties of materials are closely linked to the electronic structure of the atoms that compose them and to the way in which they are bonded to each other. Materials can therefore be classified in three main categories depending upon the type of bond between the atoms which compose them: metals (metallic bonds), ceramics
20 (covalent or ionic bond) and polymers (hydrogen bond). Since covalent and ionic bonds are stronger energetically than metallic bonds, ceramics are harder, have a higher melting point and higher chemical stability than metals. Moreover, the absence of free electrons means that ceramics have very low electrical and thermal conductivity. For the same reasons, there is
25 some conflict between the hardness of a material (which depends on the strength of the bond between the atoms and their ability not to move under

stress), and its resistance to shocks (which depends on the ability of the material to dissipate energy through the movement of atoms).

Ceramic materials can be defined as inorganic, non-metallic materials requiring high temperatures during manufacture. The firing or
5 sintering of ceramic materials is carried out, however, at temperatures well below their melting point. If ceramics are compared to glass, the two types of material can be obtained from the same raw materials. The difference lies, however, in the fact that, in the case of glass, the raw material is brought to its melting point and, once the liquid state is obtained, the raw
10 material is shaped, for example by blowing or moulding. Conversely, to produce a part made of ceramic material, the first phase is to shape the raw material in powder form, at ambient temperature. Very often, this shaping step is realized by mixing the powder with a liquid or by using all kinds of additives to enhance the homogeneity of the blank of the desired final part,
15 but also to influence the characteristics of said part. Next, the blank is fired at a temperature well below the melting point of the ceramic material. During this firing step, the ceramic powder particles aggregate with each other, which causes the elimination of most of the pores or cavities, and consequently the blank contracts and hardens, while maintaining its initial
20 shape. This firing step is called sintering.

Ceramic materials generally have a crystalline structure, sometimes associated with an amorphous phase. Ceramic materials can be classified according to their application:

1. conventional ceramics, which are intended for food or ornamental
25 use (pottery, tableware, earthenware, porcelain), or for construction (tiles, bricks, roof tiles);
2. so-called industrial or technical ceramics, of which the following can be mentioned:

- electronic or functional ceramics used in applications utilising low currents (dielectric (insulating) ceramics, piezoelectric ceramics, conductive ceramics, magnetic ceramics, ceramic superconductors);
- 5 • electrotechnical ceramics intended for applications utilising high electric power;
- refractory ceramics for thermal applications;
- ceramics for mechanical applications, such as structural ceramics and ceramics intended for machining operations (abrasive ceramics for polishing operations and carbide inserts for cutting tools);
- 10 • ceramics used for making catalyst supports in the chemical industry and catalytic converters particularly in the automobile industry;
- ceramics for optical applications (transparency, light emission):
- ceramics intended to be used for nuclear fuel containment.

The present invention more particularly concerns technical ceramics.

15 Ceramic products can also be classified according to their chemical composition. The category of monolithic ceramic materials includes:

1. oxides, namely
 - siliceous products made from silica SiO_2 ;
 - aluminous products containing from 30 to 100% of alumina Al_2O_3
 - 20 • basic products made from magnesia MgO ;
 - special products such as zirconia ZrO_2 or yttrium stabilized tetragonal zirconia polycrystals (Y-TZP).
2. non-oxides, namely carbides, nitrides and borides.

There also exist composite ceramic materials, such as ceramic matrix
25 materials reinforced with a ceramic, for example with zirconia ZrO_2 , or ceramic matrix materials reinforced with a metal.

The present invention concerns both oxides and non-oxides.

Ion implantation processes consist of the surface bombardment of the treated object, for example by means of a source of singly or multiply charged ions of the electron cyclotron resonance type. This type of device is
5 also known as an ECR ion source.

An ECR ion source makes use of electron cyclotron resonance to create a plasma. A volume of low pressure gas is ionised by means of microwaves injected at a frequency corresponding to the electronic cyclotron resonance defined by a magnetic field applied to an area located
10 inside the volume of gas to be ionised. The microwaves heat the free electrons present in the volume of gas to be ionised. Under the effect of thermal agitation, these free electrons will collide with the atoms or molecules of gas and cause them to ionise. The ions produced correspond to the type of gas used. This gas may be pure or compound. It may also be
15 a vapour obtained from a solid or liquid material. The ECR ion source is capable of producing singly charged ions, i.e. ions whose degree of ionisation is equal to 1, or multiply charged ions, i.e. ions whose degree of ionisation is higher than 1.

An ECR type ion source is schematically illustrated in Figure 1
20 annexed to the present Patent Application. Designated as a whole by the general reference numeral 1, an ECR ion source includes an injection stage 2 into which a volume 4 of gas to be ionised is introduced and a hyperfrequency wave 6, a magnetic confinement stage 8 in which a plasma
10 is created, and an extraction stage 12, which allows the ions to be
25 extracted and accelerated from plasma 10 by means of an anode 12a and a cathode 12b between which a high voltage is applied. An ion beam 14 produced at the output of ECR ion source 1 strikes a surface 16 of a part to be treated 18 and penetrates more or less deeply the volume of part to be treated 18.

Ion implantation by bombarding the surface of a treated object has many effects including modifying the microstructure of the material from which the treated object is made, improving corrosion resistance, improving tribological properties and, more generally, improving mechanical
5 properties. Several studies have thus evidenced the increase in hardness of copper and bronze by nitrogen ion implantation. It has also been demonstrated that nitrogen or neon implantation in copper increases its fatigue resistance. Likewise, studies have shown that nitrogen implantation, even at a low dose (1.10^{15} and 2.10^{15} ions.cm⁻²) is sufficient to significantly
10 modify the shear modulus of copper.

It is thus understood that ion implantation by bombarding the surface of a treated object offers great advantages from a scientific as well as a technical and industrial viewpoint.

Nevertheless, studies carried out to date have only concerned the
15 treatment of solid objects. Yet, these solid objects are necessarily limited by the shapes and geometry that they can be given by means of conventional machining techniques (drilling, milling, boring, etc.).

There therefore existed a need in the state of the art for objects whose mechanical properties could be significantly improved while imposing
20 almost no limit on the shape that such objects could take.

Summary of the invention

It is an object of the present invention to meet the aforementioned need, in addition to others, by proposing a method for surface treatment of a
25 ceramic material making it possible to realize objects whose geometric shapes are practically free of any constraint, while offering modified and improved physical and chemical properties.

To this end, the present invention therefore concerns a method for surface treatment of a ceramic material, this method comprising the step

consisting in providing a powder formed of a plurality of particles of a ceramic material, and in directing towards a surface of these particles a beam of singly or multiply charged ions produced by a source of singly or multiply charged ions, the particles having a generally spherical shape.

5 According to preferred embodiments of the invention:

- the source of singly or multiply charged ions is of the electronic cyclotron resonance (ECR) type;

- the ceramic powder particles are agitated throughout the duration of the ion implantation process;

10 - the grain size of the ceramic powder particles used is such that substantially 50% of all said particles have a dimension smaller than 2 micrometres, the dimension of the ceramic powder particles used not exceeding 60 micrometres;

15 - the material to be ionised is chosen from among carbon, nitrogen and boron;

- the singly or multiply charged ions are accelerated at a voltage comprised between 15,000 and 35,000 volts;

- the implanted ion dose is comprised between 1.10^{14} and 5.10^{17} ions.cm⁻², preferably between 1.10^{16} and 1.10^{17} ions.cm⁻²

20 - the maximum ion implantation depth is from 150 to 250 nm;

- the ceramic material treated according to the ion implantation process of the present invention is a carbide, in particular a titanium carbide TiC or a silicon carbide SiC;

25 - the ceramic material of the carbide type is bombarded with nitrogen ions N to form a carbonitride, particularly titanium carbonitride TiCN or silicon carbonitride SiCN;

- the ceramic material treated according to the ion implantation process of the invention is a nitride, in particular a silicon nitride Si₃N₄;

- the ceramic material of the nitride type is bombarded with an ion dose comprised between $1 \cdot 10^{16} \text{ cm}^{-2}$ and $1 \cdot 10^{17} \text{ cm}^{-2}$.

- the ceramic material treated according to the ion implantation process of the invention is an oxide, particularly zirconia ZrO_2 or alumina
5 Al_2O_3 ;

- the ceramic material of the oxide type is bombarded with nitrogen ions to form an oxynitride, particularly zirconium oxynitrate hydrate $\text{ZrO}(\text{NO}_3)_2$, or zirconium nitride ZrN if the ion bombardment is continued for a sufficiently long time, or aluminium oxynitride AlO_xN_y ;

10 - the oxide ceramic material is bombarded with carbon ions to form a carbonitride, particularly zirconia carbide ZrO_2C , or zirconium carbide ZrC ;

- the oxide ceramic material is bombarded with boron ions to form an oxyboride, particularly zirconia boride ZrO_2B , or zirconium diboride ZrB_2 if the ion bombardment is continued for a sufficiently long time,

15 The present invention also concerns a ceramic powder particle with a ceramic surface and a ceramic core, and more particularly with a surface that is a carbide, a nitride or a boride of the ceramic material from which the ceramic powder particles are made.

As a result of these features, the present invention provides a method
20 for treating a ceramic material in powder form, wherein the particles forming this powder maintain their initial ceramic structure at their core, whereas, at the surface and to a certain depth, the singly or multiply charged ions with which the ceramic powder particles are bombarded modify the surface properties of the ceramic powder particles, improving, in particular, the
25 compactability and sinterability of said ceramic powder particles, which, at a later stage, improves the machining properties and the tribological properties of parts made with these ceramic powder particles.

It will be noted that, after ion implantation treatment, the ceramic powder particles are ready to be used in ceramic powder sintering

processes, such as sintering at atmospheric pressure or hot isostatic pressing known as HIP. Further, because the surface of the ceramic powder particles is transformed into a boride, carbide or nitride of the ceramic material that forms the particles, the initial physical and mechanical
5 properties of these powders, such as rheology, fluidity or wettability, are modified. Consequently, the properties of surface coatings and of solid parts made with such powders, such as hardness, tribology or aesthetic appearance, are improved.

Preferably, the particles forming the ceramic powder are agitated
10 throughout the duration of the ion implantation treatment, so that these particles are exposed to the ions of the implantation beam homogeneously over their entire surface.

Brief description of the drawings

15 Other features and advantages of the present invention will appear more clearly from the following detailed description of an example implementation of the method according to the invention, this example being given purely by way of non-limiting illustration with reference to the annexed drawing, in which:

20 - Figure 1, cited above, is a schematic representation of an ECR ion source;

- Figure 2 is a cross-sectional view of an alumina particle Al_2O_3 whose radius is around 1 micrometre, and which has been bombarded with a nitrogen ion beam N^+ , and

25 - Figure 3 is a schematic representation of an ECR ion source used within the scope of the present invention.

Detailed description of one embodiment of the invention

The present invention proceeds from the general inventive idea which consists subjecting ceramic powder particles to a process of ion implantation treatment in the surface of said particles. When bombarding the particles of a ceramic powder with highly accelerated, singly or multiply charged ions at electrical voltages on the order of 15,000 to 35,000 volts, it becomes clear that these ions combine with the atoms of the ceramic material to form a new type of ceramic. To a certain depth from the surface of the ceramic powder particles, the latter are transformed, for example, into a carbide or nitride of the ceramic material from which the particles are made. Advantageously, the mechanical and physical properties, especially the hardness, tribological properties and machinability of these ceramic powder particles are substantially improved. The improvement in the mechanical and physical properties of the ceramic powder particles provided with a boride, carbide or nitride ceramic surface layer is maintained when these ceramic powders are used to make solid parts by powder sintering techniques, such as sintering at atmospheric pressure or HIP.

Figure 2 is a cross-sectional view of an alumina particle Al_2O_3 . For the sake of clarity, it will be assumed for the purposes of demonstration that this alumina particle Al_2O_3 is substantially spherical, it being understood that, in reality, such alumina particles Al_2O_3 actually have a polyhedral shape. Designated as a whole by the general reference number 20, this alumina particle Al_2O_3 has a radius R of around 1 micrometre. This alumina particle 20 was bombarded with a nitrogen ion beam N^+ designated by the reference number 22. As shown in Figure 2, alumina particle 20 has a core 24 of pure alumina and an external layer or shell 26 mainly formed of aluminum oxynitride $\text{Al}_x\text{O}_y\text{N}_z$ whose stoichiometry varies as a function of depth from the surface of alumina particle 20.

The thickness $\underline{e}$ of this external layer 26 is on the order of 7% of radius R of alumina particle 20, i.e. around 70 nanometres. This external layer 26 is mostly formed of aluminum oxynitride $\text{Al}_x\text{O}_y\text{N}_z$, which is a

ceramic material. According to the invention, the concentration of $\text{Al}_x\text{O}_y\text{N}_z$ increases from external surface 28 of alumina particle 20 to around 15% of radius R of alumina particle 20, i.e. around 140 nanometres, and then decreases to a depth of around 200 nm under the surface of alumina particle 20 where it is substantially zero.

More specifically, the composition of two samples of alumina Al_2O_3 , referred to as A and B respectively, was analysed by X-ray photoelectron spectroscopy (XPS). These two alumina samples A and B were bombarded with nitrogen ions N^+ , and the nitrogen concentration from the surface towards the core of these samples was then examined by XPS analysis.

With regard to the XPS analysis of alumina sample A, tests show that the nitrogen atoms that bombard and penetrate the original alumina particle Al_2O_3 bond, on the one hand, to the aluminium atoms that form part of the composition of aluminium oxynitride $\text{Al}_x\text{O}_y\text{N}_z$, and, on the other hand, do not bond to the aluminium atoms. More specifically, XPS analyses show that the atomic weight concentration of nitrogen bonded in the aluminium oxynitride particles $\text{Al}_x\text{O}_y\text{N}_z$ has two levels from the surface towards the core of the alumina particles $\text{Al}_x\text{O}_y\text{N}_z$:

- the first nitrogen concentration level appears at a depth of approximately 70 nm from the external surface of the particles. The average atomic percent concentration of nitrogen bonded to the aluminium of the aluminium oxynitride $\text{Al}_x\text{O}_y\text{N}_z$ is on the order of 6.3%. Further, the average stoichiometry of the oxynitride layer at this level is close to $\text{AlO}_{1.2}\text{N}_{0.16}$.
- the second nitrogen concentration level appears at a depth of around 140 nm. The average atomic percent concentration of nitrogen bonded to aluminium is on the order of 3.6%, i.e. almost half less than the concentration of nitrogen bonded to aluminium observed at a depth of 70 nm. The average stoichiometry of the aluminium oxynitride layer at this level is close to $\text{AlO}_{1.3}\text{N}_{0.08}$.

- Finally, beyond a depth in excess of 140 nm, there is an exponential drop in the concentration of nitrogen bonded to the aluminium that forms part of the composition of aluminium oxynitride $\text{Al}_x\text{O}_y\text{N}_z$. At a considered depth of more than 200 nm from the surface of the alumina Al_2O_3 particles, there is a stoichiometric ratio between oxygen and aluminium that is very close to that of alumina Al_2O_3 .

With regard to alumina sample B, XPS analysis shows that, in this case too, the nitrogen atoms that bombard and penetrate the original alumina particle Al_2O_3 bond, on the one hand, to the aluminium atoms that form part of the composition of aluminium oxynitride $\text{Al}_x\text{O}_y\text{N}_z$, and, on the other hand, do not bond to the aluminium atoms. More specifically, XPS analyses show that the atomic weight concentration of nitrogen bonded in the aluminium oxynitride particles $\text{Al}_x\text{O}_y\text{N}_z$ has two levels from the surface towards the core of the alumina particles $\text{Al}_x\text{O}_y\text{N}_z$:

- the first nitrogen concentration level appears at a depth of approximately 25 nm from the external surface of the particles. The average atomic percent concentration of nitrogen bonded to aluminium is on the order of 3.6%. Further, the average stoichiometry of the aluminium oxynitride layer at this level is close to $\text{AlO}_{1.3}\text{N}_{0.09}$.
- the second nitrogen concentration level appears at a depth of around 120 nm. The average atomic percent concentration of nitrogen bonded to aluminium is on the order of 4.7%, i.e. slightly more than at a depth of 25 nm. The average stoichiometry of the aluminium oxynitride layer at this level is close to $\text{AlO}_{1.3}\text{N}_{0.11}$.
- Finally, beyond a depth in excess of 120 nm, there is an exponential drop in the concentration of nitrogen bonded to the aluminium that forms part of the composition of aluminium oxynitride $\text{Al}_x\text{O}_y\text{N}_z$. At a considered depth of more than 200 nm from the surface of the alumina Al_2O_3 particles, there is a stoichiometric ratio between oxygen and aluminium that is very close to that of alumina Al_2O_3 .

It is evident that the present invention is not limited to the preceding description and that various simple modifications and variants can be envisaged by those skilled in the art without departing from the scope of the invention as defined by the annexed claims. It will be understood, in particular, that given that the ceramic particles envisaged here have a general polyhedral shape, the 'dimension' of such particles means the largest external dimension of such a particle. It will be noted finally that, according to the invention, the ECR ion source is capable of producing singly or multiply charged ions, i.e. ions whose degree of ionisation is higher than or equal to 1, wherein the ion beam can include ions that all have the same degree of ionisation or can result from a mixture of ions having different degrees of ionisation.

Nomenclature

1. ECR ion source
2. Injection stage
- 5 4. Volume of gas to be ionised
6. Hyperfrequency wave
8. Magnetic confinement stage
10. Plasma
12. Extraction stage
- 10 12a Anode
- 12b. Cathode
14. Ion beam
16. Surface
18. Part to be treated
- 15 20. Alumina particle Al_2O_3
- R. Radius
22. Nitrogen ion beam N^+
24. Core or centre
26. External layer or shell
- 20 e. Thickness
28. External surface
30. Ceramic powder particles

CLAIMS

1. Method for surface treatment of a ceramic material in powder form, said method comprising the step of providing a powder (30) formed of
5 a plurality of particles of the ceramic material to be treated, and in subjecting said ceramic powder particles (30) to an ion implantation process by directing towards an external surface of said particles a beam (14) of singly or multiply charged ions produced by a source of singly or multiply charged ions.
- 10 2. Method according to claim 1, characterized in that the ceramic powder particles (30) are agitated throughout the entire duration of the ion implantation process.
3. Method according to claim 1, characterized in that the grain size of the particles of ceramic powder (30) used is such that substantially 50%
15 of all the particles have a dimension smaller than 2 micrometres.
4. Method according to claim 2, characterized in that the grain size of the particles of ceramic powder (30) used is such that substantially 50% of all the particles have a dimension smaller than 2 micrometres.
5. Method according to claim 3, characterized in that the
20 dimension of the ceramic powder particles (30) used is comprised between 1.2 micrometres and 63 micrometres.
6. Method according to claim 4, characterized in that the dimension of the ceramic powder particles (30) used is comprised between 1.2 micrometres and 63 micrometres.
- 25 7. Method according to any of claims 1 to 6, characterized in that the ceramic material is a carbide, a nitride, a boride or an oxide.
8. Method according to claim 7, characterized in that the carbide ceramic material is bombarded with nitrogen ions N to form a carbonitride.

9. Method according to claim 8, characterized in that the ceramic material is a titanium carbide TiC or a silicon carbide SiC, and in that the product obtained after bombardment is titanium carbonitride TiCN, or silicon carbonitride SiCN respectively.

5 10. Method according to claim 7, characterized in that the nitride ceramic material is bombarded with an ion dose comprised between $1 \cdot 10^{16} \text{ cm}^{-2}$ and $1 \cdot 10^{17} \text{ cm}^{-2}$.

11. Method according to claim 10, characterized in that the ceramic material is a silicon nitride Si_3N_4 .

10 12. Method according to claim 7, characterized in that the oxide ceramic material is bombarded with nitrogen ions to form an oxynitride.

13. Method according to claim 12, characterized in that the ceramic material is zirconia ZrO_2 or alumina Al_2O_3 , and in that the product obtained after bombardment is zirconia nitride $\text{Zr}_x\text{O}_y\text{N}_z$, or zirconium nitride ZrN, or
15 aluminium oxynitride $\text{Al}_x\text{O}_y\text{N}_z$.

14. Method according to claim 7, characterized in that the oxide ceramic material is bombarded with carbon ions to form a carbonitride.

15. Method according to claim 14, characterized in that the ceramic material is zirconia ZrO_2 or alumina Al_2O_3 , and in that the product obtained
20 after bombardment is zirconia carbide ZrO_2C , or zirconium carbide ZrC respectively.

16. Method according to claim 7, characterized in that the oxide ceramic material is bombarded with boron ions to form an oxyboride, particularly zirconia boride ZrO_2B .

25 17. Method according to claim 16, characterized in that, if the ion bombardment is continued for a sufficiently long time, zirconium diboride ZrB_2 is obtained.

18. Method according to claim 1, characterized in that the ion implantation process is of the electron cyclotron resonance ECR type.

19. Method according to claim 18, characterized in that the singly or multiply charged ions are accelerated at a voltage comprised between
5 15,000 and 35,000 volts.

20. Method according to claim 18, characterized in that the implanted ion dose is comprised between 1.10^{14} and 5.10^{17} ions.cm⁻², and preferably between 1.10^{16} and 1.10^{17} ions.cm⁻².

21. Method according to claim 19, characterized in that the
10 implanted ion dose is comprised between 1.10^{14} and 5.10^{17} ions.cm⁻², and preferably between 1.10^{16} and 1.10^{17} ions.cm⁻².

22. Method according to claim 18, characterized in that the ions penetrate the particles forming the ceramic material powder to a depth corresponding to around 20% of the dimension of said particles.

15 23. Method according to claim 19, characterized in that the ions penetrate the particles forming the ceramic material powder to a depth corresponding to around 20% of the dimension of said particles.

24. Material in powder form formed of a plurality of particles having a ceramic external layer (26) and a ceramic core (24), said particles having
20 a generally polyhedral shape, the external layer (26) corresponding to a boride, a carbide or a nitride of the ceramic material from which the core (24) of the ceramic powder particles is made.

25. Material according to claim 24, characterized in that around 50% of the particles have a dimension smaller than 2 micrometres.

25 26. Material according to claim 25, characterized in that the dimension of the ceramic powder particles (30) used is comprised between 1.2 micrometres and 63 micrometres.

27. Material according to any of claims 24 to 26, characterized in that the ceramic material from which the ceramic powder particles (30) are made is a boride, a carbide, oxide or a nitride.