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(54) **Ballistic armor**

(57) Ballistic armor formed from or comprising a shaped ceramic material having a peened surface, a method of making said ballistic armor, and to the use of a shaped ceramic material having a peened surface in or as ballistic armor.

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Description

TECHNICAL FIELD

[0001] The present invention is directed to ballistic armor formed from or comprising a shaped ceramic material, a method of making said ballistic armor, and to the use of a shaped ceramic material in or as ballistic armor.

BACKGROUND OF THE INVENTION

[0002] Developments in the use of ceramic materials in ballistic protection devices for vehicles, aircraft and personnel are ongoing. For example, US-A-2011009255 describes boron and silicon carbide ceramic materials for use in bullet and shrapnel resistant armor. There is an ongoing need for further ceramic materials for use in ballistic protection devices to enhance or replace conventional armor materials, such as iron, steel and reinforced fibre materials such as Kevlar (RTM).

SUMMARY OF THE INVENTION

[0003] In accordance with a first aspect, there is provided ballistic armor formed from or comprising a shaped ceramic material, wherein the shaped ceramic material has a peened surface and compressive surface stress of at least about 80 MPa.

[0004] In accordance with a second aspect, there is provided a method of making ballistic armor, comprising:

(i) peening at least a portion of a surface of a shaped ceramic material to obtain a compressive surface stress of at least about 80 MPa; and
(ii) incorporating the peened shaped ceramic material into ballistic armor.

[0005] In accordance with a third aspect, there is provided ballistic armor prepared or obtainable by the method of the second aspect.

[0006] In accordance with a fourth aspect, the present invention is directed to the use of a shaped ceramic material defined in accordance with the first aspect in or as ballistic armor.

BRIEF DESCRIPTION OF THE FIGURES

[0007]

Figure 1 is scanning electron microscopy (SEM) images of various grain shapes, (a) angular; (b) pointed and angular; (c) cubic.

Figure 2 comprises a series of SEM images of ceramic plates peened in accordance with the present invention.

DETAILED DESCRIPTION

Ballistic armor

[0008] In accordance with the first aspect, the shaped ceramic material has a peened surface and compressive surface stress of at least about 80 MPa.

[0009] By "shaped" is meant that ceramic material has the quality of a distinct object, article or body in having an external surface or outline of specific form or figure.

[0010] In certain embodiments, the shaped ceramic material has a compressive surface stress of up to about 1000 MPa, for example, from about 150 to about 1000 MPa, or from about 150 to about 950 MPa, or from about 150 to about 900 MPa, or from about 150 to about 850 MPa, or from about 150 to about 800 MPa, or from about 150 to about 750 MPa, or from about 150 to about 700 MPa, or from about 150 to about 650 MPa, or from about 150 to about 600 MPa. The shaped ceramic material may have a compressive surface stress of at least about 200 MPa, or at least about 250 MPa, or at least about 300 MPa, or at least about 350 MPa, or at least about 400 MPa, or at least about 450 MPa, or at least about 500 MPa, or at least about 550 MPa, or at least about 600 MPa.

[0011] Without wishing to be bound by theory, it is believed that peening of the surface of the shaped ceramic material induces compressive stresses at the surface or near surface (e.g., to a depth of no more than about 80 μm below the surface) which, in turn, leads to an increase in mechanical strength, toughness and hardness. Theory suggests that the mechanical impact from peening leads to changes in cell units within the ceramic crystal lattice which leads to high compression stresses, density increase and an increase in elastic properties (e.g., plastic deformation) within the surface layer region. This may be accompanied by an increase of dislocation/dislocation density in the crystal lattice within the surface layer region.

[0012] The present inventor has surprisingly found that surface peening of the ceramic material and the resultant inducement of compressive surface stresses can enhance the ballistic performance (e.g., depth of penetration of a projectile) of the ceramic material. This in turn may enable the manufacture of ballistic armor using less ceramic material, thus reducing the weight of the armor and the manufacturing cost.

[0013] Methods for determining compressive surface stress are well known, and include, for example, the methods described in Handbook of Residual Stress, 2nd Ed. (Editor: Jian Lu), Vol. 1, Chapter 5.4, pages 274-285, the entire contents of which are hereby incorporated by reference. Compressive surface stress is sometimes referred to as 'compressive stress' or 'residual compressive stress'. In certain embodiments, the determination of compressive surface stress is carried out in accordance with the $\sin^2\Psi$ method as described in EU-norm EN 15305.2008, using a mobile diffractometer, Xstress 3000 G3, available from Stresstech Oy. The method is based on the determination of the atom distances in the crystal lattice, which are altered by stress. Further details of this apparatus and method are provided below in the Examples section.

[0014] Thus, in certain embodiments, compressive surface stress is determined to an X-ray penetration depth of no more than about 80 μm below the surface of the shaped ceramic material, for example, to a depth of no more than about 70 μm, or no more than 60 μm, or no more than about 50 μm, or no more than about 40 μm, or no more than about 30 μm, or no more than about 20 μm below the surface of the shaped ceramic material. In certain embodiments, compressive stress is determined to an X-ray penetration depth of about 16 μm below the surface of the shaped ceramic material.

[0015] The ceramic materials used in the invention are typically obtained by forming ceramic precursor material(s) into a shape, normally referred to as a "green body". The green body is then dried and heated, e.g., fired, under suitable conditions to form the desired ceramic material. This sintering process is carried out a temperature below the melting point of the ceramic.

[0016] In certain embodiments, the shaped ceramic material is formed from a ceramic precursor material comprising alumina, for example, at least about 50 wt. % alumina particulate, based on the total dry weight of the ceramic precursor material. The ceramic precursor material may comprise at least about 60 wt. % alumina, or at least about 70 wt. % alumina, or at least about 80 wt. % alumina, or at least about 85 wt. % alumina, or at least about 90 wt. % alumina, or at least about 95 wt. % alumina, or at least about 96 wt. % alumina, or at least about 97 wt. % alumina, or at least about 98 wt. % alumina, or at least about 99 wt. % alumina. In one embodiment, the ceramic precursor material consists of substantially 100 wt. % alumina. A person of skill in the art will understand that having been formed from a ceramic precursor material containing a certain amount of alumina, the shaped ceramic material formed therefrom may be described as comprising the same amount of alumina. Thus, for example, if the shaped ceramic material is formed from a ceramic precursor material comprising 85 wt. % alumina, the shaped ceramic material may be described as a shaped ceramic material comprising 85 wt. % alumina.

[0017] In an embodiment, the alumina has a d_{50} of from about 0.1 to about 20 μm, for example, a d_{50} of from about 0.5 to about 15 5μm, or from about 1 to about 15 μm, or from about 2 to about 12 μm, or from about 2 to about 10 μm, or from about 3 to about 8 μm, or from about 2 to about 6 μm, or from about 3 to about 6 μm, or from about 2 to about 5 μm, or from about 3 to about 5 μm, or from about 4 to about 10 μm, or from about 4 to about 8 μm, or from about 4 about 6 μm. In an embodiment, the alumina has a d_{50} of about 1 μm, or about 2 μm, or about 3 μm, or about 4 μm, or about 5 μm, or about 6 μm, or about 7 μm, or about 8 μm, or about 9 μm, or about 10 μm. The alumina may have a d_{90} of less than about 40 μm, for example, less than about 30 μm, or less than about 25 μm, or less than about 20 μm, or less than about 15 μm, or less than about 10 μm.

[0018] Unless otherwise stated, the mean (average) equivalent particle diameter (d_{50} value) referred to herein is as measured in a well known manner by sedimentation of the particulate material in a fully dispersed condition in an aqueous medium using a Sedigraph 5100 machine as supplied by Micromeritics Instruments Corporation, Norcross, Georgia, USA (web-site: www.micromeritics.com), referred to herein as a "Micromeritics Sedigraph 5100 unit". Such a machine provides measurements and a plot of the cumulative percentage by weight of particles having a size, referred to in the art as the 'equivalent spherical diameter' (esd), less than given esd values. The mean particle size d_{50} is the value determined in this way of the particle esd at which there are 50% by weight of the particles which have an equivalent spherical diameter less than that d_{50} value. Likewise, d_{90} is the value determined in this way of the particle esd at which there are 90% by weight of the particles which have an equivalent spherical diameter less than that d_{90} value.

[0019] In certain embodiments, the alumina comprises, consists of, or consists essentially of, calcined alumina. In embodiments described below in which the ceramic precursor material comprises a second particulate material, the calcined alumina is not a fused corundum. Hereafter, the invention may tend to be discussed in terms of calcined alumina, and in relation to aspects where the calcined alumina is processed and/or treated. The invention should not be construed as being limited to such embodiments.

[0020] The calcined alumina may have an Al_2O_3 content of at least 99 %, a Na_2O content of less than about 0.4 % and a Fe_2O_3 content of less than about 0.015 %. In an embodiment, the calcined alumina is a medium soda alumina having a Na_2O content of from about 0.15 to about 0.30 %. In another embodiment, the calcined alumina is a low soda alumina having a Na_2O content of less than about 0.15 %.

[0021] In certain embodiments, the alumina is doped with a metal, for example, a transition metal. Suitable dopants include on or more of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Y, Nb, Mo, Sn, In, Si, Ga, Ge and Pb. The level of dopant will typically be no more than about 10,000 ppm, based on the alumina content, for example, less than about 7500 ppm, or less than about 5000 ppm, or less than about 2500 ppm, or less than about 1000 ppm, or less than about 800 ppm, or less than about 600 ppm, or less than about 400 ppm, or less than about 200 ppm, or less than about 100 ppm.

[0022] In certain embodiments, the ceramic precursor material comprises at least about 50 wt. % alumina, for example, calcined alumina, and from about 1 to about 40 % by weight, based on the total dry weight of the composition, of second particulate material having a Mohs hardness of at least about 8.5 (e.g., fused corundum) and having a d_{50} which is greater than the d_{50} of the alumina, for example, a d_{50} from about 7 μm to about 500 μm. For example, the ceramic precursor material may comprise at least about 80 wt. % alumina, for example, calcined alumina, and from about 1 to about 20 % by weight of the second particulate material. In an embodiment, the d_{50} of the second particulate material, for example, fused corundum, is from about 9 μm to about 180 μm, or from about 17 μm to about 180 μm, or from about 23 μm to about 180 μm, or from about 23 μm to about 105 μm, or about 23 μm to about 75 μm, or from about 29 μm to about 125 μm, or from about 29 μm to about 105 μm, or about 29 μm to about 75 μm, or from about 29 μm to about 63 μm, or from about 37 μm to about 125 μm, or from about 37 μm to about 105 μm, or from about 37 μm to about 63 μm, or from about 45 μm to about 125 μm, or from about 40 μm to about 105 μm, or from about 40 to about 75 μm, or from about 40 to about 63 μm, or from about 53 μm to about 125 μm, or from about 53 μm to about 105 μm, or from about 53 μm to about 75 μm, or from about 53 μm to about 63 μm. In such embodiments, the d_{50} of the alumina, for example, calcined alumina may be less than about 10 μm, for example, less than about 8 μm, or less than about 6 μm, or less than about 5 μm, or less than about 4 μm, or less than about 3 μm, or less than about 2 μm, or less than about 1 μm. The weight ratio of alumina, for example, calcined alumina to second particulate material, for example, fused corundum may be from about 6:4 to about 99:1, or from about 7:3 to about 99:1, or from about 4:1 to about 99:1, or from about 5:1 to about 99:1, or from about 6:1 to about 99:1, or from about 7:1 to about 99:1, or from about 8:1 to about 99:1, or less than about 49:1, or less than about 97:3, or less than about 24:1, or less than about 19:1, or less than about 9:1.

[0023] In certain embodiments, the ceramic precursor material comprises from about 1 to about 35 % by weight second particulate material, for example, from about 2 to about 35 %, by weight, or from about 2 to about 30 % by weight, or from about 3 to about 25 % by weight, or from about 4 to about 20 % by weight, or from about 5 to about 20 % by weight, or from about 5 to about 18 % by weight, or from about 5 to about 16 % by weight, or from about 5 to about 14 % by weight, or from about 5 to about 12 % by weight, of from about 5 to about 10 % by weight, or from about 6 to about 20 % by weight, or from about 7 to about 20 % by weight, or from about 8 to about 20 % by weight, or from about 9 to about 20 % by weight, or from about 10 to about 20 % by weight second particulate material having any of the particle sizes described above. In an embodiment, the ceramic precursor material comprises about 1 % by weight fused corundum as the second particulate material, for example, about 2 % by weight, or about 3 % by weight, or about 4 % by weight, or about 5 % by weight, or about 6 % by weight, or about 7 % by weight, or about 8 % by weight, or about 9 % by weight, or about 10 % by weight, or about 12 % by weight, or about 14 % by weight, or about 16 % by weight, or about 18 % by weight, or about 20 % by weight of fused corundum having any of the particle sizes described above.

[0024] In certain embodiments, the second particulate material has a Mohs hardness of at least about 8.6, or at least about 8.7, or at least about 8.8, or at least about 8.9, or at least about 9.0.

[0025] In certain embodiments, the second particulate material is selected from fused corundum, zirconia, silicon carbide, boron carbide, tungsten carbide, titanium carbide, boron nitride, diamond, and combinations thereof. For example, in certain embodiments, the second particulate material is fused corundum. Hereafter, the invention may tend to be discussed in terms of fused corundum, and in relation to aspects where the fused corundum is processed and/or treated. The invention should not be construed as being limited to such embodiments.

[0026] In certain embodiments, the fused corundum particulate will have a hardness of about 9 Mohs and a specific gravity of at least about 3.9 g/cm^3. The fused corundum may have a bulk density in the range of from about 1.3 to about 2.0 g/cm^3, determined using the current FEPA test method, for example, from about 1.35 to about 1.90 g/cm^3, or from about 1.35 to about 1.85 g/cm^3, or from about 1.35 to about 1.80 g/cm^3, or from about 1.35 to about 1.75 g/cm^3, or from about 1.40 to about 1.75 g/cm^3, or from about 1.40 to about 1.70 g/cm^3, or from about 1.40 to about 1.65 g/cm^3, or from about 1.40 to about 1.60 g/cm^3, or from about 1.40 to about 1.55 g/cm^3, or from about 1.40 to about 1.50 g/cm^3.

[0027] In an advantageous embodiment, the morphology of the second particulate material (also referred to as grain shape) is 'angular' or 'pointed' or 'pointed and angular'. The grain shape may be determined by measuring the bulk density using the FEPA or ASTM method. Examples of second particulate materials (e.g., fused corundum) having an 'angular', 'pointed and angular', and 'cubic' grain shape are shown in Figure 1(a), (b) and (c), respectively. These are well known terms of art in this technical field and a person skilled in the art will be able to readily determine the difference between a 'cubic' particulate (grain shape) on the one hand and an 'angular' or 'pointed and angular' particulate (grain shape) on the other hand. In embodiments, the morphology of the second particulate material is a mixture of 'angular', 'pointed' and 'pointed and angular'.

[0028] In an embodiment, the second particulate material is white fused corundum, for example, white fused corundum having an Al_2O_3 content of at least about 99%, an Fe_2O_3 content of less than about 0.05%, and a Na_2O content of less than about 0.20 %. In another embodiment, the second particulate material is brown fused corundum, for example, brown fused corundum having an Al_2O_3 content of between about 95% and 98%, a TiO_2 content of at least about 1.5 % and an Fe_2O_3 content of at least about 0.10%. In another embodiment, the second particulate material is pink fused corundum, for example, pink fused corundum having an Al_2O_3 content of at least about 99 % and a CrO_2 content of about at least about 0.2%. In a further embodiment, the second particulate material is a mixture of two or more of white, brown and pink fused corundum, for example, a mixture of white and brown fused corundum.

[0029] In further embodiments, the shaped ceramic material is formed from a ceramic precursor material which comprises a major amount, e.g., at least 50 wt. %, of silicon carbide (SiC), silicon nitride (Si_3N_4), SiAlON, boron carbide (B_4C), boron nitride, fused corundum, zirconium, tungsten carbide, titanium carbide, titantium diboride, titanium silicide, diamond or combinations thereof. In embodiments, the ceramic precursor material comprises at least about 60 wt. %, or at least about 70 wt. %, or at least about 80 wt. %, or at least about 90 wt. %, or at least about 95 wt. % of silicon carbide (SiC), silicon nitride (Si_3N_4), SiAlON, boron carbide (B_4C), boron nitride, fused corundum, zirconium, tungsten carbide, titanium carbide, titantium diboride, titanium silicide, diamond or combinations thereof. Normally provided in particulate form, the morphology (also referred to as grain shape) of the particulate is in certain embodiments 'angular' or 'pointed' or 'pointed and angular'. The grain shape may be determined by measuring the bulk density using the FEPA or ASTM method. Examples of second particulate materials (e.g., fused corundum) having an 'angular', 'pointed and angular', and 'cubic' grain shape are shown in Figure 1(a), (b) and (c), respectively. In embodiments, the morphology of the particulate is a mixture of 'angular', 'pointed' and 'pointed and angular'.

[0030] In certain embodiments, the ceramic precursor material from which the shaped ceramic material is formed comprises minor amounts, e.g., less than about 20 wt. %, or less than about 15 wt. %, or less than about 10 wt. %, or less than about 8 wt. %, or less than about 6 wt. %, or less than about 5 wt. %, or less than about 4 wt. %, or less than about 3 wt. %, or less than about 2 wt. %, or less than about 1 wt. %, of materials other than those precursor materials described above. For example, the ceramic precursor material may comprise a minor amount of sintering aid (including alkali and alkali earth metal oxides such as, for example, magnesium oxide, sodium oxide (soda) and mixtures thereof), carbon (.e.g., carbon black, graphite, and/or coke) and/or silica.

[0031] In certain embodiments, the shaped ceramic material has a grain size of from about 0.1 to about 200 μm, for example, from about 0.5 to about 175 μm, or from about 1 to about 100 μm, or from about 1 to about 25 μm, or from about 25 to about 50 μm, or from about 50 to about 75 μm, or from about 75 to about 100 μm, or from about 1 to about 50 μm, or from about 50 to about 100 μm.

[0032] Grain size may be determined by visual inspection of an SEM of the shaped ceramic material. Grain size is taken to be the maximum (straight line) dimension between grain boundaries of an individual grain as shown in an SEM image of the grain.

[0033] In certain embodiments, for example, embodiments in which the shaped ceramic material is formed from a ceramic precursor material comprising at least about 85 wt. % alumina, the shaped ceramic material has a grain size of from about 0.1 to about 30 μm, for example, from about 0.1 to about 25 μm, or from about 0.1 to about 20 μm, or from about 0.1 to about 15 μm, or from about 0.1 to about 10 μm, or from about 0.1 to about 5 μm. The shaped ceramic material may have a grain size of at least about 0.5 μm, or at least about 1 μm.

[0034] In certain embodiments, the shaped ceramic material has a bimodal or multimodal grain size. Thus, in certain embodiments, the shaped ceramic material may be characterized by having 'islands' of relatively large, optionally irregular shaped, grains surrounded by a 'sea' of smaller, optionally more regular (relative to the larger grains), shaped grains.

[0035] Whilst not wishing to be bound by theory, it is believed that the presence of much larger particles, e.g., the second particulate described above, in the ceramic precursor material induces growth during firing of much larger, irregular shaped grains in the shaped ceramic material compared to a ceramic material prepared in the absence of the second particulate. Further, the presence of these larger and generally irregular shaped grains, which has the effect of increasing average grain size, in certain embodiments may provide further improvements in ballistic performance (e.g., reduced depth of penetration).

[0036] Thus, in an embodiment, the shaped ceramic material is characterized in having islands of grains having a grain size of at least about 40 μm, for example, at least about 50 μm, or at least about 60 μm, or at least about 70 μm, or at least about 80 μm, or at least about 90 μm. In certain embodiments, the grain size of the largest grain(s) is less than about 150 μm, for example, less than about 140 μm, or less than about 130 μm, or less than about 120 μm, or less than about 110 μm, or less than about 100 μm.

[0037] In certain embodiments, the shaped ceramic material comprises relatively small and large grains, in which the size ratio of the small grains to large grains is at least about 1:2, for example, at least about 1:3, or at least about 1:4, or at least about 1:5. By 'small' is meant a grain size of less than about 40 μm, for example less than about 35 μm, or less than about 30 μm, or less than about 25 μm , or less than about 20 μm, or less than about 15 μm, or less than about 10 μm. By 'large' is meant a grain size of at least about 40 μm, for example, at least about 50 μm, or least about 60 μm, or at least about 70 μm, or at least about 80 μm. Grain size may be determined in accordance with the method described above.

[0038] In certain embodiments, in any given surface area of the shaped ceramic material, the ratio (i.e., quantity) of small grains to large grains is at least about 50:50, for example, at least about 60:40, or at least about 70:30, or at least about 80:20, or at least about 90:10, or at least about 95:5, or at least about 96:4, or at least about 97:3, or at least about 98:2, or at least about 99:1.

[0039] The shaped ceramic material may have any form which is suitable for the ballistic application in which it is incorporated. For example, the shaped ceramic material may be in the form of a plate, panel, brick, cylinder, ring, sphere, ball, spheroid or a complex shape. The plate or panel may be planar or non-planar, i.e., curved to some degree, for example, rounded to mimic the curvature of a limb or torso of a human body. The plate or panel may have a thickness ranging from about 1 mm to about 50 mm, for example, from about 5 mm to about 40 mm, for example, from about 5 to about 30 mm, or from about 5 to about 20 mm, or form about 5 to about 10 mm. The thickness (i.e., cross-section) may be uniform across the plate or panel may vary across the plate or panel. The plate or panel may be regular in shape, e.g., circular, ovular, triangular, square, rectangular, pentagonal, hexagonal, heptagonal, octagonal, etc, or irregular in shape. The shape may be sized to fit, engage or otherwise cooperate with another article, for example, an article formed from or comprising one or more materials suitable for use in or as ballistic armor.

[0040] Ballistic armor formed from or comprising the shaped ceramic material may be in the form of body armor, for example, a bullet proof or ballistic vest. Such vests may comprise one or more ceramic bodies, such as plates, spheres or cylinders, such as small arms protective inserts used by the military, formed from or comprising the shaped ceramic material described herein.

[0041] The ballistic armor may further comprise one or more materials suitable for use in or as ballistic armor such as, for example, silicon carbide, boron carbide, Kevlar, iron and/or steel. The one or more materials may be in the form of shaped components, e.g., plates or panels. The one or more materials/shaped components may be connected to, bonded to, attached to, arranged with or otherwise engaged with the shaped ceramic material of the present invention. For example, the shaped ceramic material and one or more materials/shaped components may be arranged in a series of layers.

[0042] In other embodiments, the ballistic armor is used to protect commercial or military airplanes, or helicopters, or to protect vehicles for domestic use, such as limousines, or to protect military vehicles, such as tanks and troop carriers.

[0043] Typically, in the ballistic armor of the present invention, the shaped ceramic material will be orientated such that the peened surface faces towards the direction of impact of a ballistic projectile.

Method of making ballistic armor

[0044] In accordance with the second aspect of the present invention, at least a portion of a surface of a shaped ceramic material is peened to obtain a compressive surface stress of at least about 80 MPa. The shaped ceramic material is described above in connection with the first aspect of the present invention, save that prior to peening it will have a compressive surface of less than about 80 MPa, for example, less than about 70 MPa, or less than about 60 MPa, or less than about 50 MPa. Thus, at least a portion of the surface of the shaped ceramic material is peened in order to increase compressive surface stress at the surface.

[0045] In certain embodiments, the surface is peened to obtain a compressive surface stress of up to about 1000 MPa, for example, from about 150 to about 1000 MPa, or from about 150 to about 950 MPa, or from about 150 to about 900 MPa, or from about 150 to about 850 MPa, or from about 150 to about 800 MPa, or from about 150 to about 750 MPa, or from about 150 to about 700 MPa, or from about 150 to about 650 MPa, or from about 150 to about 600 MPa. The surface of the shaped ceramic material may be peened to obtain a compressive surface stress of at least about 200 MPa, or at least about 250 MPa, or at least about 300 MPa, or at least about 350 MPa, or at least about 400 MPa, or at least about 450 MPa, or at least about 500 MPa, or at least about 550 MPa, or at least about 600 MPa.

[0046] At least a portion of a surface of the shaped ceramic material may be peened by a technique selected from shot-peening, ultrasonic peening, laser peening or a combination thereof. These methods are traditionally used in finishing procedures to modify or enhance strength of metal components. In advantageous embodiments, at least a portion of a surface of the shaped ceramic material is peened by shot-peening.

[0047] In certain embodiments, the surface of the shaped ceramic material is shot-peened with impact elements formed from a material having a hardness comparable to the hardness of the shaped ceramic material and a density greater than the density of the shaped ceramic material.

[0048] In certain embodiments, the surface is shot-peened with a material having a hardness of greater than 8, for example, greater than 8.5, or greater than 9.

[0049] In certain embodiments, the surface is shot-peened with a material having a specific gravity of greater than 5, for example, greater than 10, or greater than 12, or greater than 15.

[0050] The impact elements may comprise or consist of spherical elements, such as beads or balls (otherwise known as 'shot'). In certain embodiments, the impact elements are formed from tungsten carbide (WC). In certain embodiments, the spherical WC impact elements have a diameter of from about 50 to about 1500 μm, for example, a diameter of from about 50 to about 800 μm or, for example, a diameter of at least about 70 μm, or at least about 90 μm, or at least about 120 μm, or at least about 150 μm, or at least about 200 μm, or at least about 250 μm, or at least about 300 μm, or at least about 350μ m, or at least about 400 μm, or at least about 450 μm, or at least about 500 μm, or at least about 550 μm, or at least about 600 μm, or at least about 650 μm, or at least about 700 μm, or at least about 750 μm, or at least about 850 μm, or at least about 1000 μm, or at least about 1200 μm, or at least about 1400 μm. In certain embodiments, the spherical WC impact elements have a diameter of from about 80 to about 100 μm, for example, about 90 μm. In other embodiments, the WC impact elements have a diameter of from about 610 to 690 μm, for example, about 650 μm.

[0051] The surface will be peened for a sufficient time and under suitable conditions to obtain a desired compressive surface stress, e.g., a compressive surface stress of at least about 80 MPa. Persons skilled in the art will understand that the duration of peen will vary depending on the velocity of the impacting elements, the peening load, i.e., the total weight of impacting elements peened at the surface over the duration of the peening process, the form and size of impact elements, the type of shaped ceramic material and the desired compressive stress to be induced.

[0052] Typical peening times range from about 100 seconds to about 30 minutes, for example, from about 200 seconds to about 25 minutes, or from about 200 seconds to about 20 minutes, or from about 200 seconds to about 1000 seconds, or from about 300 seconds to about 900 seconds, or between 200 and 300 seconds, or between about 300 and 400 seconds, or between about 400 and 500 seconds, or between about 500 and 600 seconds, or between about 600 and 700 seconds, or between about 700 and 800 seconds, or between about 800 and 900 seconds, or between about 900 and 1000 seconds.

[0053] In shot-peening the velocity of the impact elements is determined in part by the air pressure applied to the impact elements in the nozzle of the shot-peening apparatus. In embodiments, the air pressure is from about 2 to about 5 bar, for example, from about 2-4.5 bar, or from about 2-4 bar, or from about 2-3.5 bar, or from about 2-3 bar, or from about 2-2.5 bar. In certain embodiments, the air pressure is about 2 bar, or about 2.25 bar, or about 2.5 bar, or about 2.75 bar, or about 3 bar, or about 3.25 bar, or about 3.5 bar, or about 3.75 bar, or about 4 bar, or about 4.25 bar, or about 4.5 bar, or about 4.75 bar, or about 5 bar.

[0054] The peening load may be from about 0.5 kg to about 10 kg, for example, from about 1 kg to about 8 kg, or from about 1 kg to about 6 kg, or from about 1.5 kg to about 5 kg, or from about 1.5 kg to about 4 kg, or from about 1.5 kg to about 3.5 kg, or from about 1.5 kg to about 3 kg, or from about 2 kg to about 3 kg. In certain embodiments, the peening load is about 1 kg, or about 1.5 kg, or about 2 kg, or about 2.5 kg, or about 3 kg, or about 3.5 kg, or about 4 kg, or about 4.5 kg.

[0055] In certain embodiments, the surface of the shaped ceramic material is shot-peened with WC beads/balls having a diameter of from about 80 to about 100 μm, for example, about 90 μm, at an air pressure of about 2-4 bar, for example, from about 2-3 bar, or about 2 bar, or about 2.5 bar, or about 3 bar, and a peening load of from about 1.5-3 kg, for example, about 2 kg or about 2.5 kg. Peening time may range from about 200 seconds to about 1000 seconds. In these embodiments, the shaped ceramic material may be formed from a ceramic precursor material comprising at least about 85 wt. % alumina, for example, at least about 95 wt. % alumina, or at least about 98 wt. % alumina.

[0056] In certain embodiments, the surface of the shaped ceramic material is shot-peened with WC beads/balls having a diameter of from about 610 to 690 μm, for example, about 650 μm, at an air pressure of about 2-4 bar, for example, from about 2-3 bar, or about 2 bar, or about 2.5 bar, or about 3 bar, and a peening load of from about 2-5 kg, for example, about 3 kg, or about 3.5 kg, or about 4 kg. Peening time may rage from about 200 seconds to about 1000 seconds. In these embodiments, the shaped ceramic material may be formed from a ceramic precursor material comprising at least about 85 wt. % alumina, for example, at least about 95 wt. % alumina, or at least about 98 wt. % alumina.

[0057] In accordance with the method of the second aspect of the present invention, the peened shaped ceramic material is incorporated into ballistic armor, for example, a ballistic armor assembly. Types of ballistic armor are many and various, including, for example, bullet proof or ballistic vests. Such vests may comprise one or more ceramic bodies, such as plates, spheres or cylinders, such as small arms protective inserts used by the military, formed from or comprising the peened shaped ceramic material described herein. In other embodiments, the peened shaped ceramic material is incorporated into ballistic armor suitable for protecting commercial or military airplanes or helicopters, for example, the cockpit of military airplanes or helicopters, or suitable for protecting vehicles for domestic use, such as limousines, or suitable for protecting military vehicles, such as tanks, troop carriers, and the like.

[0058] The method of making ballistic may further comprise incorporating one or more materials (other than the peened shaped ceramic material of the present invention) into the ballistic armor, for example, materials such as silicon carbide, boron carbide, Kevlar, iron and/or steel. The one or more materials may be in the form of shaped components, e.g., plates or panels. The one or more materials/shaped components may be connected to, bonded to, attached to, arranged with or otherwise engaged with the shaped ceramic material of the present invention. For example, the shaped ceramic material and one or more materials/shaped components may be arranged in a series of layers in the ballistic armor. The ballistic armor may comprise a series of layers of the peened shaped ceramic material. Typically, the peened shaped ceramic material will be incorporated in the ballistic armor such that the peened surface is orientated such that it faces towards the direction of impact of a ballistic projectile.

[0059] The method of the second aspect of the present invention may comprise sizing the peened shaped ceramic material to fit, engage or otherwise cooperate with another article, for example, an article formed from or comprising one or more materials suitable for use in or as ballistic armor.

[0060] For the avoidance of doubt, the present application is directed to the subject-matter described in the following numbered paragraphs:

1. Ballistic armor formed from or comprising a shaped ceramic material, wherein the shaped ceramic material has a peened surface and compressive surface stress of at least about 80 MPa.

2. Ballistic armor according to numbered paragraph 1, wherein the shaped ceramic material has a compressive surface stress of from about 150 to about 1000 MPa, optionally from about 150 to about 600 MPa.

3. Ballistic armor according to any preceding numbered paragraph, wherein the shaped ceramic material comprises alumina, for example, at least about 85 wt. % alumina, optionally at least about 95 wt. % alumina.

4. Ballistic armor according to numbered paragraph 1 or 2, wherein the shaped ceramic material is formed from a ceramic precursor material comprising at least about 50 wt. % alumina other than fused corundum and from about 1-40 wt. % of a second particulate material having a Mohs hardness of at least about 8.5 and a d_{50} which is greater than the d_{50} of the alumina.

5. Ballistic armor according to numbered paragraph 3 or 4, wherein the shaped ceramic material is formed from a ceramic precursor material comprising alumina having a d_{50} of from about 0.1 μm to about 20 μm, optionally wherein the second particulate material has a d_{50} of from about 7 μm to about 500 μm.

6. Ballistic armor according to numbered paragraph 1 or 2, wherein the shaped ceramic material comprises a major amount of silicon carbide (SiC), silicon nitride (Si_3N_4), SiAlON, boron carbide (B_4C), boron nitride, fused corundum, zirconium, tungsten carbide, titanium carbide, titantium diboride, titanium silicide, diamond or combinations thereof.

7. Ballistic armor according to any preceding numbered paragraph, wherein the shaped ceramic material has a grain size of from about 0.1 to about 200 μm, for example, from about 0.5 to about 100 μm, or from about 1 to about 100 μm, or from about 0.1 to about 30 μm, or from about 0.1 to about 10 μm.

8. Ballistic armor according to any preceding numbered paragraph, wherein the shaped ceramic material has a bimodal or multimodal grain size.

9. Ballistic armor according to any preceding numbered paragraph, wherein the shaped ceramic material is in the form of a plate, panel, brick, cylinder, ring, ball, or complex shape.

10. Ballistic armor according to any preceding numbered paragraph, wherein the shaped ceramic material is in the form of a plate or panel which is circular, triangular, square, rectangular, pentagonal, hexagonal, heptagonal, octagonal or of irregular shape.

11. Ballistic armor according to any preceding numbered paragraph, wherein the surface is peened using a technique selected from shot-peening, ultrasonic peening, laser peening or a combination thereof.

12. Ballistic armor according to numbered paragraph 11, wherein the surface is shot-peened, with a material having a hardness of greater than 8, and optionally greater than 8.5, and optionally greater than 9.

13. Ballistic armor according to numbered paragraph 11, wherein the surface is shot-peened with a material having a specific gravity of greater than 5, and optionally greater than 10, and optionally greater than 12, and optionally greater than 15.

14. Ballistic armor according to numbered paragraph 11, wherein the surface is shot-peened, optionally with tungsten

carbide impact elements.

15. Ballistic armor according to numbered paragraph 14, wherein the impact elements are spheres having a diameter of from about 50 to about 1500 μm, for example, spheres having a diameter of from about 50 to about 800 μm.

16. Ballistic armor according to numbered paragraph 15, wherein the spheres have a diameter of about 90 μm or a diameter of about 650 μm.

17. Ballistic armor according to any preceding numbered paragraph, further comprising one or more other components suitable for use in ballistic armor, optionally wherein said one or more components is connected to, bonded to, attached to, arranged with or otherwise engaged with the shaped ceramic material.

18. A method of making ballistic armor, comprising:

(i) peening at least a portion of a surface of a shaped ceramic material to obtain a compressive surface stress of at least about 80 MPa; and
(ii) incorporating the peened shaped ceramic material into ballistic armor.

19. The method of numbered paragraph 18, wherein the surface of the shaped ceramic material is peened using a technique selected from shot-peening, ultrasonic peening, laser peening or a combination thereof.

20. The method of numbered paragraph 19, wherein the surface is shot-peened, optionally with tungsten carbide impact elements.

21. The method of numbered paragraph 20, wherein the impact elements are spheres having a diameter of from about 50 to about 1500 μm, for example, spheres having a diameter of from about 50 to 800 μm.

22. The method of numbered paragraph 21, wherein the spheres have a diameter of about 90 μm or a diameter of about 650 μm.

[0061] Embodiments of the present invention will now be described by way of illustration only, with reference to the following non-limiting examples.

EXAMPLES

Example 1

[0062] A number of alumina ceramic plates, each comprising 98 wt. % Al_2O_3, were subjected to shot-peening under varying conditions (as summarized in Tables 1 and 2 below).

[0063] The peening apparatus used was an injector blasting apparatus of MHG, Düsseldorf. In this apparatus, the pressurised air and the impact elements are led to the blasting gun via two separate tubes. The impact elements are accelerated in the blasting nozzle. The impact elements are filled into a container, which is arranged above the blasting cabin. Due to its own weight, the impact elements fall into the blasting nozzle. With this method, a uniform and impact-free discharge of impact elements is ensured at a comparatively low blasting pressure. Due to the peening treatment, some of the impact elements may break up and may not be returned to the blasting process due to the sharp edges formed. This is ensured through a so-called "inclined belt sorting apparatus".

[0064] The blasting nozzle had a diameter of 8 mm and the blasting distance in the experiments was 200 mm. This resulted in a blasting stain on the sample with a homogeneous degree of overlap with a diameter of about 30 mm. The plates were led through the blasting cone using a shifting unit. A trace with a width of 45 mm was blasted with each passage. Afterwards, the next trace with an overlap of 5 mm with the previous trace was blasted. The data regarding resulting accuracy (mean blasting amount of 2 and 4 kg) are based on a blasting stain with a diameter of about 50 mm. The outer regions of the blasting stain display a lower degree of overlap. This was compensated by overlapping of the traces.

[0065] Compressive surface stress for each ceramic plate was determined by XRD in accordance with the $\sin^2\Psi$ method as described in EU-norm EN 15305.2008, using a mobile diffractometer, Xstress 3000 G3, available from Stresstech Oy. The method is based on the atom distances in the crystal lattice, which are altered by stress. Compressive surface stress was determined to a depth of 16 μm below the surface. The specified penetration depth of the radiation indicates the thickness of the boundary layer, from which 67% of the information originates.

[0066] Details of the experimental parameters are summarized in Table 1.

Table 1.

E =	340 GPa
v =	0.23
Penetration depth	16 μm
Radiation source	Mn
2 theta	146.208
lattice plane	{0 2 10}

[0067] The plate prior to peening had a compressive surface stress of 41±26 MPa. The resulting compressive surface stresses versus the applied peening conditions are summarized in Table 2 below.

Table 2.

Impact pressure/peenload/shot diameter	2 bar 2 kg	3 bar 2 kg	2 bar 4 kg	3 bar 4 kg
90 μm	168±32 MPa	195±30 MPa	138±50 MPa	186±37 MPa
650 μm	583±32 MPa	571±63 MPa	501±52 MPa	617±35 MPa

[0068] SEM images of a plate prior to peening and after penning are provided in Figure 1:

- Figure 2(a) is an SEM image of the ceramic plate prior to peening
- Figure 2(b) is an SEM image of the ceramic plate following peening with 90 μm diameter WC spheres, 2 bar, 2 kg peening load
- Figure 2(c) is an SEM image of the ceramic plate following peening with 90 μm diameter WC spheres, 3 bar, 2 kg peening load
- Figure 2(d) is an SEM image of the ceramic plate following peening with 90 μm diameter WC spheres, 3 bar, 4 kg peening load
- Figure 2(e) is an SEM image of the ceramic plate following peening with 650 μm diameter WC spheres, 2 bar, 2 kg peening load
- Figure 2(f) is an SEM image of the ceramic plate following peening with 650 μm diameter WC spheres, 2 bar, 4 kg peening load
- Figure 2(g) is an SEM image of the ceramic plate following peening with 650 μm diameter WC spheres, 3 bar, 2 kg peening load
- Figure 2(h) is an SEM image of the ceramic plate following peening with 650 μm diameter WC spheres, 3 bar, 4 kg peening load

Example 2 - ballistic testing

[0069] Depth of Penetration (DoP) tests were performed to measure the ballistic performance of peened ceramic plates by measuring penetration of bullets into a polycarbonate target after impacting and passing through the sample ceramic plate. Six to ten samples, i.e., 6 mm thick plates, were tested for each material and the results were averaged. In the DoP test, ballistic efficiency of a ceramic armour increases with a decrease in the DoP value.

[0070] DoP tests were performed on two peened alumina samples. Sample A was peened with 650 micron WC spheres with a nozzle discharge pressure of 2 bars and a 4 kg peening load. Sample A had a stress depth of 65-70 microns and a residual stress at a depth of 16 microns of 500 MPa. Sample B was peened with 90 micron WC spheres with a nozzle discharge pressure of 2.5 bars and a 2 kg peening load. Sample B had a stress depth of 30-40 microns and a residual stress at a depth of 16 microns of 170 - 195 MPa. Unpeened alumina and SSiC samples are provided as controls. Results are summarized in Table 3 below.

Table 3.

Sample	Depth of Penetration (mm)	SD	Mean Residual Velocity (m/s)	SD
Unpeened Alumina 98% Control (10 shots)	45	13	382	72
Peened Alumina 98% Sample A (7 shots)	28	8	319	106
Peened Alumina 98% Sample B (7 shots)	28	4	302	119
Commercial SSiC Control (6 shots)	32	6	442	31

[0071] Peened alumina sample A was observed to result in some break up of the bullet cores in some cases. Peened alumina sample B was observed to result in considerable breakup of the bullet cores m some cases

Claims

1. Ballistic armor formed from or comprising a shaped ceramic material, wherein the shaped ceramic material has a peened surface and compressive surface stress of at least about 80 MPa.

2. Ballistic armor according to claim 1, wherein the shaped ceramic material has a compressive surface stress of from about 150 to about 1000 MPa, optionally from about 150 to about 600 MPa.

3. Ballistic armor according to any preceding claim, wherein the shaped ceramic material comprises alumina, for example, at least about 85 wt. % alumina, optionally at least about 95 wt. % alumina.

4. Ballistic armor according to claim 3, wherein the shaped ceramic material is formed from a ceramic precursor material comprising alumina having a d_{50} of from about 0.1 μm to about 20 μm, optionally wherein a second particulate material, when present, has a d_{50} of from about 7 μm to about 500 μm.

5. Ballistic armor according to any claims 1 or 2, wherein the shaped ceramic material comprises a major amount of silicon carbide (SiC), silicon nitride (Si_3N_4), SiAlON, boron carbide (B_4C), boron nitride, fused corundum, zirconium, tungsten carbide, titanium carbide, titantium diboride, titanium silicide, diamond or combinations thereof.

6. Ballistic armor according to any preceding claim, wherein the shaped ceramic material has a grain size of from about 0.1 to about 200 μm, for example, from about 0.5 to about 100 μm, or from about 1 to about 100 μm, or from about 0.1 to about 30 μm, or from about 0.1 to about 10 μm.

7. Ballistic armor according to any preceding claim, wherein the surface is peened using a technique selected from shot-peening, ultrasonic peening, laser peening or a combination thereof.

8. Ballistic armor according to claim 7, wherein the surface is shot-peened, with a material having a hardness of greater than 8, and optionally greater than 8.5, and optionally greater than 9.

9. Ballistic armor according to claim 7, wherein the surface is shot-peened with a material having a specific gravity of greater than 5, and optionally greater than 10, and optionally greater than 12, and optionally greater than 15.

10. Ballistic armor according to claim 7, wherein the surface is shot-peened, optionally with tungsten carbide impact elements.

11. Ballistic armor according to claim 10, wherein the impact elements are spheres having a diameter of from about 50 to about 1500 μm, for example, spheres having a diameter of from about 50 to about 800 μm.

12. Ballistic armor according to any preceding claim, further comprising one or more other components suitable for use in ballistic armor, optionally wherein said one or more components is connected to, bonded to, attached to, arranged with or otherwise engaged with the shaped ceramic material.

13. A method of making ballistic armor, comprising:

(i) peening at least a portion of a surface of a shaped ceramic material to obtain a compressive surface stress of at least about 80 MPa; and
(ii) incorporating the peened shaped ceramic material into ballistic armor.

14. The method of claim 13, wherein the surface of the shaped ceramic material is peened using a technique selected from shot-peening, ultrasonic peening, laser peening or a combination thereof.

15. The method of claim 14, wherein the surface is shot-peened, optionally with tungsten carbide impact elements.

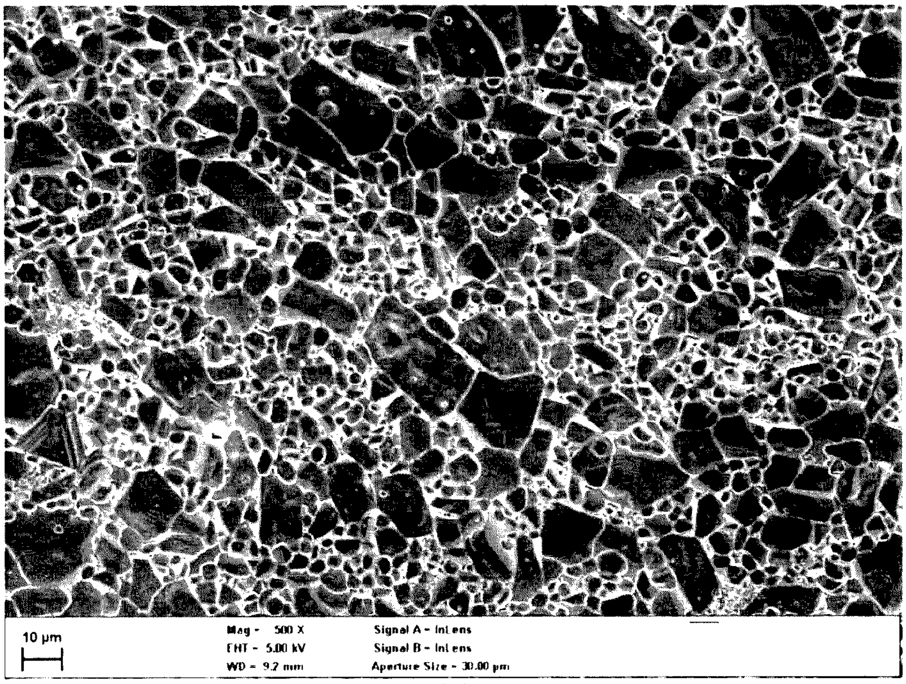
FIGURE 1

Figure 1(a)

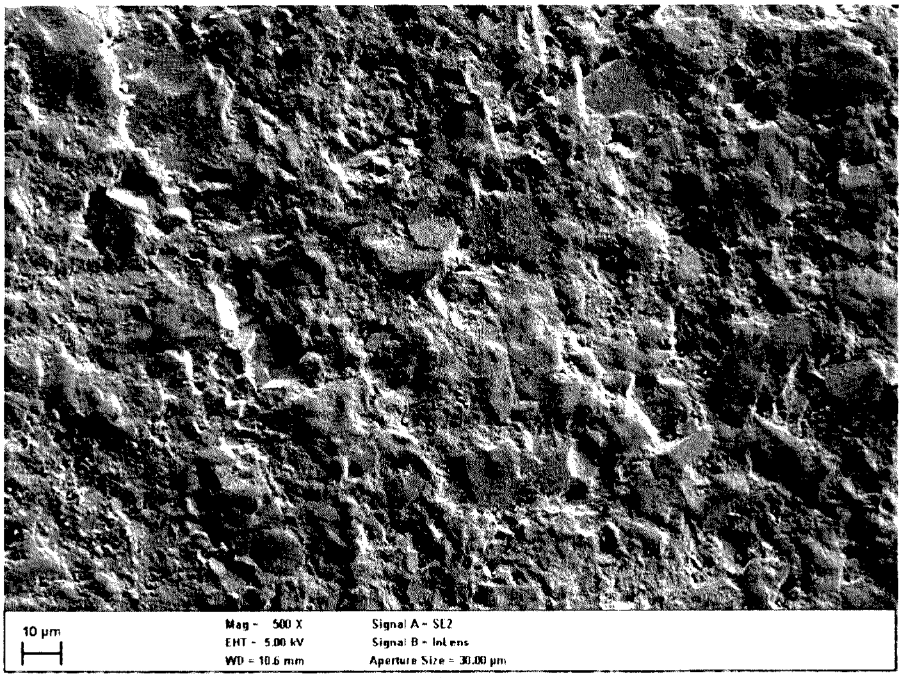
Figure 1(b)

Figure 1(c)

FIGURE 2


10 µm
Mag = 500 X
EHT = 5.00 kV
WD = 9.2 mm
Signal A = InLens
Signal B = InLens
Aperture Size = 30.00 µm

(a)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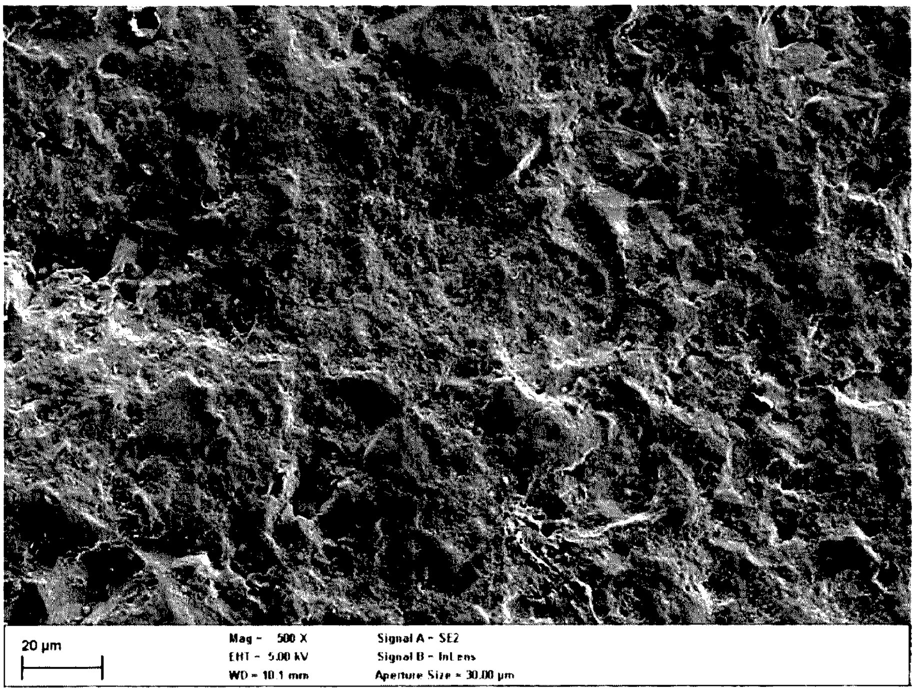
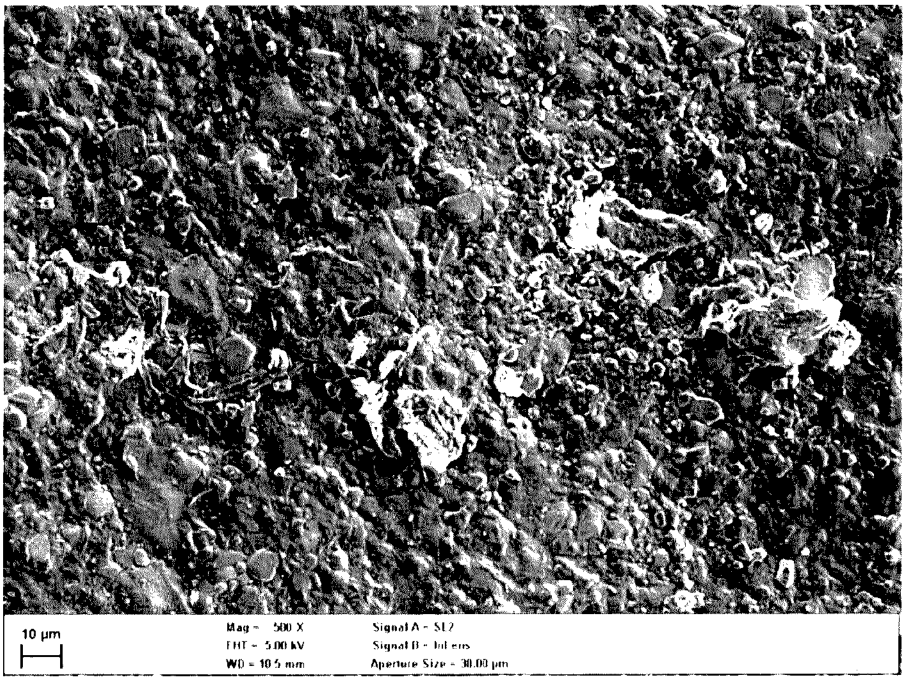
Mag = 500 X
EHT = 5.00 kV
WD = 10.6 mm
Signal A = SE2
Signal B = InLens
Aperture Size = 30.00 µm

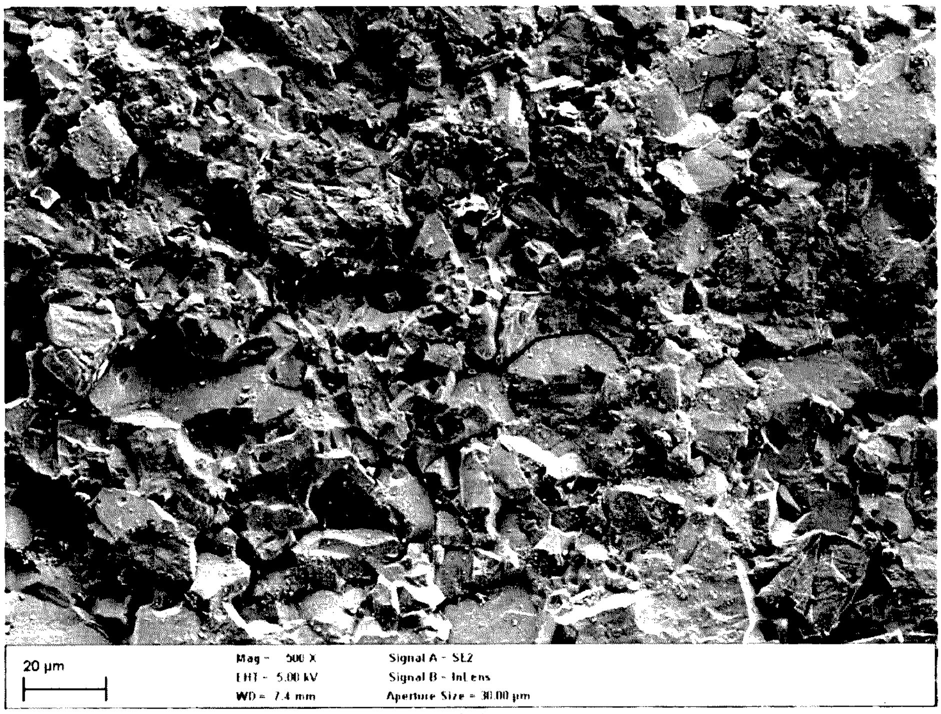
(b)


20 µm
Mag = 500 X
EHT = 5.00 kV
WD = 10.1 mm
Signal A = SE2
Signal B = InLens
Aperture Size = 30.00 µm

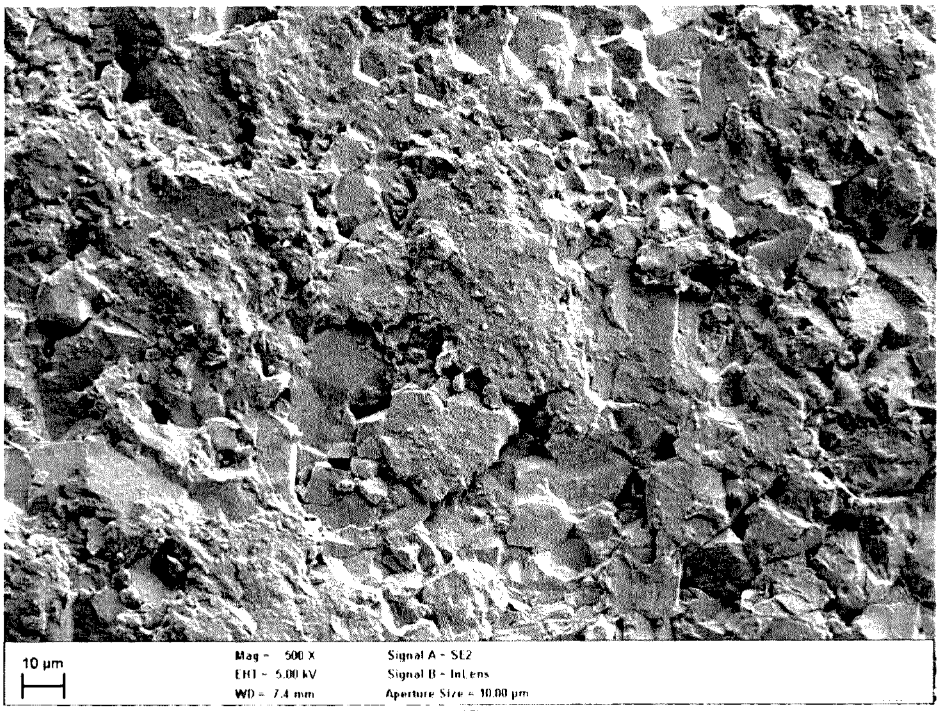
(c)


10 µm
Mag = 500 X
EHT = 5.00 kV
WD = 10.5 mm
Signal A = SE2
Signal B = InLens
Aperture Size = 30.00 µm

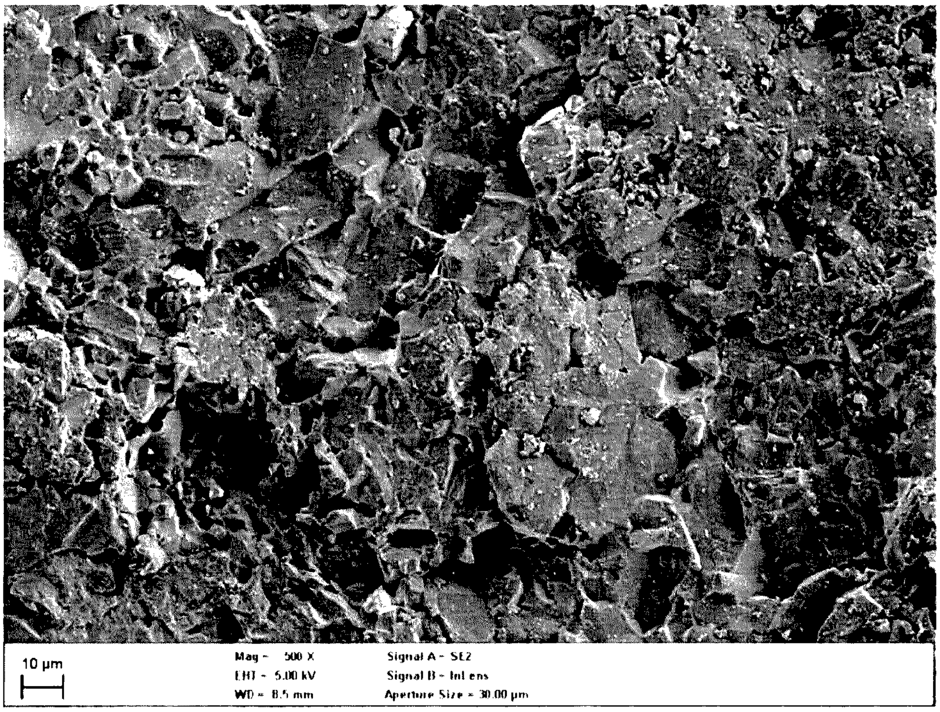
(d)


20 μm
Mag = 500 X
EHT = 5.00 kV
WD = 7.4 mm
Signal A = SE2
Signal B = InLens
Aperture Size = 30.00 μm

(e)


10 μm
Mag = 500 X
EHT = 5.00 kV
WD = 7.4 mm
Signal A = SE2
Signal B = InLens
Aperture Size = 10.00 μm

(f)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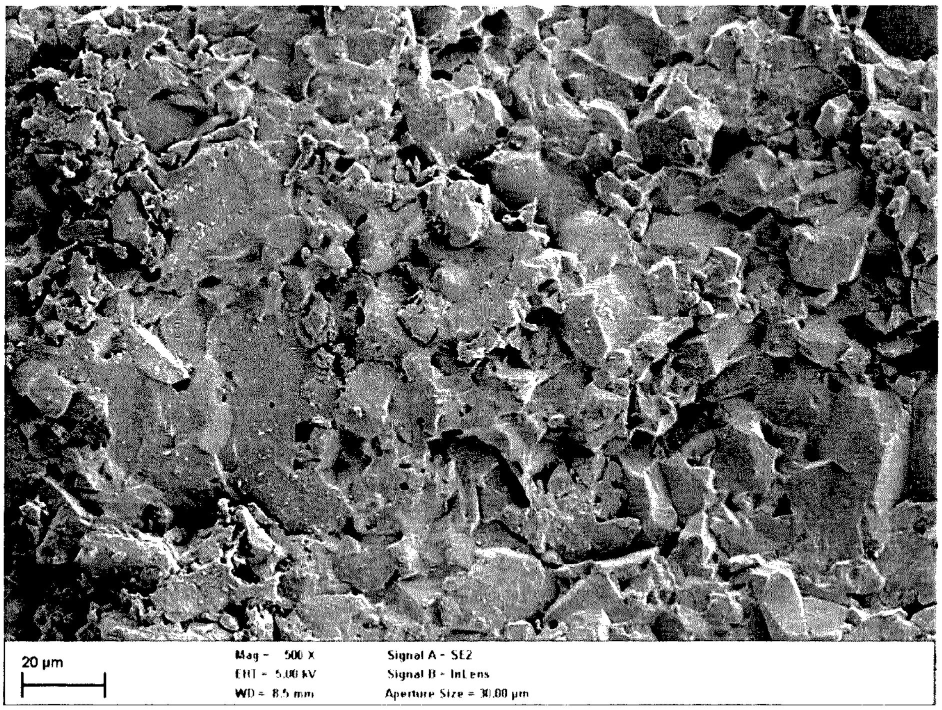
WD = 8.5 mm
Signal A = SE2
Signal B = InLens
Aperture Size = 30.00 µm

(g)


20 µm
Mag = 500 X
EHT = 5.00 kV
WD = 8.5 mm
Signal A = SE2
Signal B = InLens
Aperture Size = 30.00 µm

(h)

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EUROPEAN SEARCH REPORT

Application Number
EP 12 40 0034

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	WO 2007/124396 A2 (ORMOND LLC [US]; BUTLER THOMAS J [US]; ALBERTS DANIEL G [US]) 1 November 2007 (2007-11-01) * columns 24-33,46; figure 2 * -----	1,2,5,13	INV. F41H5/04 C04B41/80
Y	WO 2008/063697 A2 (SIKORSKY AIRCRAFT CORP [US]; BIRD CONNIE E [US]; HOLOWCZAK JOHN E [US]) 29 May 2008 (2008-05-29) * page 4, line 11 - page 7, line 2; figure 2 * -----	1-15	
Y	US 3 573 023 A (THOMAS DAVID A ET AL) 30 March 1971 (1971-03-30) * column 1, line 41 - column 3, line 68; figure 1 * -----	1-15	
A	US 2002/079602 A1 (PFEIFFER HANS-WULF [DE]) 27 June 2002 (2002-06-27) * paragraphs [0021] - [0035] * -----	1	

TECHNICAL FIELDS SEARCHED (IPC)

F41H
C04B

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	13 December 2012	Kasten, Klaus

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13-12-2012

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WO 2007124396	A2	01-11-2007	NONE	
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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- US 2011009255 A **[0002]**

Non-patent literature cited in the description

- Handbook of Residual Stress. vol. 1, 274-285 **[0013]**