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(54) **Metallic alloy nanocomposite for high-temperature structural components and methods of making**

(57) A nanocomposite comprising a plurality of nanoparticles dispersed in a metallic alloy matrix, and a structural component formed from such a nanocomposite. The metallic matrix comprises at least one of a nickel-based alloy and an iron-based alloy. The nanocomposite contains a higher volume fraction of nanoparticle

dispersoids than those presently available. The structural component include those used in hot gas path assemblies, such as steam turbines, gas turbines, and aircraft turbine. A method of making such nanocomposites is also disclosed.

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Description

[0001] The invention relates to a nanocomposite comprising a plurality of nanoparticles dispersed in a metallic alloy matrix and structural components comprising such nanocomposites. More particularly, the invention relates to method of making such nanocomposites.

[0002] The continuing effort to design and build more powerful and more efficient turbo-machinery, such as gas turbines, steam turbines, and aircraft engines, requires the use of materials having enhanced high temperature performance capabilities. Such performance enhancements require state-of-the-art materials with vastly improved mechanical properties such as strength and creep resistance.

[0003] High temperature structural materials can be strengthened in a number of ways such as, for example, grain refinement, solid solution strengthening, precipitate strengthening, composite strengthening, and dispersoid strengthening. One method of strengthening alloys called Orowan strengthening incorporates a fine distribution of hard particles into a metallic alloy matrix. Orowan strengthening depends upon the formation of an array of dispersoid particles that serve as obstacles for impeding dislocation motion within the alloy matrix. The strength of these particle-reinforced alloys is inversely proportional to the spacing between these particles, which can be controlled in turn by controlling the size of the dispersoid particles. Thus, the use of nanoparticles as dispersoids offers the potential of substantially enhancing alloy strength.

[0004] The introduction of hard dispersoid nanoparticles during the processing of the nanodispersoid-reinforced alloys presents a technical challenge. Current processes to disperse particles include powder metallurgy routes, such as mechanical alloying of micron-sized particles, in combination with secondary processes, which include hot-isostatic pressing and thermomechanical processing by hot-forging or extrusion. In the mechanical alloying process, nanoparticles are created by repeated fracture of the micron-size dispersoid particles during milling. While this is a well-established process for oxide-dispersion strengthened (ODS) alloys in iron- and nickel-based alloys (such as, for example, Inconel MA alloys), the process fails to produce a homogeneous of distribution of the particles in the alloy matrix, especially for large components. In addition, the loading of the particles in the alloy composites produced by this process is typically limited to less than 2% by volume.

[0005] Current processes are unable to produce alloy nanocomposites having sufficiently high loadings of nanoparticles. Therefore, what is needed is an alloy nanocomposite in which dispersoid nanoparticles are homogeneously distributed throughout the metallic alloy matrix. What is also needed is an alloy nanocomposite having a sufficiently high loading of dispersoid nanoparticles having high temperature performance capabilities

that adequate for use in hot gas path assemblies, such as turbine assemblies. What is further needed is a method of making alloy nanocomposites having high loadings of dispersoid nanoparticles, wherein the dispersoid nanoparticles are homogeneously distributed throughout the alloy nanocomposite.

[0006] The present invention meets these and other needs by providing a nanocomposite comprising a plurality of nanoparticles dispersed in a metallic alloy matrix, and a structural component formed from such a nanocomposite. The nanocomposite contains a higher volume fraction of nanoparticle dispersoids than those presently available. The nanocomposite may be used to fabricate structural components, such as those used in hot gas path assemblies, such as steam turbine, gas turbine, and aircraft turbine. The present invention also discloses a method of making such nanocomposites.

[0007] Accordingly, one aspect of the invention is to provide a structural component used in a hot gas path assembly comprising a nanocomposite. The nanocomposite comprises: a metallic matrix; and a plurality of nanoparticles dispersed throughout the metallic matrix, wherein the plurality of nanoparticles comprises from about 4 volume percent to about 30 volume percent of the nanocomposite.

[0008] A second aspect of the invention is to provide a nanocomposite. The nanocomposite comprises a metallic matrix and a plurality of nanoparticles dispersed throughout the metallic matrix. The plurality of nanoparticles comprises from about 4 volume percent to about 30 volume percent of the nanocomposite and is formed by a thermomechanical process followed by severe plastic deformation.

[0009] A third aspect of the invention is to provide a structural component comprising a nanocomposite. The nanocomposite comprises: a metallic matrix, wherein the metallic matrix comprises at least one of a nickel-based alloy, an iron-based alloy, and combinations thereof; and a plurality of nanoparticles dispersed throughout the metallic matrix. The plurality of nanoparticles comprises from about 4 volume percent to about 30 volume percent of the nanocomposite, and the nanocomposite is formed by a thermomechanical process followed by severe plastic deformation.

[0010] A fourth aspect of the invention is to provide a method of making a nanocomposite. The nanocomposite comprises a metallic matrix and a plurality of nanoparticles dispersed throughout the metallic matrix, wherein the metallic matrix comprises at least one of a nickel-based alloy, an iron-based alloy, and combinations thereof, and wherein the plurality of nanoparticles comprises from about 4 volume percent to about 30 volume percent of the nanocomposite. The method comprises the steps of: providing a nanocomposite powder, wherein the nanocomposite powder comprises a plurality of nanoparticles and a metallic matrix material; consolidating the nanocomposite powder; and thermomechanically processing the nanocomposite powder to

form the bulk nanocomposite.

[0011] The invention will now be described in greater detail, by way of example, with reference to the drawings, in which:-

FIGURE 1 is a transmission electron microscopy (TEM) image of a nanocomposite of the present invention;

FIGURE 2 is a flow chart illustrating the method of making a nanocomposite according to the present invention; and

FIGURE 3 is a scanning electron microscopy (SEM) image of a nickel-based alloy nanocomposite powder of the present invention containing 5 volume percent yttrium oxide.

[0012] In the following description, like reference characters designate like or corresponding parts throughout the several views shown in the figures. It is also understood that terms such as "top," "bottom," "outward," "inward," and the like are words of convenience and are not to be construed as limiting terms.

[0013] Referring to the drawings in general and to Figure 1 in particular, it will be understood that the illustrations are for the purpose of describing a preferred embodiment of the invention and are not intended to limit the invention thereto. Figure 1 is a transmission electron microscopy (TEM) image of a nanocomposite 100 of the present invention. Nano composite 100 comprises a metallic matrix 110 and a plurality of nanoparticles 120 dispersed throughout the metallic matrix 110. The plurality of nanoparticles 120 comprises from about 4 volume percent to about 30 volume percent of nanocomposite 100. In particular, Figure 1 shows a nanocomposite 100 in which metallic matrix 110 comprises a nickel-based alloy and plurality of nanoparticles 120 comprises yttrium oxide (Y_2O_3). In the sample shown in Figure 1, the yttrium oxide nanoparticles comprise about 5 volume percent of nanocomposite 100.

[0014] Metallic matrix 110 comprises at least one of a nickel-based alloy, an iron-based alloy, and combinations thereof. Non-limiting examples of such nickel-based alloys that may be used to form metallic matrix 110 include Ni-Cr based alloys, Ni-Cr-Al based alloys, and combinations thereof. Iron-based alloys that may be used to form metallic matrix 110 include, but are not limited to Fe-Cr based alloys, Fe-Cr-Al based alloys, and combinations thereof.

[0015] The plurality of nanoparticles 120 comprises at least one of an inorganic oxide, an inorganic carbide, an inorganic nitride, an inorganic boride, an inorganic oxycarbide, an inorganic oxynitride, an inorganic silicide, an inorganic aluminide, and combinations thereof. Inorganic oxides that may comprise the plurality of nanoparticles 120 include, but are not limited to, yttria, alumina, zirconia, hafnia, and combinations thereof. The inorgan-

ic carbides that may comprise the plurality of nanoparticles 120 include, but are not limited to, carbides of hafnium, tantalum, molybdenum, zirconium, niobium, chromium, titanium, tungsten, and combinations thereof.

[0016] In one embodiment, each of the plurality of nanoparticles 120 is substantially spherical in shape. In other embodiments of the invention, each of the plurality of nanoparticles may be rods, needles, spheroidal shapes, and the like. Alternatively, plurality of nanoparticles 120 may comprise a mixture of nanoparticles having a variety of such shapes. Each of the plurality of nanoparticles has at least one dimension that is in a range from about 10 nm to about 500 nm. In one embodiment, a dimension of each one of the plurality of nanoparticles 120 is in a range from about 10 nm to about 30 nm.

[0017] One method of strengthening of alloys is a mechanism known as Orowan strengthening, in which a fine distribution of hard particles is incorporated into an alloy. In this strengthening mechanism, an array of such dispersoid particles impedes dislocation motion. The strength of such particle-reinforced alloys is inversely proportional to the spacing between the dispersoid particles. Spacing of the dispersoid particles can, in turn, can be controlled by controlling the size of the dispersoid particles. For a given volume of dispersoid particles, using dispersoid particles with sizes in the nanometer range can decrease spacing and thus substantially enhance alloy strength.

[0018] Currently, powder metallurgy routes in combination with secondary processes, such as mechanical alloying processes, are used to disperse particles. In the mechanical alloying process, nanoparticles are created by repeated fracture of micron-size dispersoid particles during milling. Such processes fail to achieve a homogeneous particles distribution within the alloy, particularly for large components. In addition, the loading of the particles in the alloys formed by such processes is typically limited to less than 2% by volume.

[0019] Accordingly, the nanocomposite 100 provided by the present invention overcomes the loading and dispersion limitations encountered with current dispersoid strengthened alloys. The invention provides a nanocomposite 100 with superior mechanical properties achieved through dispersoid strengthening by a providing a higher volume fraction of nanoparticle dispersoids than those presently available. The plurality of nanoparticles 120 comprises from about 4 volume percent to about 30 volume percent of nanocomposite 100. In one embodiment, the plurality of nanoparticles 120 comprises from about 10 volume percent to about 30 volume percent of nanocomposite 100.

[0020] The higher volume loadings of the plurality of nanoparticles 120 of the present invention provide nanocomposite 100 with mechanical properties that are superior to those of current state-of-the art materials. Nanocomposite 100 also exhibits greater microstructural stability at elevated temperatures, allowing strength and creep resistance to be retained at much higher tem-

peratures than those provided by current oxide dispersion strengthened (ODS) alloys. Nanocomposite 100 is thermally stable up to about 1200°C.

[0021] As described herein, the nanocomposite 100 of the present invention may be formed into high-temperature structural components for use in hot gas path assemblies, such as steam turbines, gas turbines, and aircraft engines. Such components include, but are not limited to: rotating components, such as turbine airfoils and turbine disks; static components, such as ducts, frames, and casings; combustors; and the like. Forming techniques, such as powder metallurgy techniques, thermomechanical processing, and the like, that are well known the art, can be used to form nanocomposite 100 into the desired structural component.

[0022] In addition to nanocomposite 100 and a structural component made from nanocomposite 100, the present invention also provides a method of making nanocomposite 100. A flow chart illustrating the method 200 of making nanocomposite 100 is shown in Figure 2.

[0023] Referring to Step 210 in Figure 2, a plurality of nanoparticles 120 is first combined with a metallic matrix material, such as, for example, an alloy powder, to form a nanocomposite powder. In one embodiment, the nanocomposite powder is produced by blending at least one metallic alloy powder with a predetermined volume fraction of hard dispersoid nanoparticles. Each of the dispersoid nanoparticles has at least one dimension ranging from about 10 nm to about 500 nm. Techniques, such as, mechanofusion, mechanical alloying, cryomilling, and the like, are used separately or in combination with each other to form the nanocomposite powder. Such methods, particularly mechanofusion and cryomilling, act to coat and surround individual particles of the metallic alloy powder with a plurality of dispersoid nanoparticles. A SEM image of a nickel-based alloy nanocomposite powder, containing 5 volume percent yttrium oxide, of the present invention is shown in Figure 3.

[0024] In one embodiment, the nanocomposite powder is produced by in-situ formation of a plurality of nanoparticles 120 within an alloyed metallic matrix 110. This is achieved by cryomilling micron-sized particles of the metallic alloy matrix material in a reactive atmosphere, comprising, for example, at least one of nitrogen, and a hydrocarbon, such as, but not limited to, methane. The gases present in the reactive atmosphere may additionally serve as the coolant for cryomilling. Alternatively, cryomilling may be performed in an inert atmosphere that comprises, for example, at least one of argon and helium.

[0025] The cryomilling feedstock comprises at least one alloyed metal powder that comprises at least one metallic element. The at least one metallic element may be either reactive or refractory in nature. Such metallic elements include, but are not limited to, Al, Cr, Ti, Mo, Nb, Ta, W, B, Zr, Hf, Ta, combinations thereof, and the like. The plurality of nanoparticles 120 comprising the

metallic elements is formed by cryomilling such metallic alloys. The cryomilling action separates highly reactive nanosize particles from the micron-size particles of metallic alloy matrix material. When cryomilled in a reactive atmosphere, the metallic nanoparticles react with the reactive gases to form hard dispersoid nanoparticles, such as oxides, carbide, nitrides, combinations thereof, and the like. The hard dispersoid nanoparticles surround each of the micron-size particles of metallic alloy matrix material to achieve the fine distribution incorporation that is needed for Orowan strengthening.

[0026] The nanocomposite powder is then consolidated (Step 220) and thermomechanically processed (Step 230) to form a bulk dispersoid nanoparticle-reinforced metallic alloy nanocomposite 100. Consolidation of the nanocomposite powder (Step 220) into a compact is performed using techniques, such as cold pressing, hot pressing, forging, extruding, canning, and the like, that are known in the metallurgical arts. Step 230 is carried out using techniques such as, but not limited to, forging, hot-extrusion, and hot-rolling, either separately or in combination with each other. In another embodiment, dispersoid nanoparticle-reinforced metallic alloy nanocomposite 100 is formed from the consolidated nanocomposite powder compact by subjecting the nanocomposite powder compact to severe plastic deformation. Such severe plastic deformation may be accomplished by one of equiaxial channel angular processing, torsion extrusion, and twist extrusion of the nanocomposite powder.

[0027] The following example illustrates the various features and advantages offered by the present invention, and in no way is intended to limit the invention thereto.

Example 1

[0028] For the purpose of this example, the alloys Ni-20Cr and Fe-12.5Cr were selected as the nickel-based and iron-based matrix alloy materials, respectively, for the nanocomposite, and yttrium oxide (Y_2O_3) was selected as the reinforcing dispersoid nanoparticle.

[0029] Prototype nickel-based and iron-based metallic alloy nanocomposites were fabricated by first forming nanocomposite powders by blending -325 mesh (44 micron) of either nickel-based (Ni-20 weight percent Cr) or iron-based (Fe-12.5 weight percent Cr) alloy powder with various volume fractions (ranging from 5 to 10 volume percent) of size yttrium oxide nanopowders (particle sizes ranging from 50-100 nm). The nanocomposite powders were formed using mechanofusion, in which the yttrium oxide powder was mechanically fused or embedded into the metal powder surface. As an alternative to blending, other procedures, such as cryomilling or mechanical alloying, can be employed to make the nanocomposite powder. The nanocomposite powder was then consolidated by enclosing the nanocomposite powder in a stainless steel can, evacuating, and sealing

the can, and extruding the can against a flat faced die at a temperature of 1100°C. The extruded can was re-machined and hot extruded at a temperature of 1100°C using a 9:1 reduction ratio.

[0030] The resulting as-fabricated metallic alloy nanocomposites were examined by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) to evaluate the respective grain sizes of the matrix and the dispersoid nanoparticles, as well as distribution of the dispersoid nanoparticles in the alloy matrix and grain boundaries. A TEM image of an iron-based (Fe-12.5 weight percent Cr) alloy nanocomposite containing 5 volume percent yttrium oxide is shown in Figure 1. The microstructure of the nanocomposite 100 comprises grains of metallic alloy matrix 110, ranging from about 5 microns to about 10 microns in size, and yttrium oxide nanoparticles 120, ranging from about 100 nm to about 500 nm in size.

Claims

1. A structural component in a hot gas path assembly, said structural component comprising a nanocomposite (100), wherein said nanocomposite (100) comprises:

- a) a metallic matrix (110); and
- b) a plurality of nanoparticles (120) dispersed throughout said metallic matrix 110, wherein said plurality of nanoparticles (120) comprises from about 4 volume percent to about 30 volume percent of said nanocomposite (100).

2. The structural component according to Claim 1, wherein said metallic matrix (110) comprises at least one of a nickel-based alloy, an iron-based alloy, and combinations thereof.

3. A structural component in a hot gas path assembly comprising a nanocomposite (100), wherein said nanocomposite (100) comprises:

- a) a metallic matrix (110), wherein said metallic matrix (110) comprises at least one of a nickel-based alloy, an iron-based alloy, and combinations thereof; and
- b) a plurality of nanoparticles (120) dispersed throughout said metallic matrix (110), wherein said plurality of nanoparticles (120) comprises from about 4 volume percent to about 30 volume percent of said nanocomposite (100), and wherein said nanocomposite (100) is formed by a thermomechanical process followed by severe plastic deformation.

4. The structural component according to Claim 1, wherein each of said plurality of nanoparticles (120)

comprises at least one of an inorganic oxide, an inorganic carbide, an inorganic nitride, an inorganic boride, an inorganic oxycarbide, an inorganic oxynitride, an inorganic silicide, an inorganic aluminide, and combinations thereof.

5. The structural component according to Claim 1 or Claim 3, wherein each of said plurality of nanoparticles (120) has at least one dimension, wherein said at least one dimension that is in a range from about 10 nm to about 500 nm.

6. The structural component according to Claim 1 or Claim 3, wherein said plurality of said nanoparticles comprise from about 10 volume percent to about 30 volume percent of said nanocomposite (100).

7. A nanocomposite (100), said nanocomposite (100) comprising:

- a) a metallic matrix (110); and
- b) a plurality of nanoparticles (120) dispersed throughout said metallic matrix (110), wherein said plurality of nanoparticles (120) comprises from about 4 volume percent to about 30 volume percent of said nanocomposite (100), and wherein said nanocomposite (100) is formed by providing a nanocomposite powder, consolidating (220) said nanocomposite powder to form a green body, and thermomechanically processing (240) said green body to form said nanocomposite (100).

8. A method (200) of making a bulk nanocomposite (100), wherein the nanocomposite 100 comprises a metallic matrix (110) and a plurality of nanoparticles (120) dispersed throughout the metallic matrix (110), wherein the metallic matrix (110) comprises at least one of a nickel-based alloy, an iron-based alloy, and combinations thereof, and wherein the plurality of nanoparticles (120) comprises from about 4 volume percent to about 30 volume percent of the nanocomposite (100), the method (200) comprising the steps of:

- a) providing a nanocomposite powder, wherein the nanocomposite powder comprises a plurality of nanoparticles (120) and a metallic matrix material;
- b) consolidating (220) the nanocomposite powder; and
- c) thermomechanically processing (240) the nanocomposite powder to form the bulk nanocomposite (100).

9. The method (200) according to Claim 19, wherein the step of providing the nanocomposite powder comprises forming the plurality of nanoparticles

(120) by at least one of mechanofusion, mechanical alloying, cryomilling, and combinations thereof.

10. The method (200) according to Claim 19, wherein the step of thermomechanically processing (240) the nanocomposite powder comprises subjecting the nanocomposite powder compact to severe plastic deformation.

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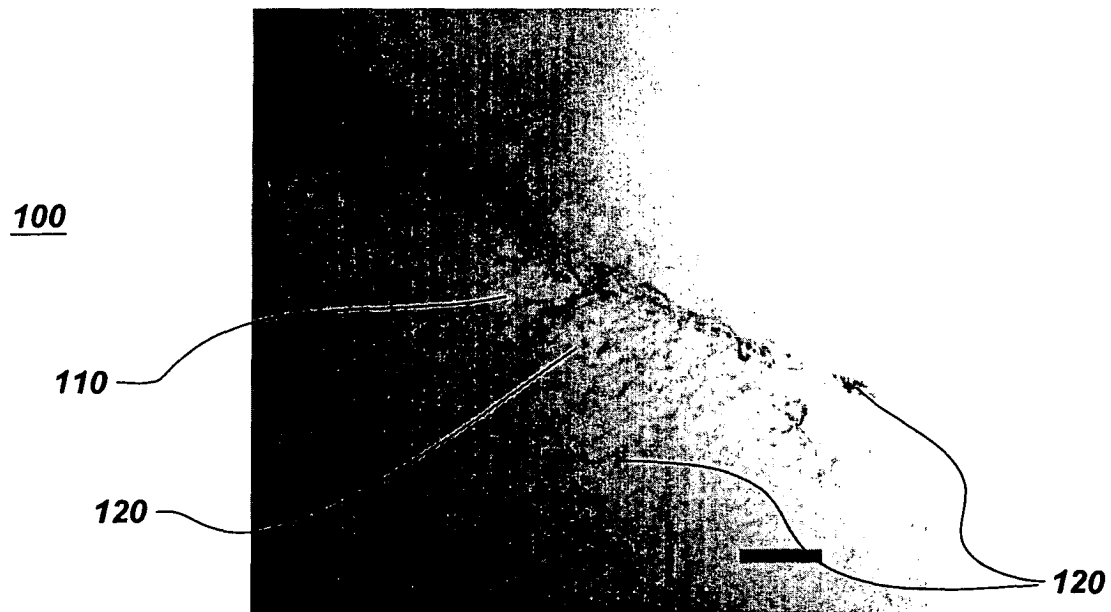


Fig. 1

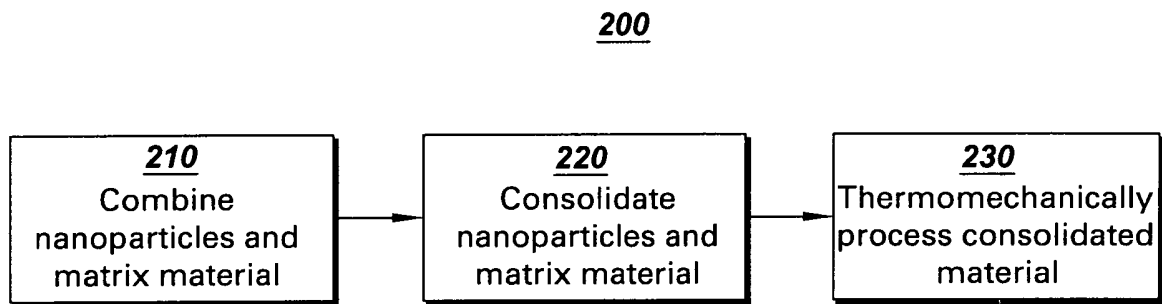


Fig. 2

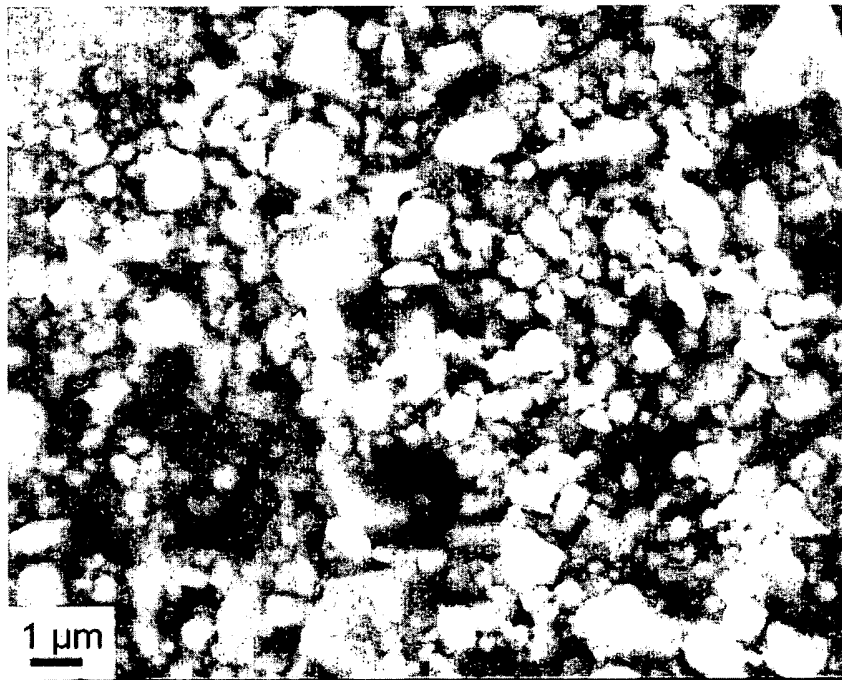


Fig. 3