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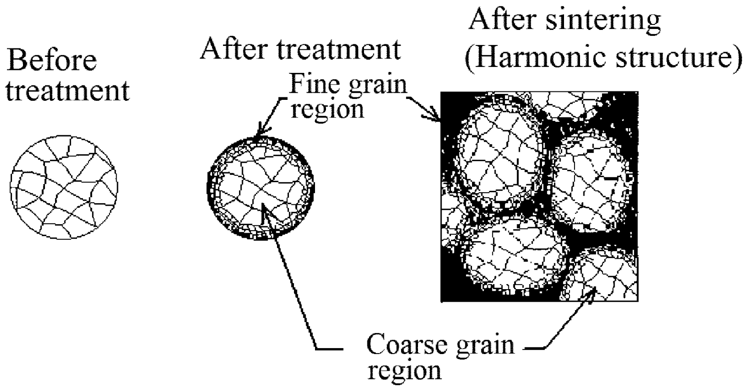
(54) SURFACE TREATMENT METHOD FOR POWDERED METAL MATERIAL

(57) Provided is a surface treatment method for safely, simply and quickly improving a powdered metal material to be used as a material in powder metallurgy, thermal spraying, or the like. The present invention involves: using a blast-machining device equipped with a dust collection means for spraying a spray powder and compressed air inside a work space and causing the same to collide with a collidable object, and removing and recovering dust by aspirating the interior of the work space; performing a blast treatment for repeatedly causing collisions at a spraying speed of 100-300 m/sec between a powdered metal material having an average particle diameter of 10-200[mu]m, and a medium material having a hardness equal to or greater than that of the powdered metal material; and detaching a surface oxide from the powdered metal material, and forming a fine-grain region which is near the surface of the powdered metal material and has a finer grain size than that of the center section thereof. The sintered metal obtained by sintering the powdered metal material subjected to the surface treatment has a concordant composition in which the fine-grain region and the large-grain region are concordantly arranged, and exhibits a balance of high ductility and high strength.

FIG. 6A FIG. 6B FIG. 6C



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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a method for surface treatment of a powdery metal material, and more particularly to a method for surface treatment of a powdery metal material used as a material in manufacture of a metal product or in formation of coating using metal powder such as powder metallurgy such as sintering or thermal spraying.

DESCRIPTION OF THE RELATED ARTS

[0002] The "sintering", i.e., obtaining sintered metal by heating and solidifying an aggregate of a powdery metal material at a temperature lower than a melting point is widely used as a type of powder metallurgy for manufacturing various mechanical components such as gears, and particularly recently, use of the powdery metal material as a shaping material in a 3D printer is proposed. It is also proposed that molding of a desired three-dimensional cubic model directly by the metal material from shape data such as CAD by irradiating a laser beam or an electron beam to a powdery metal material in a predetermined pattern and then sintering it (Non-Patent Document 1), and in the three-dimensional cubic model manufactured by sintering of the powdery metal material as above, unlike a resin model which has been manufactured by a prior-art 3D printer, application not only as a model or a sample but also a direct use as components to be incorporated in a machine or the like are expected.

[0003] However, sintered metal obtained by sintering the powdery metal material can easily have a density and strength lower than a case of melt molding due to occurrence of residual pores and the like, and it cannot be used in practice as a mechanical component as it is in many cases.

[0004] Thus, with the purpose of removing such residual pores leading to lower density and lower strength, treatment called "sinter forging" for forging the obtained sintered metal has been in practice, but as described above, if treatment of sinter forging is further required for a component manufactured by simple three-dimensional shaping using the 3D printer, the merit of simplicity is lost.

[0005] Unlike the post-treatment as the aforementioned sinter forging, researches for improving strength of the sintered metal by devising a composition or structure of the powdery metal material which is a raw material used for sintering have been promoted, and as one of them, there was a report that by applying mechanical milling treatment by stirring with a ball mill to the powdery metal material before sintering so as to change an internal structure of the material, sintered metal with high strength can be obtained (Non-Patent Documents 2 and 3).

[0006] In this method, the mechanical milling treatment by a ball mill is performed to the powdery metal material having a predetermined crystalline structure as illustrated in Fig. 6A so as to apply severe plastic deformation to the powdery metal material in a concentrated manner, a region called a shell formed by refining crystal grains (hereinafter this region shall be referred to as a "fine grain region") is generated in the vicinity of a surface of the powdery metal material as illustrated in Fig. 6B, and as a result, a powdery metal material can be obtained provided with a region at a center part called a core maintaining an original crystal grain diameter (hereinafter this region shall be referred to as a "coarse grain region") and the aforementioned fine grain region covering this coarse grain region.

[0007] By sintering the powdery metal material in which the coarse grain region and the fine grain region are formed as described above, the obtained sintered metal is metal having a structure called "harmonic structure" in which a network-state structure formed of the fine grain regions of the powdery metal materials connected to each other and the coarse grain regions arranged harmonically in the fine grain regions as illustrated in Fig. 6C (in the present invention, such metal is called "harmonic structure metal") is obtained, and it has been reported that in such harmonic structure metal, strength can be drastically improved while ductility equal to that of sintered metal having uniform equiaxed grain structure obtained by using a normal powdery metal material to which the mechanical milling treatment is not applied is maintained (Non-Patent Document 2).

[0008] In the aforementioned description, the example in which the manufacturing method of the "harmonic structure metal" is realized by "sintering" is described, but with regard to the powdery metal material provided with the aforementioned fine grain region, the formed metal coating can also be made the "harmonic structure metal" even if the metal coating is formed on the surface of a base material by "thermal spraying".

DOCUMENTS OF RELATED ART

NON-PATENT DOCUMENTS

[0009]

Non-Patent Document 1: "Special Feature 2-3D Printer 'Attracting!' 'Design/Manufacture Solution Exhibition' Report,

Diversification of Molding Materials" [issued by Nikkei BP, "Nikkei Monodukuri August issue", (published on August 1, 2013) pp. 64 to 58]
Non-Patent Document 2: "Creation of Innovative Structural Material Realizing both High Strength and High Ductility by Harmonic Structure Control" by Kei Ameyama, Tatsuya Sekiguchi ["Journals of The Japan Society for Heat Treatment" Vol. 53, No. 1 2013" issued by The Japan Society for Heat Treatment (published on February 28, 2013) pp. 1 to 2]
Non-Patent Document 3: "Tripled Renewed Brass Hardness, Chip Molding/Sintering, New Technology by Nihon Univ. Improved Conductivity to Practice" [Nikkan Kogyo Shimbun (April 30, 2013)]

DISCLOSURE OF THE INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0010] As introduced as Non-Patent Documents 2 and 3, when sintering is to be performed by using the powdery metal material subjected to stirring by a ball mill in advance, the sintered metal obtained by the sintering has the "harmonic structure" so that metal having excellent characteristics of both high ductility and high strength is obtained.
[0011] However, as described in Non-Patent Documents 2 and 3, when the powdery metal material is treated by the ball mill, treatment efficiency is extremely poor, and treatment time is 100 hours in Non-Patent Document 2 and 32 hours in Non-Patent Document 3 as examples.
[0012] Moreover, the treatment of the powdery metal material by the ball mill has a risk of powder dust explosion and is an extremely dangerous work.
[0013] That is, since the powdery metal material used for sintering and the like has a fine grain diameter at approximately 100 μm in general, if the powdery metal material is contained in the ball mill, stirred under presence of air and subject to a friction force or an impact force, discharge of static electricity generated by friction in stirring can cause powder dust explosion.
[0014] The powder dust explosion here occurs when the following three elements: presence of oxygen; generation of dusts at explosion lower limit density or more; and presence of ignition source are all satisfied and thus, if occurrence of the powder dust explosion is to be prevented, one or more of these conditions need to be eliminated. However, it is impossible to remove occurrence of friction or impact, which can be the ignition source, from the ball mill inside which the friction force and the impact force are generated in order to apply severe plastic deformation to the powdery metal material.
[0015] Thus, if the powder dust explosion is to be prevented, the work should be performed in a state in which oxygen is eliminated by filling an inside of the ball mill with an inactive gas or the like, or an input amount of the powdery metal material should be adjusted so as to be less than the explosion lower limit density, or the both should be done.
[0016] However, if the treatment is performed in a state in which the ball mill is filled with the inactive gas, a manufacturing cost is drastically raised, and considering that the explosion lower limit density of the powdery metal [200 mesh (opening: 74 μm) completely through] is 35 g/m^3 for aluminum, 45 g/m^3 for titanium, and 120 g/m^3 for iron ["Safety and Hygiene of Arc Welding (third)" extracted from WE-COM magazine No. 6 (published in October 2012), Japan Welding Engineering Society, General Incorporated Association], if stirring is to be performed at the explosion lower limit density or less, only an extremely small amount can be treated at one time. Treatment might be possible for small-scaled production at an experimental level in a lab, but treatment of a large amount of the powdery metal material by a ball mill on a commercial base is impossible.
[0017] Moreover, even if the aforementioned treatment by the ball mill can be applied to the treatment of the powdery metal material, surface oxides such as oxidized scale exfoliated from a surface of the powdery metal material are mixed in the powdery metal material treated by this method, and the oxides prevent binding between powdery metal materials during sintering and hinder improvement of strength.
[0018] That is, the powdery metal material used for sintering or thermal spraying is manufactured by an atomizing method in general, but since in this atomizing method, the powdery metal material is manufactured by spraying/scattering molten metal for refining and by instantaneously rapid cooling/solidifying it, the oxidized scale adheres to the surface of the powdery metal material.
[0019] On the powdery metal materials manufactured by methods other than the atomizing method, an oxidized film which is a surface oxide is also formed more or less by contact with oxygen in the air.
[0020] Even if these surface oxides such as the oxidized scale are exfoliated from the surface of the powdery metal material by friction or impact received during stirring in the ball mill, the oxides exfoliated as above are not eliminated even after the exfoliation but stay mixed in the powdery metal material due to a structure of the ball mill.
[0021] Moreover, since the exfoliated oxides are continuously stirred together with the powdery metal material in the ball mill, a part of the exfoliated oxides is pressed onto the surface of the powdery metal material by friction or impact caused by stirring and adheres thereto again by being embedded or the like.

[0022] Thus, if the powdery metal material treated by the ball mill is taken out as it is and used for sintering, improvement of strength is suppressed by presence of the oxides mixed in the powdery metal material.

[0023] On the other hand, in order to remove the oxides mixed in the powdery metal material, the powdery metal material after the treatment by the ball mill can be subjected to wind-power sorting or the like, for example, but with this method, another process for further eliminating the oxides needs to be provided in addition to the treatment by the ball mill, whereby productivity is further lowered.

[0024] Moreover, with this method, though the oxides mixed in the powdery metal material can be removed to some degree, the oxides re-adhering to the surface of the powdery metal material cannot be separated/removed.

[0025] Thus, if surface treatment of the powdery metal material can be performed by a method which can also remove such surface oxidized film, further improvement of strength of the obtained harmonic structure metal can be expected.

[0026] The present invention was made in order to overcome the disadvantages in the aforementioned prior-art techniques and has an object to provide a method for surface treatment of a powdery metal material which can perform treatment of forming the aforementioned fine grain region on a surface of the powdery metal material used as a material for obtaining a metal product or metal coating provided with a harmonic structure by a method such as powder metallurgy such as sintering, thermal spraying and the like without a concern of powder dust explosion and can perform exfoliation of oxides from the surface and removal of the oxides after the exfoliation easily and reliably and also efficiently in a relatively short time.

MEANS FOR SOLVING THE PROBLEMS

[0027] In order to achieve an objective of the invention, a method for surface treatment of a powdery metal material according to the present invention used for manufacture of harmonic structure metal in which a fine grain region and a coarse grain region are harmonically arranged comprises the steps of:

using a blasting machine which ejects a medium substance or a powdery metal material as ejection powder with a compressed gas in a cabinet and causes the ejection powder to collide against a medium substance or a powdery metal material as an object to be collided and comprises dust collecting means for suctioning an inside of the cabinet and removing/collecting power dusts; and

performing blasting of causing the powdery metal material as the object to be collided having an average grain diameter of 10 to 200 μm and the medium substance as the ejection powder having hardness equal to or higher than that of the powdery metal material to collide with each other repeatedly at an ejection speed of 100 to 300 m/sec, and exfoliate surface oxides from the powdery metal material and also form the fine grain region having a crystal grain diameter smaller than that of a center part of the powdery metal material in the vicinity of a surface of the powdery metal material.

[0028] The blasting machine used in said blasting has a cyclone for classifying the power dusts and the ejection powder.

[0029] Furthermore, in the dust collecting means of the blasting machine, the collected power dusts are stored with inflammable powder, such as calcium carbonate or the like.

[0030] In the method for surface treatment of a powdery metal material, the ejection powder and the object to be collided may be exchanged each other, i.e., the blasting may be performed by using the powdery metal material as the ejection powder and the medium substance as the object to be collided; and
the blasting may be performed by using the medium substance with a powdery shape as the ejection powder and the powdery metal material as the object to be collided.

[0031] Furthermore, the medium substance may be made a powdery metal material of the same material and the same average grain diameter as the powdery metal material, and the ejection powder and the object to be collided may be both made into the powdery metal material.

[0032] A material of the medium substance may be metal having hardness equal to or higher than hardness of the powdery metal material or ceramic having hardness equal to or higher than hardness of the powdery metal material after the surface treatment.

EFFECT OF THE INVENTION

[0033] According to the method for surface treatment of the powdery metal material of the present invention, the following marked effects can be obtained by means of the aforementioned constitution of the present invention.

[0034] By performing blasting of causing a powdery metal material having an average grain diameter of 10 to 200 μm and a medium substance having hardness equal to or higher than that of the powdery metal material to be collided with each other repeatedly at an ejection speed of 100 to 300 m/sec, surface oxides on the powdery metal material are removed, and repetition of rapid temperature rise and cooling occurring in the vicinity of a surface of the powdery metal material at the collision refines crystal grains in the vicinity of the surface of the powdery metal material, and the powdery metal material in which a fine grain region having a crystal grain diameter smaller than a crystal grain diameter at a center part is formed in the vicinity of the surface can be treated by a relatively simple method of blasting easily and in a large quantity in a short time.

[0035] Moreover, by performing the aforementioned blasting by means of a blasting machine with a dust collection function, mass production is made possible while a risk of powder dust explosion is avoided, and by removing and collecting surface oxides such as oxidized scale exfoliated from the surface of the powdery metal material as powder dusts by suctioning in a cabinet, a powdery metal material without mixing of the surface oxides could be obtained without separately providing a process of removing the surface oxides in a post-process.

[0036] Particularly, if means provided with a cyclone for classifying the powder dusts from the ejected powder is to be used as dust collecting means for the blasting, even if the powdery metal powder and the exfoliated surface oxides are collected in the mixed state, the surface oxides can be classified with the powder dusts from the ejected powder and collected so that the powdery metal material from which the surface oxides are removed with higher accuracy could be obtained.

[0037] Moreover, in the dust collecting means of the aforementioned blasting machine, if the removed powder dusts are stored with inflammable powder such as calcium carbonate, a risk of powder dust explosion not only in a processing chamber but also in the collecting machine could be reduced.

[0038] This blasting may be so configured that the powdery metal material as the ejection powder is ejected to the medium substance and made to collide against said medium substance, or that the medium substance as the ejection powder is ejected to the powdery metal material and is made to collide against said powdery metal material, but when it is so configured that both the ejection powder and an object to be collided are made to be a powdery metal material having the same average grain diameter and formed of the same material and the powdery metal material is ejected to and is made to collide against the powdery metal material, the surface treatment is applied to both the powdery metal powder as the ejection powder and the powdery metal powder as the object to be collided, and a throughput could be doubled.

BRIEF DESCRIPTION OF THE DRAWINGS

[0039]

Fig. 1A is schematic explanatory view of a blasting machine of a gravity type used in a method for surface treatment of the present invention;

Fig. 1B is schematic explanatory view of a blasting machine of a direct pressure type used in a method for surface treatment of the present invention;

Fig. 2 is a graph showing an X-ray diffraction result of an untreated stainless powder (SUS304 equivalent);

Fig. 3 is a graph showing an X-ray diffraction result of a stainless powder (SUS 304 equivalent) treated by a method in Example 1;

Fig. 4 is a graph showing an X-ray diffraction result of an untreated powder high-speed tool steel (SKH equivalent);

Fig. 5 is a graph showing an X-ray diffraction result of a powder high-speed tool steel (SKH equivalent) treated by a method in Example 2; and

Fig. 6A is an explanatory view explaining creation of a harmonic structure in which is a schematic view of an untreated powdery metal material;

Fig. 6B is an explanatory view explaining creation of a harmonic structure in which is a schematic view of a powdery metal material after treatment by a ball mill; and

Fig. 6C is an explanatory view explaining creation of a harmonic structure in which is a schematic view of harmonic structure metal obtained by sintering the powdery metal material in Fig. 6B.

[0040] Subsequently, embodiments of the present invention will be described below by referring to the attached drawings.

ENTIRE CONFIGURATION

[0041] The present invention is to remove surface oxides such as an oxidized scale prohibiting improvement of strength in sintering or thermal spraying from a surface of a powdery metal material and to form a fine grain region having a crystal grain diameter smaller than the crystal grain diameter at a center part in the vicinity of the surface of the powdery metal material by performing blasting of repeatedly causing the powdery metal material which is a treatment target and a medium substance which collides against the powdery metal material to collide against each other at a predetermined ejection speed by means of a known blasting machine.

[0042] As described above, a metal product obtained by a method of powder metallurgy such as sintering or metal coating manufactured by thermal spraying by using a powdery metal material in which a coarse grain region having a relatively large crystal grain diameter is formed at the center part and a fine grain region with a smaller crystal grain diameter than that of the coarse grain region is formed in the vicinity of the surface become harmonic structure metal having a crystalline structure [see Fig. 6C] in which the coarse grain regions are harmonically arranged in a network of a fine grain structure formed by binding the fine grain regions and exhibiting an excellent characteristic that both high ductility and high strength are realized.

POWDERY METAL MATERIAL

[0043] The powdery metal material which is a treatment target in the present invention is powdery metal having an average grain diameter of 10 to 200 μm to be used as a material in powder metallurgy such as sintering or thermal spraying, and various materials can be used as long as it is applicable to powder metallurgy or thermal spraying. The material may be constituted by either one of pure metal and an alloy.

[0044] As an example, metal used for powder metallurgy in general includes iron-, copper-, stainless-, titanium-, and tungsten-based metal and metal used for thermal spraying in general includes zinc, aluminum, copper and the like. They can be all included in the material of the powdery metal material in the present invention.

[0045] The powdery metal material to be used can be manufactured by various methods, e.g. spraying methods represented by an atomizing method which is a manufacturing method of the powdery metal material used in general in the powder metallurgy and thermal spraying, and various known methods such as mechanical crushing, electrolytic deposition and the like.

[0046] A shape of the powder may be spherical but this is not limiting and those with various shapes can be used.

[0047] The crystal grain diameter of the powdery metal material before treatment is a crystal grain diameter of the aforementioned coarse grain region as it is, and if the crystal grain diameter of the coarse grain region is set within a predetermined range, a powdery metal material with a corresponding crystal grain diameter is selected. Though not particularly limiting, the average crystal grain diameter of the coarse grain region is several to several tens μm as an example.

MEDIUM SUBSTANCE

[0048] As the aforementioned medium substance which collides against the powdery metal material, various substances can be used as long as it has hardness equal to or higher than that of the powdery metal material, and not only those made of metal but those made of ceramic can be used.

[0049] If the medium substance made of ceramic not subjected to work hardening is to be used, it is preferable that ceramic having hardness equal to or higher than that of the powdery metal material after the surface treatment of the present invention is used so that the powdery metal material can maintain the same or improved hardness after the work hardening.

[0050] By constituting the medium substance itself by the aforementioned powdery metal material, the aforementioned fine grain region may be formed in the both of the powdery metal material as the treatment target and the powdery metal material as the medium substance by collision between the powdery metal materials.

[0051] A shape of the medium substance needs to be constituted as powder when the medium substance is to be used as the ejection powder, but when the treatment is to be performed by using the aforementioned powdery metal material as the ejection powder, the medium substance does not have to be powder but may be constituted in a form of a plate body or the like.

BLASTING METHOD AND BLASTING MACHINE

[0052] The collision between the powdery metal material and the medium substance described above is made by blasting means of the blasting machine.

[0053] As this blasting, as described above, it may be so configured that the powdery metal material is ejected as the ejection powder to the medium substance and made to collide against said medium substance, or to the contrary, a powdery medium substance may be prepared as the ejection powder and ejected to the powdery metal material so as to cause a collision against said powdery metal material. Moreover, it may be so configured that the ejection powder and the object to be collided are both constituted by the powdery metal material having the same average grain diameter and made of the same material, and the powdery metal materials are made to collide against each other.

[0054] As the blasting machine 1 to be used, those with various known constitution can be used as long as it is a blasting machine having a cabinet 21 as a processing chamber and a dust collection function of suctioning an inside of the cabinet 21 for dust collection, and the blasting machine of either one of a direct pressure type and a gravity type may be used.

[0055] A constitution example of the gravity type blasting machine 1 and a constitution example of the direct pressure type to be used for the surface treatment of the present invention are illustrated in Fig. 1A and Fig. 1B, respectively.

[0056] An example in which the surface treatment of the present invention is performed with the blasting machine 1 by using the powdery metal material having the same material and the same average grain diameter for both the ejection powder and the object to be collided will be described below. However, the blasting machine 1 used in the method for surface treatment of the present invention is not limited to illustrated constitution.

[0057] The blasting machine 1 illustrated in Figs. 1A and 1B comprises: the cabinet 21 which becomes a processing chamber for accommodating an ejection nozzle 22 and a workpiece and performing blasting; and a dust collecting machine 38 for suctioning an inside of this cabinet 21. The blasting machine 1 is provided with a cyclone type collection tank 23 between this dust collecting machine 38 and the cabinet 21 for collecting into the collection tank 23 the powdery metal material collected by suctioning of the inside of the cabinet 21 in a state mixed with powder dusts and can collect into the dust collecting machine 38 the powder dusts separated from the powdery metal material in the cyclone type collection tank 23.

[0058] It is configured that the powdery metal material collected in the collection tank 23 as described above can be ejected again by an ejection nozzle 22 in the cabinet 21.

[0059] At a destination to which a tip end of the ejection nozzle 22 is directed inside the aforementioned cabinet 21, a barrel basket 24 which is a container rotating during ejection of the ejection powder and opened upward is provided, and the powdery metal material which is the object to be collided can be input therein.

[0060] In the example illustrated in Fig. 1A, this barrel basket 24 is depicted as a mesh with a large number of small pores formed, but the illustrated example is not limiting, and the barrel basket may be constituted without such small pores.

[0061] Prior to the treatment by means of the blasting machine 1 constituted as above, the powdery metal material is contained in the collection tank 23 and the powdery metal material is also contained in the barrel basket 24 provided in the processing chamber, and while the barrel basket 24 is rotated in this state, ejection of the powdery metal material from the ejection nozzle 22 is started at the ejection speed of 100 to 300 m/sec and then, the powdery metal material ejected from the ejection nozzle 22 collides against the powdery metal material in the rotating barrel basket 24.

[0062] An ejection pressure may be 100 m/sec or more in the treatment of a non-iron based powdery metal material, but 150 m/sec or more is preferable for the treatment of an iron-based powdery metal material.

[0063] By performing ejection of the powdery metal material as described above, the powdery metal material in the barrel basket 24 and the powdery metal material ejected from the ejection nozzle 22 mutually receive energy at the collision so that surface oxides such as oxidized scale formed on the surface of the powdery metal materials are exfoliated. Also, the temperature of the surface in the collision portion is rapidly raised and also cooled so that the crystal grains on the surface of the collision portion are refined, and a fine grain region is formed in which a crystal grain with a diameter smaller than that of the crystal grain on a center portion of the powdery metal material is formed in the vicinity of the surface of the powdery metal material.

[0064] It is empirically confirmed that the fine grain region of the powdery metal material is formed on the surface of the powdery metal material to a depth of approximately 20% at the maximum with respect to the grain diameter if the powdery metal material as the treatment target is less than 100 μm and formed to a depth of approximately 10% at the maximum with respect to the grain diameter if the powdery metal material as the treatment target is 100 μm or more, and thus, in the method for surface treatment of the present invention with the powdery metal material having an average grain diameter of 10 to 200 μm as the treatment target, the aforementioned fine grain region is formed within a range of 2 to 20 μm from the surface at the maximum depending on the grain diameter of the powdery metal material as the treatment target.

[0065] A description "in the vicinity of the surface" used herein refers to the surface including the above described range of depth.

[0066] The powdery metal material ejected from the ejection nozzle 22 collides against the powdery metal material in the barrel basket 24 and then, accumulates in the barrel basket 24 except those forced out to outside the barrel basket 24 and is stirred with rotation of the barrel basket 24 with the powdery metal material having been originally present in the barrel basket 24.

[0067] Thus, if the ejection of the powdery metal material from the ejection nozzle 22 is continued, the powdery metal material in the barrel basket 24 increases and overflows from the barrel basket 24 and drops to a bottom part of the cabinet 21.

[0068] The bottom part of the cabinet 21 is formed as a hopper having an inverted trapezoidal shape, and a lower end of the hopper communicates with the dust collecting machine 38 through an exhaust air passage 33 and the collection tank 23 and thus, when the inside of the cabinet 21 is suctioned by a ventilator 39 provided in the dust collecting machine 38, the dropped powdery metal material and powder dusts are suctioned with the air in the cabinet 21 and supplied into the cyclone type collection tank 23, the powder dusts and the powdery metal material are classified in this collection tank 23 and the powdery metal material is collected downward in the collection tank 23.

[0069] The surface oxides such as oxidized scale generated on the surface of the powdery metal material are harder and more fragile as compared with the powdery metal material. Therefore, the surface oxides are finely crushed when they are exfoliated by an impact caused by a collision between the powdery metal materials. Thus, the surface oxides are not collected in the collection tank 23 but sent to the dust collecting machine 38 as powder dusts through a pipe 32 connected to an upper part of the collection tank 23 and collected downward in the dust collecting machine 38, and clean air is discharged to the outside air by the ventilator 39.

[0070] As described above, the inside of the processing chamber formed in the cabinet 21 is suctioned at all times, and the powder dusts and the powdery metal material floating in the air are removed and kept to the explosion lower limit density or less. Thus, there is no concern of the powder dust explosion in the cabinet even by heat generation by ejection, collision and friction of the ejection powder which is the powdery metal material or generation of static electricity in this embodiment.

[0071] On the other hand, the powder dusts classified in the cyclone type collection tank 23 and collected in the dust collecting machine 38 are accommodated in the dust collecting machine 38 with an inflammable powder such as powder of calcium carbonate, for example, so that a density of flammable powder dusts in the air in the dust collecting machine 38 becomes the explosion lower limit density or less, whereby a risk of powder dust explosion in the dust collecting machine 38 is also avoided.

[0072] The powdery metal material collected in the collection tank 23 is ejected again by the ejection nozzle 22 toward the powdery metal material in the barrel basket 24, and the aforementioned process is repeated so that the surface oxides such as oxidized scale are removed from the surfaces of any powdery metal materials, and the fine grain region is formed so as to cover the entirety in the vicinity of the surface.

[0073] When the powdery metal material on which the fine grain region is formed in the vicinity of the surface as described above is used as a material for powder metallurgy such as sintering or is used for formation of a metal film of thermal spraying or the like, in the obtained sintered metal or metal coating, harmonic structure metal in which the coarse grain region is harmonically arranged in the network of the fine grain structures formed by mutually connecting parts of the fine grain regions is obtained. In such harmonic structure metal, excellent characteristics of realization of both the high ductility and high strength are obtained.

[0074] Particularly in the powdery metal material treated by the method of the present invention, the surface oxides such as oxidized scale causing lowered strength in sintering or deposition can be favorably removed and thus, strength of the obtained sintered metal or metal coating can be further improved.

[0075] In the aforementioned description, the constitution is described in which the ejection powder and the object to be collided are both the powdery metal materials and the ejection powder and the object to be collided are made to collide against each other in the barrel basket 24 provided in the cabinet 21, but a plate body formed of a material having hardness equal to or higher than that of the ejection powder is accommodated as the medium substance in the cabinet 21 instead of the aforementioned barrel basket 24, and the surface treatment of the present invention may be configured to be performed by ejecting the powdery metal material as the ejection powder to this plate body and making to collide against the same.

[0076] Moreover, it may be so constituted that the aforementioned blasting machine 1 provided with the barrel basket 24 is used, a powdery medium substance is used as the ejection powder, and the medium substance as the ejection powder is ejected to the powdery metal material contained in the barrel basket 24, and in this case, the powdery metal material and the medium substance are classified after the treatment and collected, respectively.

EXAMPLES

[0077] Examples in which the method for surface treatment of the present invention is applied to the powdery metal materials of various materials will be described below.

EXAMPLE 1

[0078] The method for surface treatment of the present invention was performed to stainless powder (SUS304 equivalent: #80) as the powdery metal material. Treatment conditions are shown in Table 1 below:

TABLE 1
Treatment conditions for Example 1 (SUS304)

Blasting machine	Type	Direct pressure type ("FD-4LD" by Fuji Manufacturing Co., Ltd.)
	Barrel basket	made of SUS304, no pores, 4 rotations per minute

(continued)

Treatment conditions for Example 1 (SUS304)

	Nozzle	Nozzle diameter: φ5 mm Oscillation: 100 mm in width, 60 times per minute
Powdery metal material	Material	Stainless powder (SUS-304 equivalent) (0.2 to 0.3%C <1.8%Si <1.0%Mn 18 to 20%Cr 8 to 10.5%Ni)
	Grain diameter	#80 (105 to 250μm / 177μm on average)
Medium substance		Same as powdery metal material
Blasting conditions	Ejection pressure	0.6 MPa
	Ejection speed	150m/sec or more
	Ejection distance	300 mm
	Ejection rate	6 kg/min
	Ejection time	3 hours
	Throughput	30 kg

[0079] The stainless powder in 10 kg was contained in the barrel basket provided in the processing chamber of the blasting machine and 20 kg into the collection tank, and the treatment of ejecting the stainless powder in the collection tank by the ejection nozzle into the barrel basket was performed continuously for 3 hours under the condition shown in the aforementioned Table 1.

[0080] As the result of the aforementioned treatment, in the stainless powder after the treatment, the oxidized scale was removed and the surface was cleaned, and moreover, hardness of the stainless powder which was 250 to 350 HV before the treatment rose to 450 to 550 HV after the treatment, and it is expected from the result that the crystal grains in the vicinity of the surface were refined.

[0081] Refining of the crystal grain diameter can be evaluated from an increase of a line width of an X-ray analysis peak using the Scherrer (Sherrer, 1918) formula. In the X-ray analysis result (Fig. 3) after the treatment by the present invention, the line width of the peak drastically increased with respect to the X-ray analysis result (see Fig. 2) of the untreated stainless powder. Thus, it was confirmed that hardness of the aforementioned powdery metal material rose, and refining of the crystal grain diameter on the surface was also confirmed from the X-ray diffraction result.

EXAMPLE 2

[0082] The method for surface treatment of the present invention was performed to a powder high-speed tool steel (SKH equivalent: #150) as the powdery metal material. The treatment conditions are shown in Table 2 below:

TABLE 2

Treatment conditions for Example 2 (Powder high-speed tool steel: SKH equivalent)

Blasting machine	Type	Gravity type ("SGK-4LD" by Fuji Manufacturing Co., Ltd.)
	Barrel basket	made of SUS304, no pores, 4 rotations per minute
	Nozzle	Nozzle diameter: φ9 mm Oscillation: 100 mm in width, 60 times per minute
Powdery metal material	Material	Powder high-speed tool steel ("SPM30" by Sanyo Special Steel Co., Ltd.) (1.3%C 4.0%Cr 5%Mo 6%W 3%V 8%Co)
	Grain diameter	#150 (44 to 125μm / 85μm on average)
Medium substance		Same as powdery metal material
Blasting conditions	Ejection pressure	0.6 MPa
	Ejection speed	150m/sec or more

(continued)

Treatment conditions for Example 2 (Powder high-speed tool steel: SKH equivalent)

	Ejection distance	200 mm
	Ejection rate	5 kg/min
	Ejection time	5 hours
	Throughput	20 kg

[0083] The powdery high-speed tool steel in 10 kg was contained in the barrel basket provided in the processing chamber of the blasting machine and 10 kg into the collection tank, and the treatment of ejecting the powdery high-speed tool steel in the collection tank by the ejection nozzle into the barrel basket was performed continuously for 5 hours under the conditions shown in the aforementioned Table 2.

[0084] As a result, hardness of the powdery high-speed tool steel at 650 to 750 HV before the treatment rose to 900 to 1000 HV after the treatment.

[0085] Moreover, in the powdery high-speed tool steel after the treatment, the oxidized scale was removed and the surface was cleaned, and from the X-ray diffraction result, the line width of the X-ray analysis peak increased (see Fig. 5) as compared with the untreated one (see Fig. 4), and the refining of the surface structure by the treatment according to the method of the present invention was confirmed (see Figs. 4 and 5).

EXAMPLE 3

[0086] The method for surface treatment of the present invention was performed to powder of an alloy steel for mechanical structure (SCM equivalent: #150) as the powdery metal material. The treatment conditions are shown in Table 3 below:

TABLE 3

Example 3: Treatment conditions for powder of alloy steel for mechanical structure (SCM equivalent)

Blasting machine	Type	Gravity type ("SGK-4LD" by Fuji Manufacturing Co., Ltd.)
	Barrel basket	made of SUS304, no pores, 4 rotations per minute
	Nozzle	Nozzle diameter: φ9 mm Oscillation: 100 mm in width, 60 times per minute
Powdery metal material	Material	Alloy steel for mechanical structure (SCM equivalent) (0.23%C 0.2%Mo 1.5%Cr)
	Grain diameter	#150(44 to 125μm / 85μm on average)
Medium substance		Same as powdery metal material
Blasting conditions	Ejection pressure	0.6 MPa
	Ejection speed	150 m/sec or more
	Ejection distance	200 mm
	Ejection rate	5 kg/min
	Ejection time	5 hours
	Throughput	20 kg

[0087] The power of alloy steel for mechanical structure in 10 kg was contained in the barrel basket provided in the processing chamber of the blasting machine and 10 kg into the collection tank, and the treatment of ejecting the powder of the alloy steel for mechanical structure in the collection tank by the ejection nozzle into the barrel basket was performed continuously for 5 hours under the conditions shown in the aforementioned Table 3.

[0088] As a result, hardness of the powder of alloy steel for mechanical structure at 150 to 200 HV before the treatment rose to 300 to 350 HV after the treatment.

[0089] Moreover, in the powder of the alloy steel for mechanical structure after the treatment, the oxidized scale was removed and the surface was cleaned, and it is considered from the aforementioned rise of hardness that the refined structure is formed on the surface.

EXAMPLE 4

[0090] The method for surface treatment of the present invention was performed to powder of the copper alloy (#150) as the powdery metal material. The treatment conditions are shown in Table 4 below:

TABLE 4

Treatment conditions for Example 4 (copper alloy)

Blasting machine	Type	Gravity type ("SGK-4LD" by Fuji Manufacturing Co., Ltd.), No barrel basket
	Nozzle	Nozzle diameter = φ9 mm Oscillation: 100 mm in width, 60 times per minute
Powdery metal material	Material	Copper alloy (21%Zn 17%Ni 0.34%Mn, the remnant Cu)
	Grain diameter	#150 (44 to 125μm / 85μm on average)
Medium substance		SKD 11 plate having diameter of 400 mm and thickness of 20 mm
Blasting conditions	Ejection pressure	0.4 MPa
	Ejection speed	100m/sec or more
	Ejection distance	200 mm
	Ejection rate	4 kg/min
	Ejection time	7 hours
	Throughput	20 kg

[0091] The copper alloy powder in 20 kg was contained in the collection tank, and the treatment of ejecting the copper alloy powder in the collection tank by the ejection nozzle toward a position where a core was shifted by 100 mm from a center of a plate (φ400 mm, thickness 20 mm) made of SKD11 arranged in the processing chamber was performed for 7 hours continuously.

[0092] As a result, hardness of the copper alloy powder at 160 to 200 HV before the treatment rose to 220 to 260 HV after the treatment.

[0093] Moreover, in the copper alloy powder after the treatment, the oxidized scale was removed and the surface was cleaned, and it is considered from the aforementioned rise of hardness that the refined structure is formed on the surface.

EXAMPLE 5

[0094] The method for surface treatment of the present invention was performed to powder of aluminum alloy (AC8A: #80) as the powdery metal material. The treatment conditions are shown in Table 5 below:

TABLE 5

Treatment conditions for Example 5: Aluminum alloy (AC8A)

Blasting machine	Type	Gravity type ("SGK-4LD" by Fuji Manufacturing Co., Ltd.)
	Barrel basket	made of SUS304, with φ1 mm pores, 4 rotations per minute
	Nozzle	Nozzle diameter: φ9 mm Oscillation: 100 mm in width, 60 times per minute
Powdery metal material	Material	Aluminum alloy (AC8A:12%Si 0.8%Fe 1.1%Cu 0.15%Mn 1%Mg 1.1 %Ni, the remnant Al)
	Grain diameter	#80 (105 to 250μm / 177μm on average)
Medium substance		Shot made of a high speed steel (#400, 45μm on average)
Blasting conditions	Ejection pressure	0.4 MPa

(continued)

Treatment conditions for Example 5: Aluminum alloy (AC8A)

Ejection speed	100 m/sec or more
Ejection distance	200 mm
Ejection rate	4 kg/min
Ejection time	7 hours
Throughput	10 kg

[0095] A barrel basket in which a large number of holes, each having a diameter of 1 mm, are formed was provided in the processing chamber, and the powder of the aluminum alloy (AC8A) was input in 10 kg into this barrel basket, and a treatment of ejecting a shot made of a high speed steel collected in the collection tank into the barrel basket was performed for 7 hours continuously.

[0096] As a result of the aforementioned treatment, hardness of the aluminum alloy powder at 120 to 140 HV before the treatment rose to 200 to 250 HV after the treatment.

[0097] Moreover, in the aluminum alloy powder after the treatment, the oxidized scale was removed and the surface was cleaned, and from the aforementioned rise of hardness, it is considered that a component of the high speed steel which is the medium substance is diffused and penetrated into the surface of the powder of the aluminum alloy and the refined structure was formed on the surface.

SINTERING TEST RESULT

[0098] Then, discharge plasma sintering was performed by using the powdery metal material treated by the method for surface treatment of the present invention described as above as Examples 1 to 5.

[0099] As a result, also in the sintered metal obtained by sintering the powdery metal material of any one of examples 1 to 5, the "harmonic structure" in which the coarse grain structures are arranged harmonically in the network formed by connecting the fine grain regions to each other is provided, and it was confirmed that the method for surface treatment of the present invention is a method for surface treatment which can treat the powdery metal material used for manufacture of the harmonic structure metal simply, in a large quantity and moreover, safely.

Descriptions of Reference Numerals

[0100]

1. Blasting machine
21. Cabinet
22. Ejection nozzle
23. Collection tank (cyclone type)
24. Barrel basket
32. Pipe
33. Exhaust air passage
38. Dust collecting machine
39. Ventilator

Claims

1. A method for surface treatment of a powdery metal material used for manufacture of harmonic structure metal in which a fine grain region and a coarse grain region are harmonically arranged comprising the steps of:

using a blasting machine which ejects ejection powder with a compressed gas in a cabinet and causes the ejection powder to collide against an object to be collided and comprises dust collecting means for suctioning an inside of the cabinet and removing/collecting power dusts ; and
performing blasting of causing a powdery metal material having an average grain diameter of 10 to 200 μm and a medium substance having hardness equal to or higher than that of the powdery metal material to collide with each other repeatedly at an ejection speed of 100 to 300 m/sec, and exfoliate surface oxides from the

powdery metal material and also form the fine grain region having a crystal grain diameter smaller than a crystal grain diameter of a center part of the powdery metal material in the vicinity of a surface of the powdery metal material.

2. The method for surface treatment of a powdery metal material according to claim 1, wherein
the dust collecting means of the blasting machine comprises a cyclone for classifying the power dusts and the ejection powder.

3. The method for surface treatment of a powdery metal material according to claim 1 or 2, wherein
in the dust collecting means of the blasting machine, the collected power dusts are stored with inflammable powder.

4. The method for surface treatment of a powdery metal material according to any one of claims 1 to 3, wherein
the blasting is performed by using the powdery metal material as the ejection powder and the medium substance as the object to be collided.

5. The method for surface treatment of a powdery metal material according to any one of claims 1 to 3, wherein
the blasting is performed by using the medium substance with a powdery shape as the ejection powder and the powdery metal material as the object to be collided.

6. The method for surface treatment of a powdery metal material according to any one of claims 1 to 3, wherein
the medium substance is made a powdery metal material of the same material and the same average grain diameter as the powdery metal material, and the ejection powder and the object to be collided are both made into the powdery metal material.

7. The method for surface treatment of a powdery metal material according to any one of claims 1 to 5, wherein
a material of the medium substance is metal having hardness equal to or higher than hardness of the powdery metal material or ceramic having hardness equal to or higher than hardness of the powdery metal material after the surface treatment.

FIG. 1A

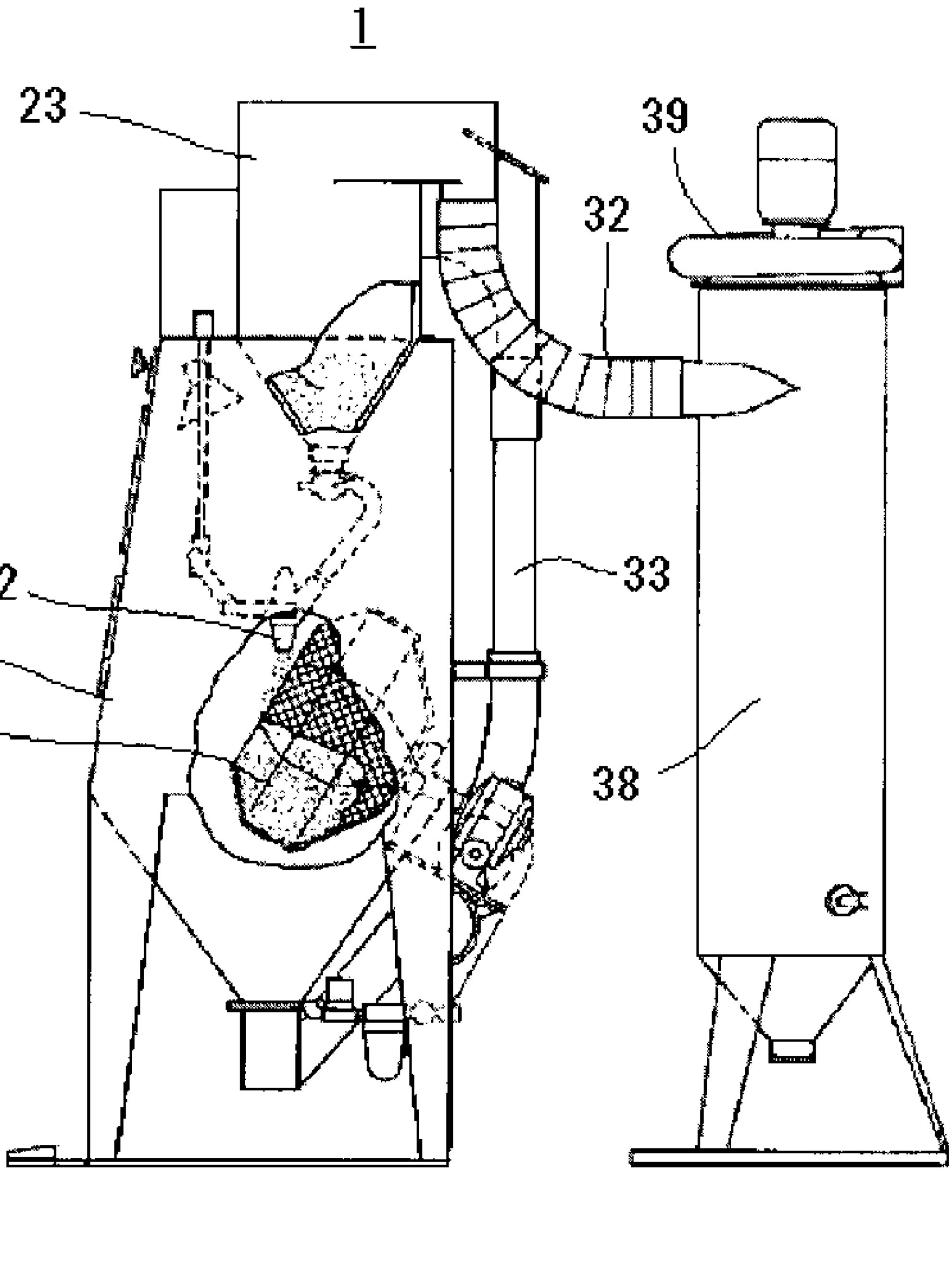


FIG. 1B

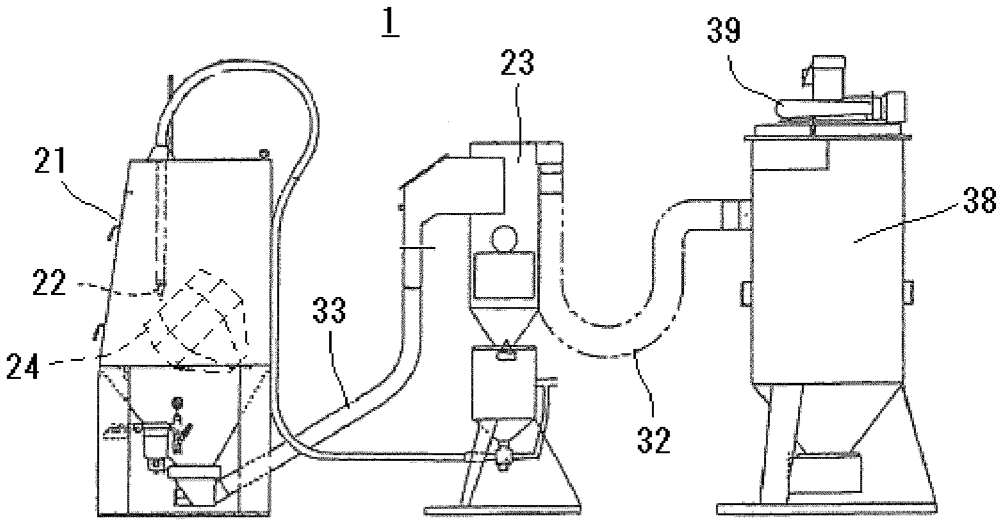


FIG. 2

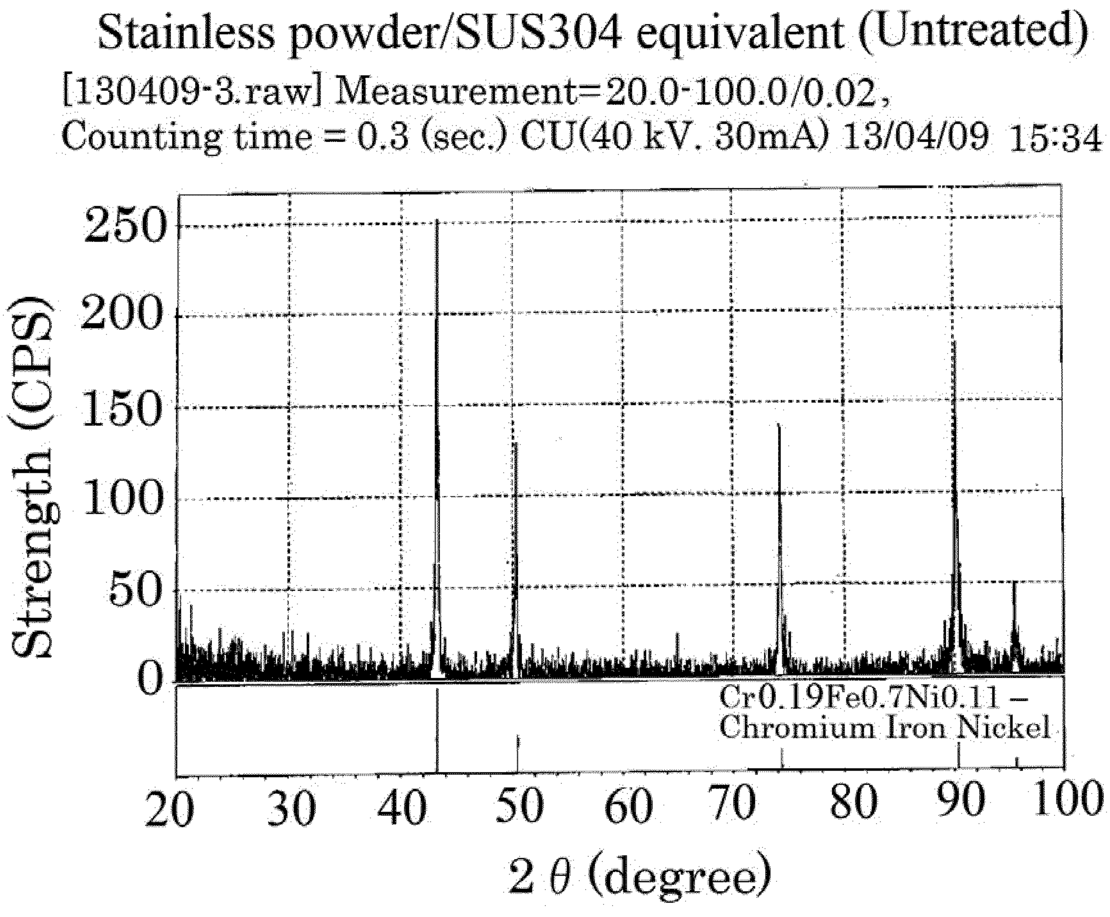

Stainless powder/SUS304 equivalent (Untreated)
[130409-3.raw] Measurement=20.0-100.0/0.02,
Counting time = 0.3 (sec.) CU(40 kV. 30mA) 13/04/09 15:34
Strength (CPS)
250
200
150
100
50
0
Cr0.19Fe0.7Ni0.11 –
Chromium Iron Nickel
20
30
40
50
60
70
80
90
100
2 θ (degree)

FIG. 3

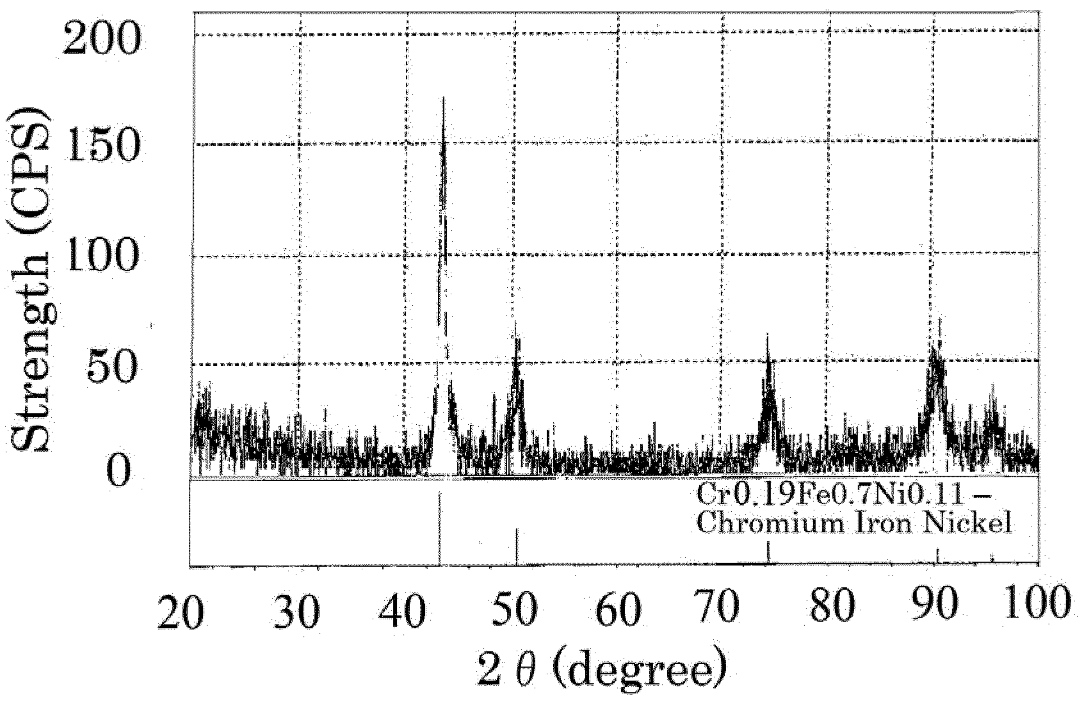
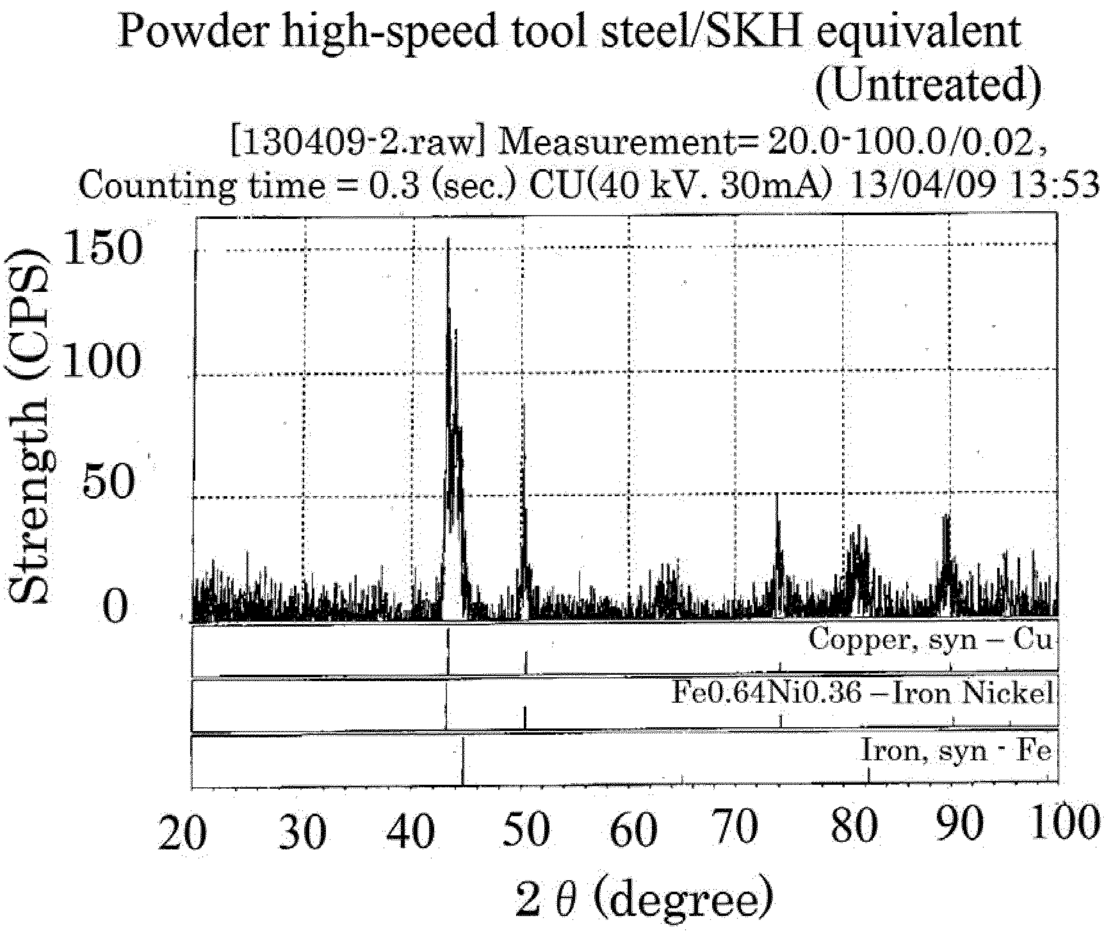

Stainless powder/SUS304 equivalent (Example 1)
[130409-4.raw] Measurement= 20.0-100.0/0.02,
Counting time = 0.3 (sec.) CU(40 kV. 30mA) 13/04/09 16:24
Strength (CPS)
200
150
100
50
0
Cr0.19Fe0.7Ni0.11 –
Chromium Iron Nickel
20
30
40
50
60
70
80
90
100
2 θ (degree)

FIG. 4



Powder high-speed tool steel/SKH equivalent (Untreated)
[130409-2.raw] Measurement= 20.0-100.0/0.02,
Counting time = 0.3 (sec.) CU(40 kV. 30mA) 13/04/09 13:53
Strength (CPS)
150
100
50
0
Copper, syn – Cu
Fe0.64Ni0.36 –Iron Nickel
Iron, syn - Fe
20
30
40
50
60
70
80
90
100
2 θ (degree)

FIG. 5

Powder high-speed tool steel/SKH equivalent (Example 2)

[130409-1.raw] Measurement=20.0-100.0/0.02,
Counting time = 0.3 (sec.) CU(40 kV. 30mA) 13/04/09 13:25

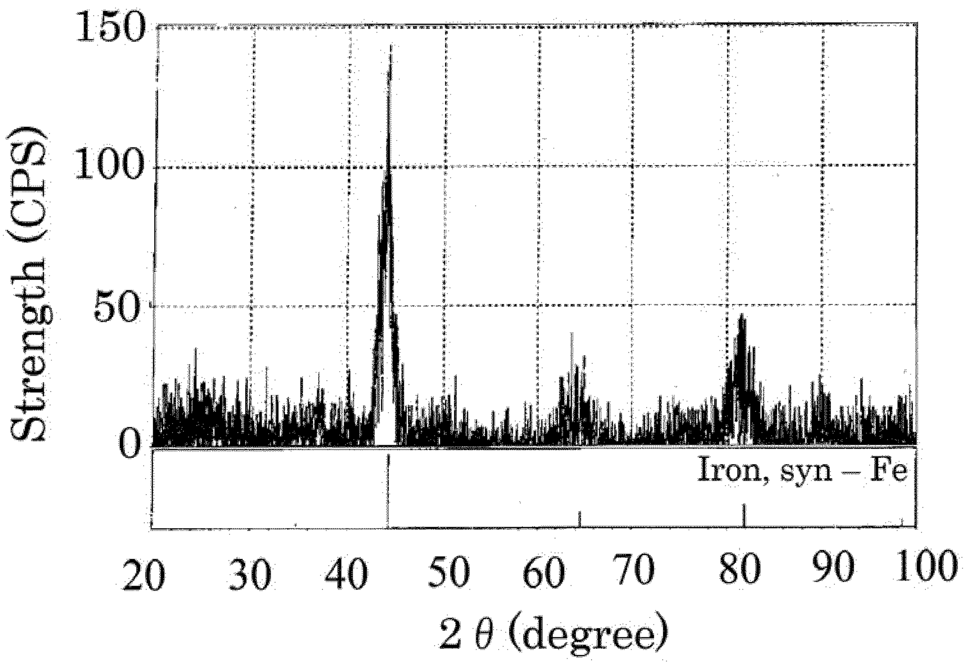
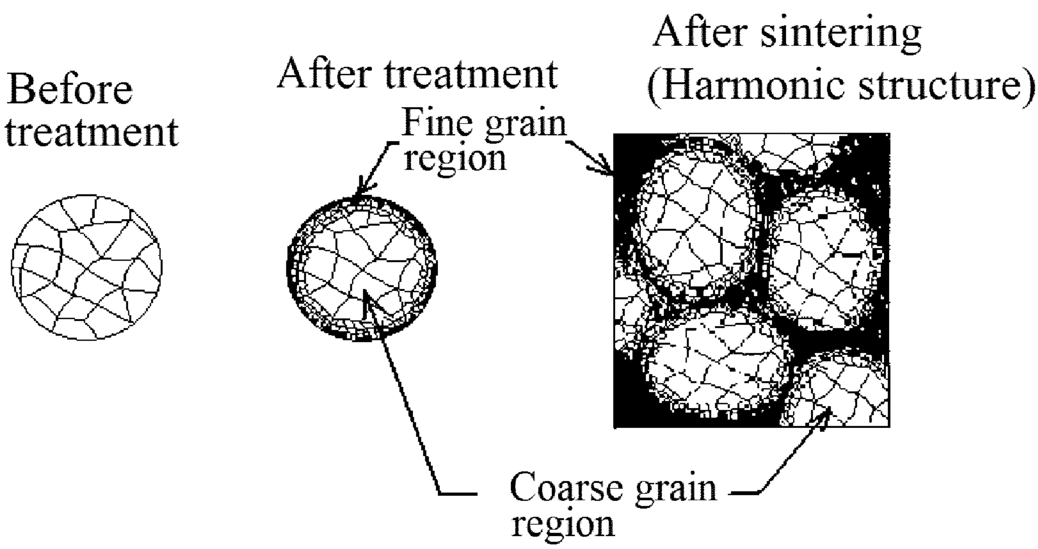


FIG. 6A FIG. 6B FIG. 6C



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2014/074518

A. CLASSIFICATION OF SUBJECT MATTER
B22F1/00(2006.01)i, *B22F7/06*(2006.01)i, *B24C1/00*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B22F1/00, B22F7/06, B24C1/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2014
Kokai Jitsuyo Shinan Koho	1971-2014	Toroku Jitsuyo Shinan Koho	1994-2014

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
JSTPlus(JDreamIII), JST7580(JDreamIII), JSTChina(JDreamIII)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Masato ISHIWATA (Fuji Manufacturing Co., Ltd.), "Improvement of Metal Surface Strength by Fine Particle Bombarding Treatment", Marine engineering, vol.46, no.5, 01 September 2011 (01.09.2011), pages 684 to 687	1-7
Y	JP 63-312071 A (Nippon Mining Co., Ltd.), 20 December 1988 (20.12.1988), page 3, lower left column, line 17 to lower right column, line 6 (Family: none)	1-7
A	JP 2007-297651 A (Kabushiki Kaisha Fuji WPC), 15 November 2007 (15.11.2007), entire text; all drawings (Family: none)	1-7

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
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Date of the actual completion of the international search	Date of mailing of the international search report
02 December, 2014 (02.12.14)	09 December, 2014 (09.12.14)

Name and mailing address of the ISA/	Authorized officer
Japanese Patent Office	
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2014/074518

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2001-225270 A (Fuji Manufacturing Co., Ltd.), 21 August 2001 (21.08.2001), entire text; all drawings (Family: none)	1-7

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

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Non-patent literature cited in the description

- Special Feature 2-3D Printer 'Attracting!' 'Design/Manufacture Solution Exhibition' Report, Diversification of Molding Materials. Nikkei Monodukuri August issue. Nikkei BP, 01 August 2013, 64-58 **[0009]**
- **KEI AMEYAMA ; TATSUYA SEKIGUCHI.** Creation of Innovative Structural Material Realizing both High Strength and High Ductility by Harmonic Structure Control. *Journals of The Japan Society for Heat Treatment,* 28 February 2013, vol. 53 (1), 1-2 **[0009]**
- Tripled Renewed Brass Hardness, Chip Molding/Sintering, New Technology by Nihon Univ. Improved Conductivity to Practice. Nikkan Kogyo Shimbun, 30 April 2013 **[0009]**