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(11) **EP 1 577 402 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(43) Date of publication:
21.09.2005 Bulletin 2005/38

(51) Int Cl.7: **C21D 7/06, B24C 1/10**

(21) Application number: **03768204.4**

(86) International application number:
PCT/JP2003/016669

(22) Date of filing: **25.12.2003**

(87) International publication number:
WO 2004/059015 (15.07.2004 Gazette 2004/29)

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IT LI LU MC NL PT RO SE SI SK TR**
Designated Extension States:
AL LT LV MK

(30) Priority: **25.12.2002 JP 2002374610**
18.12.2003 JP 2003421143

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(54) **METHOD OF REFINING METAL SURFACE AND METAL PRODUCT BY THE METHOD**

(57) This invention relates to a method for fining a surface of a metal product to form crystal grains having sizes less than 1 μm at their surfaces and the metal product produced thereby. The method is comprised of a process for forming crystal grains having sizes less than 1 μm at the surface of the metal product by project-

ing or peening shots or projectiles while a power per unit of area of the surface, which power is caused by projecting or peening shots or projectiles, is controlled at a predetermined value.

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Description

Technical Field

5 **[0001]** This invention relates to a method for fining a surface of a metal product to form crystal grains having sizes less than 1 μm at its surface and for producing a metal product thereby.

Background of the Invention

10 **[0002]** It is well known that when a surface of a metal product has been projected upon by shot peening, the micro-structure of the surface can be fined. (See Literature 1.) Literature 1 discloses that a micro-structure having fine grain sizes in a surface layer with a high dislocation density that is formed by shot peening is useful to improve the fatigue characteristics of a metal product.

15 **[0003]** Literature 1: A. Niku-Lari, First International Conference on Shot Peening, United Kingdom, Pergamon Press, 1981, p. 192.

Disclosures of Invention

20 **[0004]** However, Literature 1 does not disclose forming crystal grains having sizes of less than 1 μm . Namely, it does not disclose mechanisms and conditions to form crystal grains having sizes of less than 1 μm .

[0005] This invention is directed to solve this problem. Namely, the purpose of this invention is to provide a method for fining a surface of a metal product to form crystal grains having sizes of less than 1 μm at its surface.

[0006] Further, the purpose of this invention is to provide a metal product that is treated by the method.

25 **[0007]** To achieve the purpose, the method according to this invention is comprised of a process for forming crystal grains having sizes of less than 1 μm at the surface of the metal product by projecting or peening shots or projectiles while the power per unit of area of the surface is controlled at a predetermined value.

[0008] According to this invention, it is possible to improve fatigue strength, hardness, and a corrosion resistance of a metal product by forming crystal grains having sizes of less than 1 μm at the surface of the metal product.

30 **[0009]** As explained above, this invention is comprised of a method for forming crystal grains having sizes of less than 1 μm at the surface of the metal product by projecting or peening shots or projectiles while the power per unit of area of the surface, which power is caused by projecting or peening shots or projectiles, is controlled at a predetermined value. The metal product is treated by this method. Thus, according to this invention, the fatigue strength, the hardness, and the corrosion resistance of the metal product can be improved by forming crystal grains having sizes of less than 1 μm at the surface of the metal product.

Brief Descriptions of the Drawings

[0010]

40 Fig. 1 shows a perspective view of an apparatus for projecting projectiles of a first embodiment.

Fig. 2 shows a perspective view of an apparatus for dropping a weight to treat the surface of a metal product of the second embodiment.

45 Fig. 3 shows a cross-sectional view of the apparatus for shot-peening of the third and fourth embodiment.

Fig. 4 shows a photomicrograph of the surface of the metal product that is treated by the method of this invention.

50 Fig. 5 shows a photomicrograph of the crystal grain that is fined by the method of this invention.

Preferred Embodiments of the Invention

55 **[0011]** Below, the preferred embodiments of this invention are explained. This invention relates to a method comprising a process for forming crystal grains having sizes of less than 1 μm at the surface of the metal product by projecting or peening shots or projectiles while the power per unit of area of the surface, which power is caused by projecting or peening shots or projectiles, is controlled at a predetermined value.

[0012] A steel or non-ferrous metal can be used as the material for the metal product of this invention. The surface of the metal product is defined as a portion near the surface that can be affected by projecting the shots or projectiles.

The depth of the portion that is affected by projecting the shots or projectiles depends on the velocity and mass of the shots or projectiles and the period for projecting them when the surface of the metal product is projected upon by them.

[0013] It is preferable that the hardness of the shots or projectiles be equal to or higher than that of the metal product. It is also acceptable that the hardness of the shots or projectiles be lower than that of the metal product, if its surface can be hardened.

[0014] The reason the power per unit of area of the surface, which power is caused by projecting or peening shots or projectiles, is controlled at a predetermined value, is as follows:

Literature 1 says that when the surface of the metal product is projected upon by shot peening, a degree of fining the micro-structure of the surface of the metal product depends on the dislocation density and the arrangement of the dislocations, grain sizes, and phase changes of the micro-structure. However, its mechanisms are not explained in Literature 1.

[0015] In this invention, it is found that the power per unit of area of the surface, which power is caused by projecting the shots or projectiles, affects the fining of the micro-structure of the surface of the metal product.

[0016] Namely, it is possible to produce nanocrystals without repeatedly projecting the shots or projectiles, such as by the shot-peening.

[0017] "A unit of area" of the surface is defined as the sum of the contact surfaces that are projected upon by the shots or projectiles. Namely, "a unit of area" is calculated by multiplying the contact surface from a projectile or a shot by the number of the shots or projectiles, based on the assumption that the marks (surfaces contacted by the shots or projectiles) on the surface by projecting the shots or projectiles do not overlap. Thus, when the marks on the surface do overlap, "a unit of area" is calculated by subtracting the overlapped areas calculated based on the number of shots or projectiles that have their contact surfaces overlap from the sum of the contact surfaces. Thus, basically "the unit of area" does not correspond to the surface that is treated by the shot-peening.

[0018] However, it is possible to use a surface area of the metal product treated by the shot-peening as "the unit of area," under a certain assumption.

[0019] Below, the first embodiment is explained.

[0020] Fig. 1 shows an apparatus of the first embodiment of this invention. This apparatus 10 for projecting the projectiles can project a metal ball 11 having a diameter of 4 mm on the surface of the metal product 12 through the nozzle 13 with compressed gas at a high speed. Table 1 shows the working conditions for projecting the projectiles and the results of the treatment. This treatment increases the strength of the portion of the surface since the process is instantaneously completed. Namely, nanocrystals can be formed because the small area of the surface of the metal product 12, which is projected upon by the ball 11, is quickly processed.

[0021] In comparison with the area hardened by ordinary working or made from base materials, the growth of the grain size in the area having nanocrystals is very slow. Thus, the area having nanocrystals is clearly distinguished from the other areas hardened by ordinary working or made from base materials, based on the change of the state of the micro-structure of the surface or its hardness by heating them. Since the grain size in the area hardened by working become very coarse, and the hardness of the area is reduced by heating it (the hardness of the surface is reduced from 450 Hv to 310 Hv in Vickers hardness), it is recognized that the growth of the grain sizes in the area having nanocrystals is very slow, and the decrease of the hardness of the area is little (the hardness of the area is reduced from 700 Hv to 650 Hv) by heating it.

[0022] It can be seen that an area having nanocrystals is formed, by investigating the behavior of a recrystallization.

[0023] Now, the second embodiment is explained.

[0024] Fig. 2 shows an apparatus of the second embodiment of this invention. This apparatus 20 for dropping a weight can freely drop a weight 21 made of metal on the surface of the metal product 22 and cause a collision between the surface of the metal product 22 and the weight 21, to treat its surface. Table 1 shows the working conditions for dropping the weight and the results of the treatment. In this apparatus 20, the metal product 22 to be treated to form nanocrystals on the surface 22A is located in the bottom of the cylinder (not shown in the Figs.).

[0025] In this embodiment, the metal product 22 is already machined so that it has a final configuration and cannot move in the cylinder since the configuration of the outside of the metal product closely corresponds to that of the inside of the cylinder (not shown). The metal weight 21 is placed at the upper part in the cylinder. As explained below, a protrusion 21A is disposed at the surface of the metal weight 21, and the protrusion has a predetermined height (3 mm) from the surface of the weight 21. The protrusion 21A is disposed at the location on the weight that is opposite the point where nanocrystals should be formed on the surface 22A of the metal product 22.

[0026] The metal weight, which is placed at the upper part in the cylinder, drops freely. Consequently, the protrusion 21A of the metal weight collides with the predetermined portion of the surface 22A of the metal product 22. If the mass of the metal weight is defined as M (Kg), and the velocity of the metal weight 21 when it collides with the surface of the metal product 22 is defined as V (m/sec), then V is given as follows:

$$V = \sqrt{2gH}$$

(g: acceleration of gravity; H: distance that the weight falls) Namely, the protrusion 21A of the metal weight 21 collides with the surface 22A of the metal product 22 at the following kinetic momentum:

$$M * \sqrt{2gH} \quad (\text{Kg} * \text{m/sec})$$

[0027] Consequently, the force, which is defined as a temporal response to the kinetic momentum, acts on the portion of the metal product 22 with which the protrusion 21A collides. Since the collision is completed in a short time, the strength of the portion of the metal product with which the protrusion collides increases significantly.

[0028] Namely, since the small area of the metal product is intensively worked in a very short time by the collision of the protrusion 21A of the metal weight 21, it is easy to form nanocrystals.

[0029] According to the result of the examination of this embodiment, the power per unit of area, that is, the power per depressed area produced by the protrusion or the contact area of it, should be at least 11 KJ/sec * mm².

[0030] Namely, the accumulated kinetic momentum of the metal weight is not important, but the power per depressed area is important.

[0031] If the power per depressed area is less than 11 KJ/sec * mm², no nanocrystal is formed at the surface 22A of the metal product 22. Namely, when the protrusion 21A collides with the surface 22A of the metal product 22 with a power per depressed area of more than 11 KJ/sec * mm², a nanocrystal is formed at the portion with which the protrusion 21A collides.

[0032] It is preferable that the protrusion be a hemispherical protrusion that projects at a height (h) of 1-10 mm from the surface of the metal weight 21. The protrusion may have a shape of an ellipse. If a plurality of the portions on the surface of the metal product to be treated to form nanocrystals are required, the plurality of the protrusions 21A opposite the portions may be disposed at the surface of the metal weight.

[0033] The kinetic momentum explained above is defined as a function of the mass (M) of the metal weight 21 and the speed (V) of it at the moment that the protrusion collides. When the metal weight 21 having the protrusion 21A, which has a hemispherical configuration and a height of 1-10 mm, is used in the experiments of this invention, the mass (M) of the metal weight 21 is set between 0.1-10 Kg, and the speed of the weight at the moment that the protrusion collides is set at more than 1 m/sec, the power per depressed area of more than 11 KJ/sec * mm² is achieved, and the nanocrystals can be formed at the surface of the metal product.

[0034] When the metal weight 21 having the plurality of the protrusions 21A is used, it is necessary to set the weight colliding with the surface 22A of the metal product 22 to the value that equals the product of the number of protrusions times the mass of the weight having a protrusion (between 0.1-10 Kg). Then, the process is completed by dropping the weight at a speed of more than 1 m/sec. Since the value of the kinetic momentum divided by the total depressed area caused by all the protrusions 21A and the deformation period satisfies the power per depressed area of more than 11 KJ/sec * mm², the nanocrystals can be formed at the portions of the surface of the metal product.

[0035] Next, the third embodiment is explained.

[0036] Fig. 3 shows an apparatus of the third embodiment of this invention. This shot-peening apparatus 30 can project shots 31 having a diameter of 50 μm, which shots 31 are made from steel, on the surface of the metal product 32 with compressed air through a nozzle 33. Table 1 shows the working conditions of the shot peening and the results of the treatment. From Table 1, it is found that the power per unit of area of the third embodiment to produce nanocrystals is larger than that of the first and the second embodiments.

[0037] In this embodiment, the pressure of the compressed air is controlled so that the projecting speed of the shots 31 at the metal product becomes 150-200 m/sec. If it is required that the entire area of the surface of the metal product be treated by shot peening, it can be treated by moving the metal product 32 so that the shots are projected over the entire area. A layer constituted of a fine crystal having grain sizes of less than 100 nm is formed at the surface of the metal product 32 by means of this shot peening process. It is found that the hardness of the layer having the fine crystal is significantly increased. Fig. 4 shows a photomicrograph of the surface of the metal product that is treated by the method of the third embodiment of this invention. Fig. 5 also shows a photomicrograph of the crystal grain that is fined by the method of the third embodiment of this invention.

[0038] As explained above, since the layer constituted of a fine crystal can be formed at the surface of the metal product 32 by using the method of the third embodiment of this invention, its hardness significantly increases. Thus, the strength of the metal product 32 also increases, and the fatigue strength and corrosion resistance of the metal product can be improved.

[0039] Now, the fourth embodiment is explained.

[0040] Fig. 3 shows an apparatus of the fourth embodiment of this invention, which figure is the same figure as that

shown for the third embodiment. This shot-peening apparatus 30 can project shots 31 having a diameter of 50-300 μ m and made from stainless steel on the surface of the metal product 32 with compressed air through a nozzle 33. Table 1 shows the working conditions of the shot peening and the results of the treatment. From Table 1, it is found that the power per unit of area of this embodiment to produce nanocrystals is larger than that of the first and the second embodiments.

[0041] In this embodiment, the pressure of the compressed air is controlled so that the projecting speed of the shots 31 on the metal product becomes 80 m/sec. If it is required that the entire area of the surface of the metal product be treated by the shot peening, it can be treated by moving the metal product 32 so that the shots are projected at the entire area. As well as in the third embodiment, a layer constituted of a fine crystal having grain sizes of less than 100 nm is formed at the surface of the metal product 32 by means of this shot peening process. It is found that the hardness of the layer having the fine crystal is significantly increased. Shots made not only from stainless steel, but also from high-carbon steel or ferrous metallic glass, can be used. Further, shots having a range of diameters of 30 μ m to 2000 μ m can be used.

[0042] As explained above, since a layer constituted of a fine crystal can be formed at the surface of the metal product 32 by using the method of the fourth embodiment of this invention, its hardness significantly increases. Thus, as well as in the third embodiment, the strength of the metal product 32 also increases, and the fatigue strength and corrosion resistance of the metal product can be improved.

[0043] Generally, when a surface of a metal product is treated by shot peening, a work hardening is caused at the surface. It is well known that the degree of the work hardening of the metal is proportional to the square root of its dislocation density. When the process for working the metal product is continued, since the speed of the disappearance of its dislocations caused by a merger between the dislocations of grains increases, the rate of the work hardening decreases gradually as the degree of working increases. However, when the metal product is worked hard at a high strain rate, since no disappearance of the dislocations of grains is caused, the dislocation density of the grains increases. Then, when the dislocation density reaches a critical value, a dislocation-cell structure changes to a grain-boundary structure.

[0044] Further, the fining of the micro-structure of the surface of the metal product is improved by projecting the projectiles or the shots to the surface while the temperature of the metal surface is controlled to be between room temperature and -150 °C. It is difficult for the number of the dislocations of the grains to reach the critical dislocation density. This allows the grains to be recrystallized, since the recovery rate of the dislocations of the grains increases with the increased temperature of the surface due to the continuous projection of the projectiles or the shots. However, in the condition at low temperature, since the recovery rate of the grain structure which is fined by projecting the projectiles or the shots decreases, it becomes easy for the number of the dislocations of the grain to increase. Namely, it becomes easy for the dislocation density to reach the critical value, which value allows the grain to be fined.

[0045] In this embodiment, liquid nitrogen (temperature: -196 °C) and liquid carbon dioxide (temperature: -79 °C) can be used to cool the metal product. It is preferable to control the temperature of the metal product to be between room temperature and about -150 °C based on the material of the product. It is possible to form finer grains by using this method compared to the method for projecting the projectiles or the shots at room temperature.

Industrial Applicability

[0046] This invention relates to a method for fining a surface of a metal product to form crystal grains having sizes less than 1 μ m at its surface and to produce the metal product by the method. By this method, since the fatigue strength, the hardness, and the corrosion resistance of the metal product can be improved, the method possesses a possibility of industrial applicability.

Table 1 Working Conditions for Each Processing

	Method of Projecting Projectiles (Embodiment 1)	Method of Dropping Weight (Embodiment 2)	Method of Shot Peening (Embodiment 3 and 4)
Diameter of Ball or Projectile ϕ (mm)	4	6	0.05
Velocity of Ball or Projectile (m/sec)	120	4.4	190
Working Energy per One Shot (J)	1.9	49	9.2×10^{-6}
Depth of Deformation (μ m)	500	1000	5
Contact Area (mm ²)	6.3	19	7.9×10^{-4}
Deformation Time (s)	4.2×10^{-6}	2.3×10^{-5}	2.6×10^{-8}
Strain Rate (1/s)	2.4×10^6	4.4×10^4	3.8×10^7
Power/ Contact Area (kJ/s * mm ²)	72	11	450

Claims

1. A method for fining a metal surface, comprising a process for forming crystal grains having sizes less than $1\mu\text{m}$ at the surface of a metal product by means of projecting or peening shots or projectiles to the surface while a

power per unit of area of the surface is controlled at a predetermined value.

2. A method for fining a metal surface according to claim 1, wherein the shots or projectiles are made from high-carbon steel, ferrous metallic glass, or stainless steel, and the diameters of the shots or projectiles are 30 μ m to 2000 μ m.
3. A method for fining a metal surface according to either of claims 1 and 2, wherein the power per unit of area is greater than 11 KJ/sec * mm².
4. A method for fining a metal surface according to any of claims 1, 2, and 3, wherein the process for projecting or peening shots or projectiles to the surface is carried out while the temperature of the metal surface is controlled to be between room temperature and -150 °C.
5. A method for fining a metal surface according to any of claims 1-4, wherein the unit area is calculated by multiplying a contact surface of a projectile or a shot by a number of the shots or projectiles.
6. A method for fining a metal surface according to claim 5, wherein the unit area is calculated by subtracting the overlapped areas that is calculated based on the number of shots or projectiles that have their contact surfaces overlap from the sum of the contact surfaces.
7. A metal product having surfaces hardened by the method for fining a metal surface according to any of claims 1-6.

Fig. 1

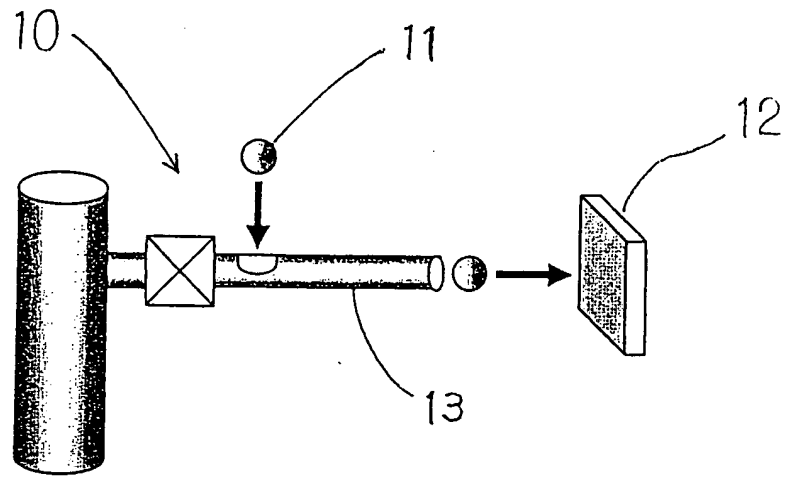


Fig. 2

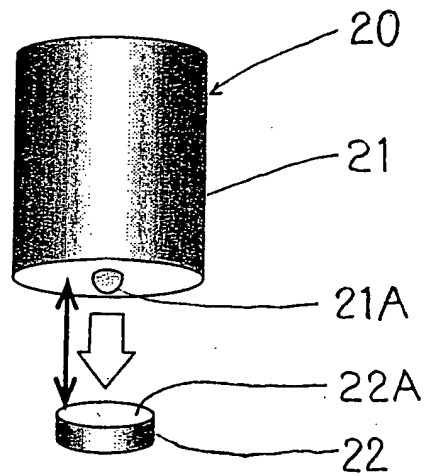


Fig. 3

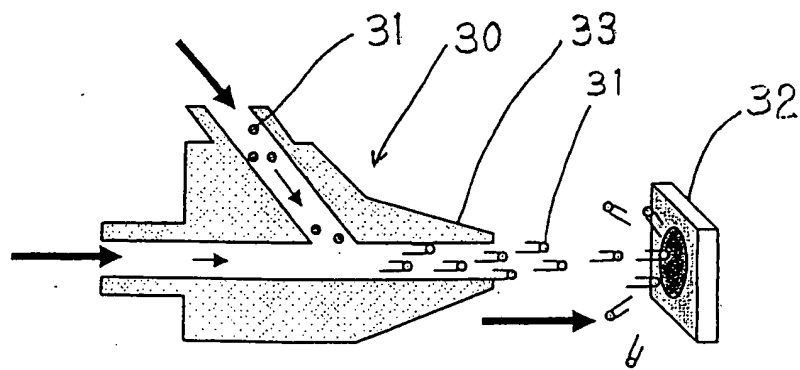


Fig. 4

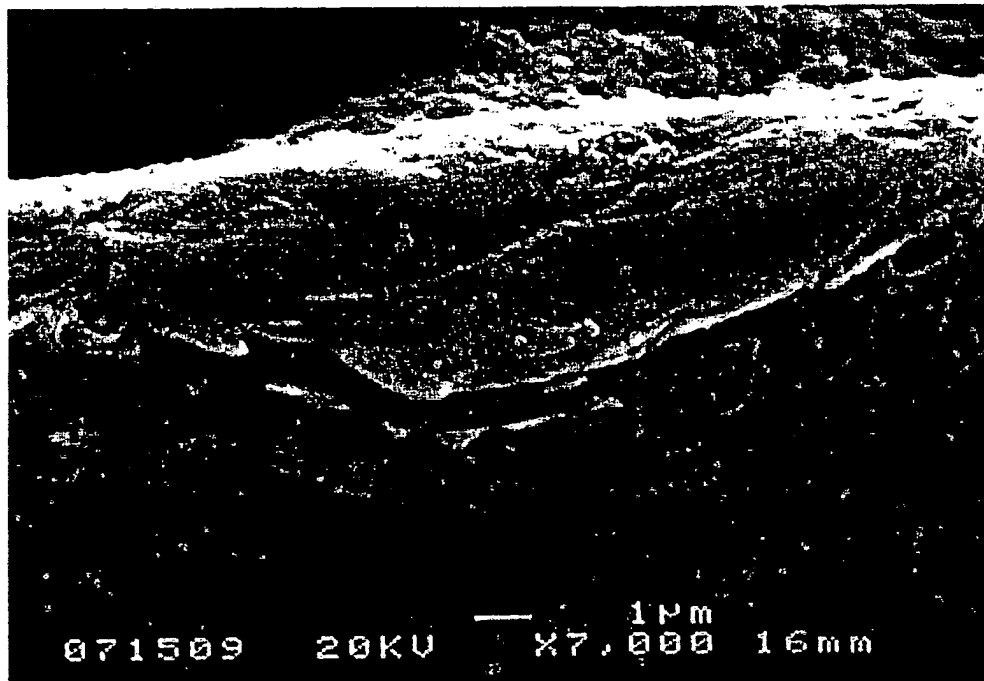
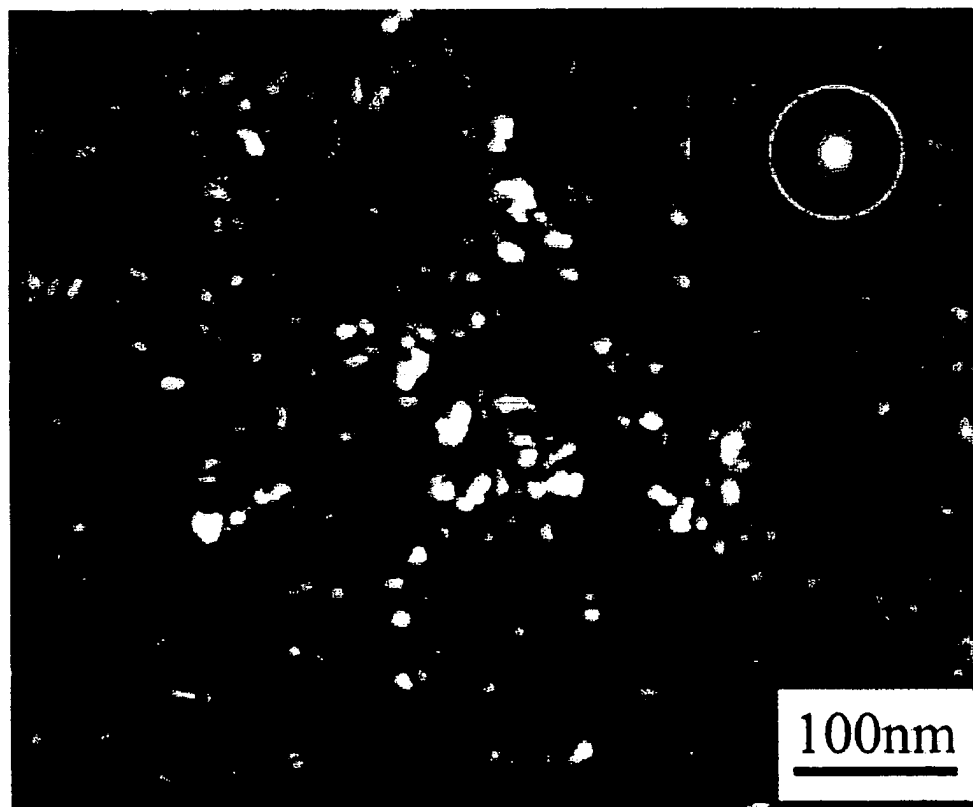


Fig. 5



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP03/16669

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁷ C21D7/06, B24C1/10		
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) Int.Cl ⁷ C21D7/04, 7/06, B24C1/00-1/10		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-2004 Kokai Jitsuyo Shinan Koho 1971-2004 Jitsuyo Shinan Toroku Koho 1996-2004		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 8-1514 A (Toshiba Corp.), 09 January, 1996 (09.01.96), Column 3, lines 4 to 22 (Family: none)	1-7
A	JP 1-240615 A (Nissan Motor Co., Ltd.), 26 September, 1989 (26.09.89), Claims (Family: none)	4
A	JP 2000-94330 A (Sinto Kogyo Ltd.), 04 April, 2000 (04.04.00), Claims (Family: none)	3, 5, 6
☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 26 March, 2004 (26.03.04)		Date of mailing of the international search report 13 April, 2004 (13.04.04)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP03/16669

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 02/9908 A1 (Sinto Kogyo Ltd.), 07 February, 2002 (07.02.02), Claims & EP 1306165 A1 & US 2003-5736 A1 & JP 2002-36115 A	2
X	Minoru UMEMOTO "Shot Peening nado no Hyomen Shori to Kessho Ryubisaika", The Japan Society for Heart Treatment Taikai Koen Gaiyoshu, Vol.55, pages 47 to 48	1-7
X	Minoru UMEMOTO et al., "Tekko Zairyo no Ball Mill ni yoru Nano Kesshoka Kiko no Kaimei to sono Bulk-Zai Hyomen Nano Kesshoka heno Oyo", Japan Society of Powder and Powder Metallurgy Koen Gaiyoshu, Vol.2002, Shuki page 158	1-7
X	Liu G. et al., "Low carbon steel with nano structured surface layer induced by high energyshot peening", Scr.Mater, Vol.44, No.8/9, pages 1791 to 1795	1-7

Form PCT/ISA/210 (continuation of second sheet) (July 1998)