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(71) Applicant: **Honda Motor Co., Ltd.**
Minato-ku
Tokyo 107-8556 (JP)

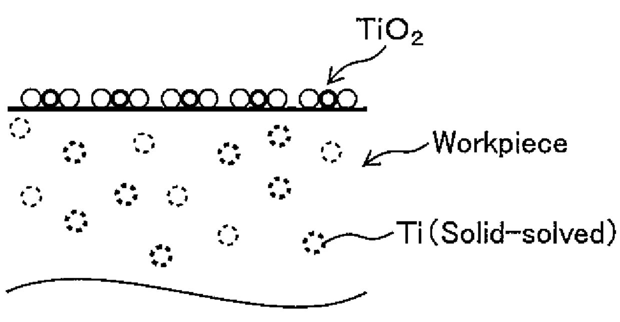
(72) Inventors:
- **TAKAGAKI, Masashi**
  Tochigi 321-3395 (JP)
- **MASE, Hiroaki**
  Tochigi 321-3395 (JP)
- **Narita, Naoki**
  Tokyo 107-8556 (JP)

(74) Representative: **Rupp, Christian**
Mitscherlich & Partner
Patent- und Rechtsanwälte
Sonnenstraße 33
80331 München (DE)

(54) **NITRIDING PROCESS FOR MARAGING STEEL**

(57) A nitriding process for a maraging steel is provided in order to increase the compressive residual stress of the maraging steel. A workpiece is made of maraging steel in which titanium is solid solved, and a partial amount of the titanium is oxidized at the surface of the workpiece so that titanium oxide ($Ti0_2$) is positively generated and concentrated at the surface (a solution heat treating step). Then, since titanium in an oxide state does not combine with nitrogen in a nitriding step, a reducing treatment is sufficiently performed as a pretreatment of the nitriding step, thereby removing oxygen. As a result, surface concentration of the titanium in an activated state is increased. Next, by performing the nitriding treatment, the reduced titanium and the solid solved titanium combine with nitrogen as titanium nitride (TiN). The titanium is in the activated state and is thereby easily nitrided. Moreover, the surface concentration of the titanium in the activated state is high, whereby a large amount of nitrogen infiltrates into the workpiece.

Fig. 1A



EP 2 518 177 A1

Fig. 1B

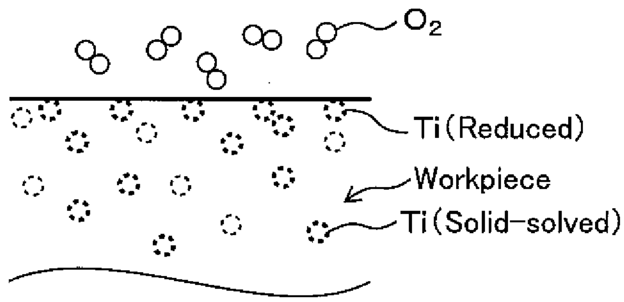
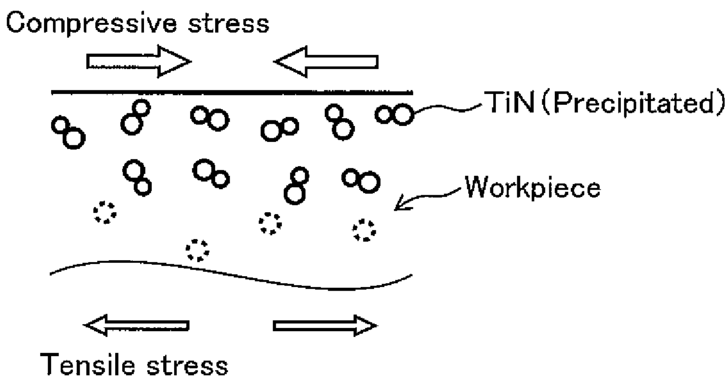

O_2
Ti (Reduced)
Workpiece
Ti (Solid-solved)

Fig. 1C


Compressive stress
TiN (Precipitated)
Workpiece
Tensile stress

Description

Technical Field

[0001] The present invention relates to a nitriding process for a maraging steel containing titanium, and specifically, the present invention relates to an improvement in a technique for controlling the degree of compressive residual stress.

Background Art

[0002] In order to improve strengths of steels, compressive residual stress may be generated at the surface of the steels by a nitriding treatment. In this case, if excessive degrees of the compressive residual stress are generated, there may be cases in which notch sensitivity is increased or toughness is decreased. Therefore, it is necessary to generate an appropriate degree of the compressive residual stress.

[0003] When a nitriding treatment is performed on a steel with low nitridability, an oxide layer existing at the surface of the steel prevents nitriding of the steel. For example, in a case of maraging steel, if surface concentrations of atoms that easily combine with oxygen, such as titanium, are high, oxide layers of the atoms are formed in a solution heat treating step. Therefore, nitriding is prevented by the oxide layers in a nitriding step, whereby sufficient degree of the compressive residual stress cannot be generated in the steel. In regard to this, a method is disclosed in Japanese Unexamined Patent Application Laid-open No. 2004-162134. In this method, a solution heat treatment is performed in a specific atmosphere which prevents oxidation as much as possible, thereby preventing increase of the surface concentrations of the atoms that easily combine with oxygen.

[0004] However, according to the technique disclosed in Japanese Unexamined Patent Application Laid-open No. 2004-162134, compressive residual stress cannot be sufficiently generated at the surface of a maraging steel. Moreover, a reducing treatment is used as a pretreatment of a nitriding treatment, but it is not sufficiently performed. Therefore, the nitriding treatment is performed on a maraging steel with a surface in which oxygen is not sufficiently removed. As a result, improvement of the compressive residual stress is limited.

Disclosure of the Invention

[0005] Accordingly, an object of the present invention is to provide a nitriding process for a maraging steel, by which greater compressive residual stress is generated in the maraging steel.

[0006] The inventors of the present invention conducted an intensive research on a nitriding process for a maraging steel containing titanium. As a result, the following findings were obtained, and the present invention has been completed. In the technique disclosed in Japanese Unexamined Patent Application Laid-open No. 2004-162134, the solution heat treating step is performed so as not to increase surface concentration of titanium, which easily combines with oxygen. In contrast, in the present invention, a solution heat treating step is performed so as to facilitate increase of surface concentration of titanium oxide, and a reducing treatment is performed according to the surface concentration of the titanium oxide before a nitriding step. As a result, nitriding is facilitated, whereby the degree of the compressive residual stress is controlled.

[0007] The present invention provides a nitriding process for a maraging steel containing titanium, and the nitriding process includes a solution heat treating step for generating and concentrating titanium oxide at the surface of the maraging steel by a solution heat treatment. The nitriding process also includes a reducing step for reducing the titanium oxide so as to concentrate the titanium at the surface of the maraging steel. The nitriding process further includes a nitriding step for nitriding the maraging steel, in which the titanium is concentrated at the surface, thereby applying compressive residual stress at the surface of the maraging steel.

[0008] In the nitriding process for the maraging steel of the present invention, first, a solution heat treatment is performed on a maraging steel containing titanium (Ti), whereby titanium oxide (TiO_2) is formed at the surface thereof (a solution heat treating step). Specifically, as shown in Fig. 1A, a workpiece is made of a maraging steel in which titanium is solid-solved, and a partial amount of the titanium is oxidized at the surface of the workpiece. Therefore, titanium oxide is positively generated and is concentrated at the surface of the workpiece. Accordingly, the surface concentration of the titanium is increased. Thus, the titanium oxide is positively generated in the solution heat treating step, which is a great difference from the technique disclosed in Japanese Unexamined Patent Application Laid-open No. 2004-162134 in technical concept.

[0009] Then, the titanium oxide is reduced so as to concentrate the titanium at the surface of the maraging steel (a reducing step). Specifically, since titanium in an oxide state does not combine with N in a nitriding treatment, a reducing treatment is sufficiently performed as a pretreatment of the nitriding treatment. As a result, as shown in Fig. 1B, oxygen is removed. Accordingly, the surface concentration of the titanium in an activated state is increased.

[0010] Next, the maraging steel, in which the titanium is concentrated at the surface, is subjected to a nitriding treatment, whereby compressive residual stress is applied at the surface (a nitriding step). Specifically, as shown in Fig. 1C, the reduced titanium and the solid-solved titanium combine with nitrogen and form titanium nitride (TiN) by the nitriding treatment. In this case, since the titanium is in the activated state, the titanium is easily nitrided. In addition, since the surface concentration of the titanium in the activated state is high, a large amount of nitrogen infiltrates into the workpiece. As a result, greater compressive residual stress is applied at the surface of the workpiece by nitriding the titanium, whereby strength of the workpiece is greatly improved.

[0011] The nitriding process for the maraging steel of the present invention may be performed in various manners. In the solution heat treating step of the maraging steel, by controlling the atmosphere, the surface concentration of the titanium oxide is controlled. In addition, in the reducing step before the nitriding step, by controlling the reducing conditions, the amount of the oxygen to be removed is controlled. By controlling both the surface concentration and the reduction amount as described above, a necessary degree of the compressive residual stress is applied at the surface of the maraging steel. In this case, in order to obtain higher compressive residual stress than a conventional degree, for example, the surface titanium concentration of the maraging steel after the solution heat treating step is preferably set to be not less than 13.0 at %. The reducing step is preferably performed by using reducing gas at a flow rate of not less than 24.7 L/m^3.

[0012] The solution heat treatment may be performed by vacuum treatment, atmosphere treatment, or the like. As a furnace for the solution heat treatment, a batch furnace, a continuous furnace, a mesh belt furnace, etc., may be used. The reducing step may be performed by using NF_3 gas or the like. The nitriding process for the maraging steel of the present invention is suitably applied to parts such as, for example, an endless metal belt which may be used in a continuously variable transmission (CVT).

Effects of the Invention

[0013] According to the nitriding process for the maraging steel of the present invention, the surface concentration of the titanium oxide is increased by the solution heat treatment. Moreover, by performing the reducing treatment before the nitriding treatment, the surface titanium concentration is increased. Therefore, nitriding of the maraging steel is facilitated. As a result, high compressive residual stress is obtained, whereby the strength of the maraging steel is further improved.

Brief Description of the Drawings

[0014]

Figs. 1A to 1C are schematic drawings of a surface part of a maraging steel of an embodiment in each step relating to the nitriding process for the maraging steel of the present invention. Fig. 1A is a schematic drawing of a solution heat treating step, Fig. 1B is a schematic drawing of a reducing step, and Fig. 1C is a schematic drawing of a nitriding step.

Fig. 2 is a schematic flow diagram that shows a production process of an endless metal belt relating to practical examples, which were subjected to the nitriding process for the maraging steel of the present invention.

Fig. 3 is a graph that shows results of practical examples, which were subjected to the nitriding process for the maraging steel of the present invention.

Reference Numerals

[0015] 1 denotes a sheet, 2 denotes a drum, 3 denotes a heating furnace, and 4 denotes a ring.

Examples

[0016] The present invention will be described in detail with reference to specific practical examples hereinafter. In the Examples, the nitriding process for the maraging steel of the present invention is applied to the production method of an endless metal belt.

[0017] In the production of the endless metal belt, as shown in Fig. 2, first, a sheet 1 made of maraging steel is welded at both ends so as to have a cylindrical shape, thereby forming a drum 2 (a welding step). In this case, the drum 2 has a portion 2a that is hardened by the heat of the welding. Therefore, the drum 2 is subjected to a first solution heat treatment in a heating furnace 3, whereby the hardness of the drum 2 is homogenized (a first solution heat treating step). Next, the drum 2 is cut into predetermined widths, thereby forming plural rings 4 with an endless belt shape (a drum cutting step). Then, the rings 4 are rolled so as to have a predetermined thickness (a ring rolling step). In this case, the metallic structure of the rings 4 is deformed by the rolling. Therefore, the rings 4 are subjected to a second solution heat treatment so that the metallic structure of the rings 4 is recrystallized (a second solution heat treating step). In the second solution heat treating step, by controlling the atmosphere, titanium oxide is formed and is concentrated at the surface of the rings 4.

[0018] Next, the rings 4 are corrected so as to have a predetermined perimeter (a ring perimeter correcting step). In this case, the correction is performed so that the perimeters of the rings 4 differ slightly from each other. Then, the rings 4 are subjected to an aging treatment and subsequent nitriding treatment, whereby the hardness and the wear resistance of the rings 4 are improved (an aging and nitriding step). In this case, a reducing treatment is performed on the rings 4 before the nitriding treatment, thereby increasing the surface concentration of the titanium in an activated state (a reducing step). Then, by laminating the rings 4, an endless metal belt is produced (a ring laminating step).

[0019] In the Examples, the steps from the welding step to the second solution heat treating step in the above production method of the endless metal belt were performed, and obtained rings 4 were used as test pieces 11 to 13.

[0020] The test pieces 11 to 13 were made of maraging steel consisting of, by mass %, 0.004 % of C, 0.02 % of Si, 0.01 % of Mn, 0.002 % of P, less than 0.001 % of S, 18.58 % of Ni, 0.02 % of Cr, 4.99 % of Mo, 9.28 % of Co, 0.01 % of Cu, 0.12 % of Al, 0.47 % of Ti, 0.0004 % ofN, and the balance of Fe and inevitable impurities. The maraging steel having the above compositions was used in the Examples, but other maraging steels may be used as long as the compositions are in the following ranges. For example, a maraging steel consisting of, by mass %, not more than 0.01 % of C, not more than 0.10 % of Si, not more than 0.10 % of Mn, not more than 0.005 % of P, not more than 0.005 % of S, not more than 0.05 % of Cr, not more than 0.04 % of Cu, 17 to 19 % of Ni, 4.5 to 5.5 % ofMo, 9.2 to 9.5 % of Co, 0.05 to 0.15 % of Al, 0.40 to 0.50 % of Ti, and the balance of Fe and inevitable impurities, may be used.

[0021] In the first and the second solution heat treating steps, a heating furnace shown in Table 1 was used and the atmosphere was set with respect to each of the test pieces 11 to 13. The first and the second solution heat treating steps were performed at a temperature in the range of not less than the recrystallizing temperature of the maraging steel and not more than 850 °C. In the second solution heat treating step, the oxygen concentration was controlled so as to be in the range of 0.1 to 14 ppm, whereby the surface titanium concentration was controlled so as to be in the range of 4.1 to 31.4 atm %. The surface titanium concentration was measured by analyzing the surface of each test piece with μ ESCA (manufactured by Ulvac-phi, Inc., "Quantera SXM"). The surface titanium concentrations are shown in Table 1 and are maximum titanium concentrations (at %) in the region from the surface to 50 nm depth of the test pieces. The reducing treatment before the nitriding treatment was performed by using NF_3 gas as a reducing gas. The NF_3 gas was used in the range of 0 to 61.7 L/m^3 based on a unit flow of 12.3 liters per volume.

Table 1

	Furnace	Atmosphere	Oxygen Concentration ppm	Titanium concentration after solution heat treating step at %
Test piece 11	Mesh belt furnace	$N_2 + H_2$ (N_2 71.4 %) (H_2 28.6 %)	0.1	4.1
Test piece 12	Mesh belt furnace	N_2 (N_2 100 %)	5	13.0
Test piece 13	Vacuum furnace	Vacuum (Degree of vacuum 5×10^{-3} Pa)	14	31.4

[0022] The test pieces 11 to 13 of the rings thus obtained were subjected to a residual stress measurement. In the residual stress measurement, an X-ray stress measuring device (manufactured by Rigaku Corporation, "PSPC/MSF-3M") was used. The residual stress of the outer circumferential surface of the ring was measured in the thickness direction (the direction perpendicular to the circumferential direction of the outer circumferential surface). The results are shown in Table 2 and Fig. 3. Table 2 shows each surface titanium concentration after the solution heat treatment of the second solution heat treating step. Table 2 also shows compressive residual stress values after the nitriding treatment that was performed at each flow rate of the reducing gas. Fig. 3 is a graph that shows a relationship between the surface titanium concentration after the solution heat treatment and the compressive residual stress value after the nitriding treatment shown in Table 2.

Table 2

Titanium concentration after solution heat treating step at %		4.1	13.0	31.4
Flow rate of reducing gas	0 L/m3	876	1038	877
	12.3 L/m3	843	1215	1419
	24.7 L/m3	843	1297	1717
	37.0 L/m3	882	1146	1735
	61.7 L/m3	943	1160	1694

[0023] As shown in Fig. 3 and Table 2, the compressive residual stress was increased by generating the titanium oxide at the surface of the maraging steel in the solution heat treatment and by performing the reducing treatment before the nitriding treatment. Specifically, in order to obtain high compressive residual stress, the titanium concentration at the surface of the maraging steel after the solution heat treatment is preferably set to be not less than 13.0 at %. Moreover, in order to obtain high compressive residual stress, the flow rate of the reducing gas is preferably set to be not less than 24.7 L/m^3 in the reducing treatment.

Claims

1. A nitriding process for a maraging steel containing titanium, comprising:

a solution heat treating step for generating and concentrating titanium oxide at the surface of the maraging steel by a solution heat treatment;
a reducing step for reducing the titanium oxide so as to concentrate the titanium at the surface of the maraging steel; and
a nitriding step for nitriding the maraging steel, in which the titanium is concentrated at the surface, and thereby applying compressive residual stress at the surface of the maraging steel.

2. The nitriding process for the maraging steel according to claim 1, wherein the concentration of the titanium at the surface of the maraging steel after the reducing step is set to be not less than 13.0 at %.

3. The nitriding process for the maraging steel according to claim 1 or 2, wherein the reducing step is performed by using reducing gas at a flow rate of not less than 24.7 L/m^3.

Fig. 1A

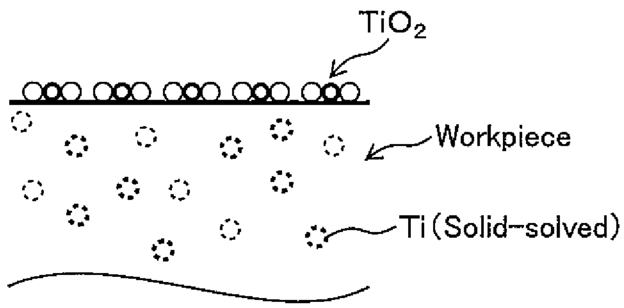


Fig. 1B

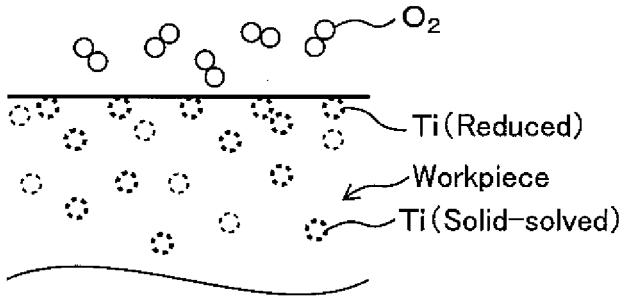


Fig. 1C

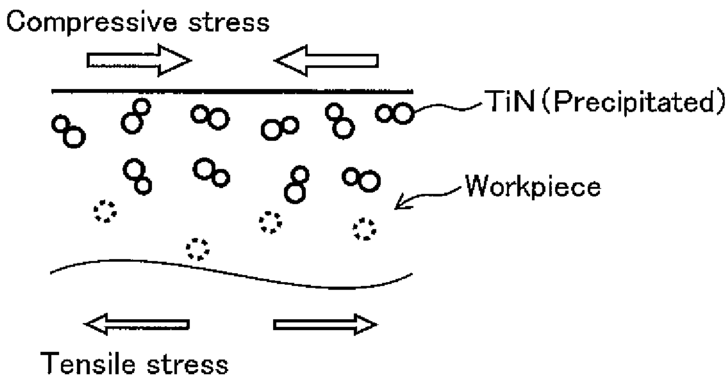


Fig. 2

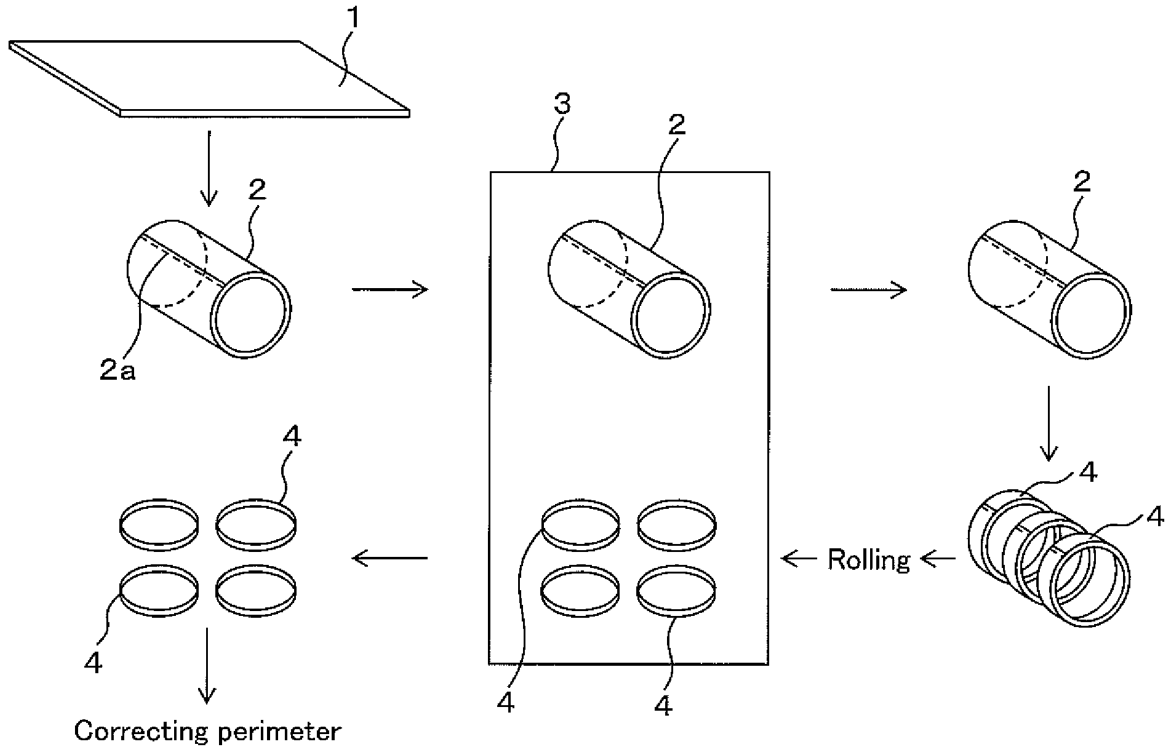
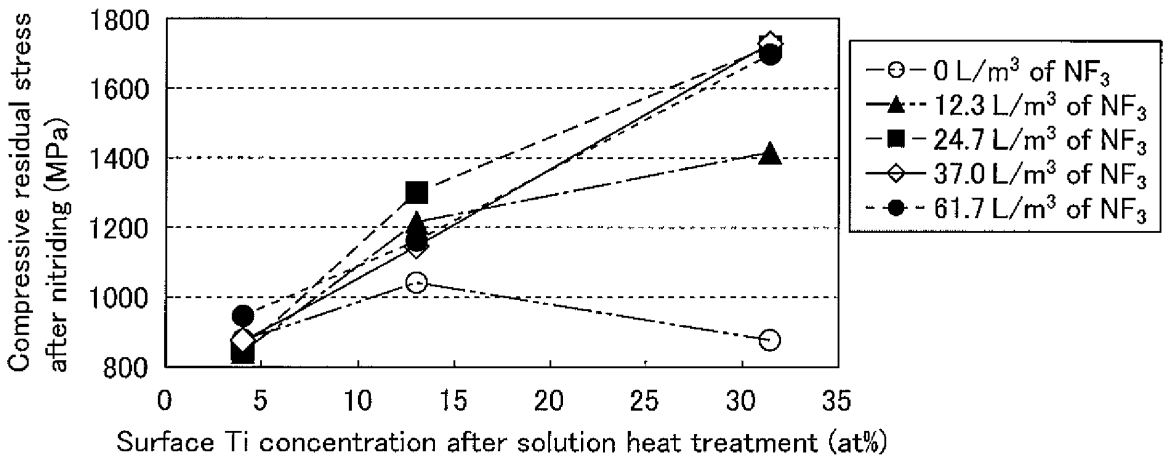

1
2
2a
3
2
2
4
4
4
4
4
4
Rolling
Correcting perimeter

Fig. 3


Compressive residual stress after nitriding (MPa)
1800
1600
1400
1200
1000
800
0
5
10
15
20
25
30
35
Surface Ti concentration after solution heat treatment (at%)
0 L/m³ of NF₃
12.3 L/m³ of NF₃
24.7 L/m³ of NF₃
37.0 L/m³ of NF₃
61.7 L/m³ of NF₃

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2010/071924

A. CLASSIFICATION OF SUBJECT MATTER
C23C8/26(2006.01)i, *C21D1/06*(2006.01)i, *C22C38/00*(2006.01)i, *C23C8/02*(2006.01)i, *C21D9/40*(2006.01)n, *C22C38/52*(2006.01)n

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)
C23C8/26, C21D1/06, C22C38/00, C23C8/02, C21D9/40, C22C38/52

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	1996-2011
Kokai Jitsuyo Shinan Koho	1971-2011	Toroku Jitsuyo Shinan Koho	1994-2011

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.
Y A	JP 2000-087214 A (Daido Hoxan Inc.), 28 March 2000 (28.03.2000), claims; paragraphs [0002], [0005] to [0007], [0015] to [0017], [0024], [0029], [0030] (Family: none)	1,3 2
Y A	JP 2006-124757 A (Toyota Motor Corp.), 18 May 2006 (18.05.2006), claim 1; paragraphs [0001] to [0007] (Family: none)	1,3 2
A	JP 2002-167652 A (Daido Steel Co., Ltd.), 11 June 2002 (11.06.2002), paragraph [0002] (Family: none)	2

☒ 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
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"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 10 February, 2011 (10.02.11)	Date of mailing of the international search report 22 February, 2011 (22.02.11)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

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

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2010/071924

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 07-188896 A (Toyota Motor Corp.), 25 July 1995 (25.07.1995), claims (Family: none)	2

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

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2004162134 A **[0003] [0004] [0006] [0008]**