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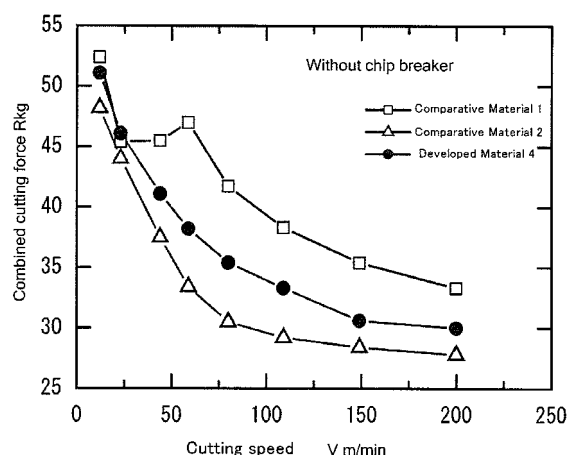
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(54) **FREE-CUTTING STAINLESS-STEEL CAST PRODUCT AND PROCESS FOR PRODUCING SAME**

(57) [Object] An object of the present invention is to provide a free-cutting stainless steel cast product capable of ensuring all of excellent machinability, environmental friendliness, and corrosion resistance, and a production method thereof.

[Means for solving] A stainless steel cast product, which contains a free-cutting additive, which is h-BN particles, where the h-BN particles are uniformly dispersed and precipitated in steel. A production method thereof, which contains: heating a stainless steel cast product in which h-BN particles are precipitated, followed by quenching to eliminate the h-BN particles by a solution treatment; and tempering to again disperse and precipitate h-BN particles.

FIG. 4



Description

Technical Field

5 **[0001]** The present invention relates to a stainless steel cast product to which a free-cutting additive has been added, and to a production method thereof.

Background Art

10 **[0002]** A stainless steel cast product to which corrosion resistance is important, for example, pipe couplings (e.g. elbows, sockets, and nipples) used in plumbing, vacuum equipments and analytical equipments, valves, and flanges for coupling, is produced by casting. Products having complicated shapes are not subjected to plastic working such as forging and rolling, but are subjected to cutting work (machining), such as flattening, piercing, and threading with as-cast structure. These products are required to have excellent corrosion resistance, and therefore austenitic stainless steel, such as SUS 304, and SUS 316, is often used. However, the austenitic stainless steel is prone to work hardening. The austenitic stainless steel is therefore known to have poor machinability, due to work hardening occurred adjacent to the cutting surface.

15 **[0003]** In the conventional art, there is provided free-cutting stainless steel to which sulfur (S), lead (Pb), or selenium (Se) is added as a free-cutting additive, for the purpose of improving machinability. A use of Pb however brings an environmental issue, and is not suitable for couplings of food and beverage machinery in view of safety. Se has been known as an environmentally hazardous element, and a use thereof has been prohibited. SUS 303, commercially available sulfur-added free-cutting stainless steel, contains about 0.3% of S. S is known as an element even a trace of which adversely affects corrosion resistance. Therefore, a use of SUS 303 is not suitable for equipments to which corrosion resistance is important.

25 **[0004]** The sulfur-added free-cutting stainless steel can be used only in a low corrosiveness environment, or for products that do not require corrosion resistance. From these reasons, a free-cutting stainless steel cast product, which ensures both excellent machinability and corrosion resistance, has not yet been provided to date.

30 **[0005]** PTL 1 discloses free-cutting stainless steel ensuring excellent machinability, corrosion resistance, and mechanical properties at the same time, and a production method thereof. In order to ensure all of the machinability, corrosion resistance, and mechanical properties, this invention improved machinability of the free-cutting stainless steel by about 25% compared to a conventional stainless steel material, by performing forging and rolling on an ingot after casting to eliminate a cast structure, and re-precipitating hexagonal boron nitride (h-BN) particles.

35 **[0006]** Although the stainless steel whose machinability has been improved by a heat treatment after forging and rolling is developed as disclosed in PTL 1, there is not disclosed a stainless steel cast product whose machinability has been improved with maintaining the cast structure.

Summary of Invention

Technical Problem

40 **[0007]** Accordingly, the present invention aims to provide a free-cutting stainless steel cast product, which can ensure all of the excellent machinability, environmental friendliness, and corrosion resistance, as a cast steel product that does not require mechanical properties so much, but requires machinability for giving complicated shapes, and to provide a production method thereof.

Solution to Problem

50 **[0008]** The present invention is accomplished based on the insight that a stainless steel cast product having excellent machinability and corrosion resistance and production method thereof can be provided by effectively utilizing characteristics of hexagonal boron nitride (h-BN) particles that are excellent as a solid lubricant, chemically stable, and not damaged by either acid or alkali, and by utilizing precipitation, or solid solution/re-precipitation of h-BN by performing a particular heat treatment even in the state of the cast structure.

55 **[0009]** Invention 1 is an embodiment, which is a stainless steel cast product contains a free-cutting additive, which is hexagonal boron nitride (h-BN) particles, in which the h-BN particles have particle diameters of 200 nm to 10 μ m, are spherical particles, and are uniformly dispersed and precipitated in steel.

[0010] Invention 2 is an embodiment, which is a production method of the stainless steel cast product of Invention 1, and the production method contains controlling a cooling rate of molten stainless steel in a temperature range of 1,250°C to 850°C during casting solidification, to thereby disperse and precipitate the h-BN particles therein.

[0011] Invention 3 is an embodiment, which is a production method of the stainless steel cast product of Invention 1, and the production method contains: heating cast stainless steel, in a cast structure of which h-BN particles are unevenly precipitated, followed by quenching the cast stainless steel to turn into a state of a solid solution, whereby eliminating the h-BN particles; and tempering the cast stainless steel to again disperse and precipitate h-BN particles.

[0012] Invention 4 is an embodiment which is a production method of the stainless steel cast product of Invention 1, and the production method contains: quenching molten stainless steel in a temperature range of 1,250°C to 850°C during casting solidification, to give a cast structure where no h-BN particle is precipitated; and tempering the cast stainless steel at temperature ranging from 950°C to 1,100°C to disperse and precipitate h-BN particles therein.

[0013] Invention 5 is an embodiment which is the production method of the stainless steel cast product according to Inventions 2 to 4, in which the boron (B) is added in an amount of 0.003% by mass to 0.5% by mass, and the nitrogen (N) is added in an amount that a molar ratio of N/B becomes 1 or more.

[0014] Invention 6 is an embodiment which is the production method of the stainless cast product according to Invention 5, in which the B is added to the molten stainless steel in the form of ferroboration or metallic boron, and the N is added to the molten stainless steel by providing a mixed gas of argon and nitrogen (argon + nitrogen) or reduced-pressure nitrogen as a melting atmosphere for the molten stainless steel.

[0015] Invention 7 is an embodiment which is the production method of the stainless steel cast product according to Invention 5, in which the B is added to the molten stainless steel in the form of ferroboration or metallic boron, and the N is added to the molten stainless steel in the form of a compound or ferroalloy containing nitrogen.

Advantageous Effects of Invention

[0016] There can be provided a stainless steel cast product whose machinability is improved without deteriorating of corrosion resistance as a result of uniformly dispersing and precipitating h-BN particles as excellent solid lubricants, which are chemically stable and are not damaged by either acid or alkali, as well as provided a production method thereof.

[0017] Invention 1 can ensure not only excellent machinability and environmental friendliness, but also corrosion resistance.

[0018] These effects are obtained by effectively applying h-BN particles having excellent properties as a solid lubricant for cast stainless steel. This application of the h-BN particles makes it possible to realize a stainless steel cast product, which ensures not only machinability, but also environmental friendliness as environmentally hazardous elements, e.g., Pb and Se, are not used, and inhibits deterioration of corrosion resistance.

[0019] As a result of the improvement in machinability, electric power consumption in a cutting machine can be reduced. This reduction in the electric energy consumption leads to reduction in carbon dioxide gas emissions. Further, an improvement in productivity can be expected as such stainless steel cast product can be machined at high speed.

Brief Description of Drawings

[0020]

FIG. 1 is a SEM micrograph depicting a precipitation and dispersion state of the precipitates on a fracture surface of Developed Material 1.

FIG. 2 is a SEM micrograph depicting a precipitation and dispersion state of the precipitates on a fracture surface of Developed Material 3.

FIG. 3 is a SEM micrograph depicting a precipitation and dispersion state of the precipitates on a fracture surface of Comparative Material 2.

FIG. 4 is a graph depicting a relationship between cutting speed and combined cutting force of Developed Material 4 and Comparative Materials 1 and 2 during turning.

FIG. 5 is a graph depicting a relationship between cutting speed and combined cutting force of Developed Materials 1 to 3 and Comparative Material 3 during turning.

FIG. 6 is a graph depicting the results of a corrosion test of Developed Material 4 and Comparative Materials 1 and 2 performed in accordance with the method of sulfuric acid test for stainless steel (JIS G 0591).

Description of Embodiments

[0021] The present invention has characteristics as described above, and embodiments thereof will be explained hereinafter.

[0022] In the production method of the present invention, melting of cast stainless steel is performed by means of a melting furnace, which is capable of adjusting melting atmosphere, and is generally used for melting of stainless steel. In the melting, ferroboration or metallic boron is used as a source of B, but use of the ferroboration having a low melting point

is technically advantageous, and is economical as a cost per unit weight of B is low.

[0023] For a general standard, the B content is determined as the final B content in the stainless steel cast product, which is preferably 0.003% by mass to 0.5% by mass, more preferably 0.01% by mass to 0.2% by mass.

[0024] As for a method for adding N, there are a method where the molten stainless steel is allowed to absorb N in a melting atmosphere, and a method in which nitride of alloying elements constituting stainless steel, such as chromium nitride, and ferrochromium nitride, is added to the molten stainless steel.

[0025] The N content in the stainless steel cast product may be an amount that a molar ratio of N/B becomes 1 or more, for a general standard. When the molar ratio of N/B in the cast stainless steel is smaller than 1, an amount of the solute B increases, which reduces an amount of precipitated h-BN particles that are useful for machinability. Accordingly, it is desired that the molar ratio of N/B is as large as possible. The N content varies depending on chemical compositions of the cast stainless steel, but as B increases, an equivalent N concentration decreases in the steel, because B increases the activity of N. In the chemical composition of SUS 304 stainless steel, the N content is 0.25% by mass or lower, exclusive of melting under pressurized nitrogen atmosphere.

[0026] The molten stainless steel containing B and N, prepared in the aforementioned manner can precipitate and distribute h-BN spherical particles having particle diameter of 200 nm to 10 μm in the cast structure, by controlling a cooling rate thereof in the precipitation temperature range of h-BN, i.e., 1,250°C to 850°C, during the solidification in a mold.

[0027] In a stainless steel cast product, h-BN coarsely grown to the size of about 20 μm to about 30 μm may be unevenly distributed and precipitated in a portion of the product, depending on a cooling rate in a cooling process after casting. To avoid uneven distribution and precipitation of coarse h-BN particles:

- (1) a cooling rate after the casting is controlled;
- (2) a metal mold is used; and
- (3) a design of a mold is considered, such as a position of teeming, and a shape of a feeder head.

[0028] The h-BN precipitated in the stainless steel cast product is decomposed into B and N and is turned into a solid solution in a matrix of the cast stainless steel by being held at the temperature of 1,200°C or higher, for a relatively short time (e.g., 0.5 hours to 1 hour, at 1,250°C). Note that, such treatment is not possible when the stainless steel cast product is melted, and therefore it is necessary to perform the treatment at temperature lower than the melting point of the steel.

[0029] By quenching from this state, a stainless steel cast product containing B and N which are in the state of a supersaturated solid solution is obtained. An operation for quenching may be water quenching, which is generally performed for stainless steel, but the cooling rate in the below-mentioned temperature range at which h-BN is precipitated needs to be adjusted to a cooling rate at which precipitation does not occur.

[0030] The supersaturated B and N are re-precipitated as h-BN during tempering at the temperature of 800°C to 1,150°C. When tempering is performed at the temperature around 800°C, nucleation of h-BN is prioritized rather than growth because of the following two factors, that are a difference between equilibrium solubility and supersaturation solubility of B and N is large at this temperature, and diffusion lengths of B and N are small because diffusion velocities of B and N are slow at this temperature. Therefore, very finely and uniformly precipitated h-BN appears in the entire material. When the tempering is performed at the temperature around 1,150°C, in contrast to the tempering at the temperature around 800°C, coarsely grown h-BN precipitates appear as growth of h-BN is prioritized rather than nucleation.

[0031] Accordingly, in order to precipitate h-BN with particle diameters and distribution suited for giving excellent machinability, a selection of the tempering temperature is important. As a result of trial experiments, the tempering temperature at which the particle diameters and distribution suited for giving excellent machinability is preferably in the range of 950°C to 1,100°C.

[0032] When the cast product can be directly quenched to the tempering temperature, h-BN is not precipitated during casting. In such casting conditions to give a solid solution of B and N, obviously, it is not necessary to perform a heat treatment at the temperature of 1,200°C or higher to decompose h-BN particles.

[0033] As for the tempering period, the higher the tempering temperature is the shorter the period is, as diffusion velocities of B and N are fast as the temperature is high. The period is therefore in the range of 0.5 hours to 3 hours, preferably 1 hour to 2 hours. In order to restrict further growth of h-BN, quenching is performed after the tempering.

Examples

(Example 1)

[0034] A commercial austenitic stainless steel (SUS 304) round bar (weight: 18 kg) was used as a melting raw material, and was melted by means of a vacuum induction melting furnace. A chemical composition (% by mass) of the melting

raw material included 0.04% of C, 0.30% of Si, 1.00% of Mn, 0.030% of P, 0.024% of S, 8.09% of Ni, and 18.05% of Cr. When melting, N gas with partial pressure of 0.07 MPa was introduced in the vacuum induction melting furnace, to adjust a concentration of N in the molten steel. After melting, a predetermined amount of commercial ferroboron (19.2% by mass of B) was added to the molten steel to adjust a concentration of B. The resultant was maintained in a reduced-pressure nitrogen atmosphere for 20 minutes, and cast at 1,600°C into a cast iron mold, to thereby produce an ingot. The target values of the B contents of Developed Materials 1 to 3 were respectively 0.02% by mass, 0.05% by mass, and 0.1% by mass, and the target values of the N contents thereof were 0.2% by mass, respectively.

[0035] Comparative Material 1 was produced (corresponding to SUS 304 cast stainless steel without h-BN) in the same melting and casting conditions to produce an ingot in the manner as in Developed Materials 1 to 3, provided that the melting raw material was melted in an Ar atmosphere. As Comparative Material 2, a material in which 0.3% by mass of S was added to Comparative Material 1 (corresponding to SUS303 cast stainless steel, sulfur-added free-cutting cast stainless steel) was produced. As Comparative Material 3, a material in which, similarly to Developed Materials 1 to 3, 0.2% by mass of N was added to Comparative Material 1 was produced.

[0036] In order to unify effects of N on machinability and corrosion resistance, the partial pressure of N in the melting atmosphere was adjusted to 0.005 MPa, to thereby produce an ingot of Developed Material 4 having the same level of N as those in Comparative Materials 1 and 2. As a melting raw material, the same material used in Developed Materials 1 to 3 was used, and the target value of the B content was 0.05% by mass, which was the same to the target value of Developed Material 2. Analysis values (unit: % by mass) of B, N and S in the produced materials (Developed Materials 1 to 4, Comparative Material 1 to 3) after casting were presented in Table 1.

Table 1

Analysis values of B, N, and S in each sample (unit: % by mass) ("-" represents that analysis was not performed)			
Sample	B%	N%	S%
Developed Material 1	0.021	0.22	-
Developed Material 2	0.049	0.20	-
Developed Material 3	0.096	0.20	-
Developed Material 4	0.047	0.065	-
Comparative Material 1	-	0.057	-
Comparative Material 2	-	0.063	0.29
Comparative Material 3	<0.001	0.21	-

[0037] To the cast ingot, an h-BN solution treatment was performed, which was the heat treatment in an electric resistance heating furnace in air for 0.5 hours at 1,250°C followed by water quenching outside the furnace. To the water-quenched ingot, an h-BN precipitation treatment was performed, which was the heat treatment in an electric resistance heating furnace in air for 1 hour at 1,050°C followed by water quenching outside the furnace. To equalize the conditions of a cast structure, this heat treatment was performed on the developed materials and comparative materials under the same conditions.

[0038] FIGs. 1 to 3 are SEM (scanning electron microscopy) micrographs depicting precipitation and dispersion states of the precipitates in Developed Material 1, Developed Material 3, and Comparative Material 2, respectively. A round bar having a diameter of 3.6 mm was cut from the heat treated sample, circumferentially notched, and bent at the notched position, and the fracture surface of the bent bar was observed by SEM. The SEM was equipped with an energy dispersive X-ray spectroscopy (EDS), and elementary analysis of nonmetallic inclusions observed on the fracture surface was performed by the EDS, to thereby determine the nonmetallic inclusions.

[0039] In FIG. 1, it was observed that some h-BN particles (indicated by solid arrows) having the size of 10 μm or smaller were dispersed at the bottom of dimples over the entire fracture surface in the visual field with the magnification of x200. Also, some spherical MnS particles (indicated by dashed arrows) having the size of about 10 μm derived from a trace of sulfur and manganese contained in the melting raw material were observed.

[0040] In FIG. 2, similarly to FIG. 1, it was observed that the h-BN particles having the size of 10 μm or smaller were dispersed in the entire fracture surface in the visual field with the magnification of x200. In FIG. 2, the number of the h-BN particles was approximately 10 times the number thereof of Developed Material 1, with proportional to the concentration of B. It was assumed from the shapes of the h-BN particles observed in FIGs. 1 and 2 that supersaturated B and N in the molten steel were precipitated as the h-BN particles in the solidification process of the molten steel.

[0041] In the case of Comparative Material 2 of FIG. 3, a large number of MnS spherical particles having the size of

about 10 μm to about 30 μm was observed at the bottom of dimples over the entire fracture surface in the visual field with the magnification of $\times 200$. These MnS particles were also observed in FIG. 1, and were assumed from their particle diameters and shapes to be crystallized when the steel was in the molten state.

[0042] As for an evaluation test for machinability, a lathe turning test was performed on a round bar sample cut out from cast steel samples, which were Comparative Materials 1 and 2, and Developed Material 4 after the heat treatment. The results are presented in FIG. 4. As depicted in Table 1, these three materials had substantially the same level of the N content, which was about 0.06% by mass. FIG. 4 depicts an effect of the h-BN particles or MnS particles dispersed in the material on the machinability. The conditions for the turning test included the cutting depth of 1.0 mm, the feed rate of 0.1 mm/rev, and the tool material of M30 (without chip breaker), no use of cutting oil, and the turning cutting speed of 12 m/min to 200 m/min. Under these conditions, the measurement values were obtained.

[0043] Developed Material 4 reduced the combined cutting force by 20% in the intermediate cutting speed region, 11% in the high cutting speed region, compared to Comparative Material 1 (corresponding to SUS 304 cast stainless steel), and the machinability thereof was significantly improved.

[0044] Comparative Material 2 was sulfur-added free-cutting cast stainless steel, and the machinability of the developed materials was lower than that of Comparative Material 2. In the case where corrosion resistance of a cast steel product is important, however, Comparative Material 2 cannot be used. Only the developed materials can ensure both excellent machinability and corrosion resistance, the superiority of the developed materials over the comparative materials cannot be denied.

[0045] FIG. 5 depicts a relationship between cutting speed and combined cutting force of the samples of Developed Materials 1 to 3, where the amount of B added was varied, and Comparative Material 3 (B was not added) in the turning process. As presented in Table 1, these four materials had substantially the same level of the N content, which was about 0.2% by mass. FIG. 5 depicts an effect of the addition of B on the machinability. Compared to Comparative Material 3 whose concentration of B was 0% by mass, it was observed that the developed materials to which B was added reduced the cutting resistance in almost all regions of the cutting speed, and therefore it was confirmed that the machinability was improved by addition of B.

[0046] As an evaluation test of stainless steel to corrosion resistance, a corrosion test was performed on samples of cast steel to which the heat treatment had been performed. The results are presented in FIG. 6. Since N contributed to corrosion resistance of stainless steel, comparison was carried out with materials having the same level of the N concentration. FIG. 6 depicts the results of the corrosion test performed in accordance with the method of sulfuric acid test for stainless steel (JIS G 0591). The conditions for the test were as follows. Each sample was immersed in boiled 5% H_2SO_4 for 6 hours consecutively. The value obtained by dividing the corrosion weight loss with the initial surface area of the sample was determined as a corrosion amount. The obtained corrosion amounts were compared.

[0047] Comparing the corrosion resistance of the materials based on the fact whether or not h-BN was added, hardly any difference was observed between Developed Material 4 and Comparative Material 1, and deterioration in corrosion resistance was not confirmed. On the other hand, Comparative Material 2 significantly increased its corrosion amount compared to Developed Material 4 and Comparative Material 1, which indicated that Comparative Material 2 could not be used when corrosion resistance was required.

[0048] The present invention is obviously not limited to the examples above, and specific details of the present invention include various embodiments.

Industrial Applicability

[0049] As explained in details above, the present invention can easily provide a stainless steel cast product, which is environmentally friendly and has improved its machinability without deteriorating its corrosion resistance, and hence the present invention can provide excellent utility of the stainless steel cast product in various processing fields.

Citation List

Patent Literature

[0050]

PTL 1 Internal Patent Application Publication No. W02008/016158

Claims

1. A stainless steel cast product, comprising:

a free-cutting additive, which is hexagonal boron nitride (h-BN) particles, wherein the h-BN particles have particle diameters of 200 nm to 10 μm , are spherical particles, and are uniformly dispersed and precipitated in the stainless steel cast product.

- 5 **2.** A production method of the stainless steel cast product of claim 1, comprising:

 controlling a cooling rate of molten stainless steel in a temperature range of 1,250°C to 850°C during casting solidification, to thereby disperse and precipitate the h-BN particles therein.
- 10 **3.** A production method of the stainless steel cast product of claim 1, comprising:

 heating cast stainless steel, in a cast structure of which h-BN particles are unevenly precipitated, to temperature equal to or higher than 1,200°C, followed by quenching the cast stainless steel to turn into a state of solid solution, whereby eliminating the h-BN particles; and
15 tempering the cast stainless steel at temperature ranging from 950°C to 1,100°C to again disperse and precipitate h-BN particles.
- 4.** A production method of the stainless steel cast product of claim 1, comprising:

20 quenching molten stainless steel in a temperature range of 1,250°C to 850°C during casting solidification, to give a cast structure where no h-BN particle is precipitated; and
 tempering the cast stainless steel at temperature ranging from 950°C to 1,100°C to disperse and precipitate h-BN particles therein.
- 25 **5.** The production method of the stainless steel cast product according to any one of claims 2 to 4, wherein boron (B) is added in an amount of 0.003% to 0.5% by mass, and nitrogen (N) is added in such amount that a molar ratio of N/B becomes 1 or more.
- 30 **6.** The production method of the stainless steel cast product according to claim 5, wherein the B is added to the molten stainless steel in the form of ferroboration or metallic boron, and the N is added to the molten stainless steel by providing a mixed gas of argon and nitrogen (argon + nitrogen) or reduced-pressure nitrogen as a melting atmosphere for the molten stainless steel.
- 35 **7.** The production method of the stainless steel cast product according to claim 5, wherein the B is added to the molten stainless steel in the form of ferroboration or metallic boron, and the N is added to the molten stainless steel in the form of a compound or ferroalloy containing nitrogen.

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FIG. 1

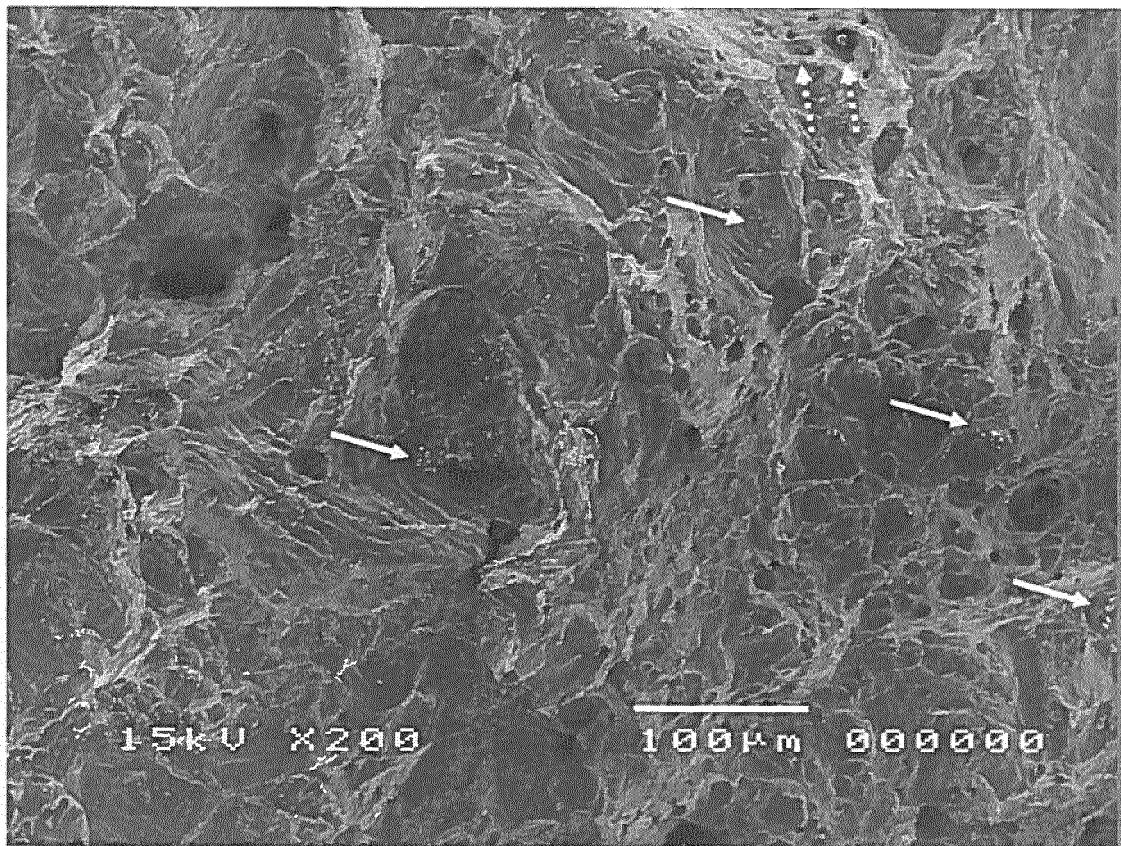


FIG. 2

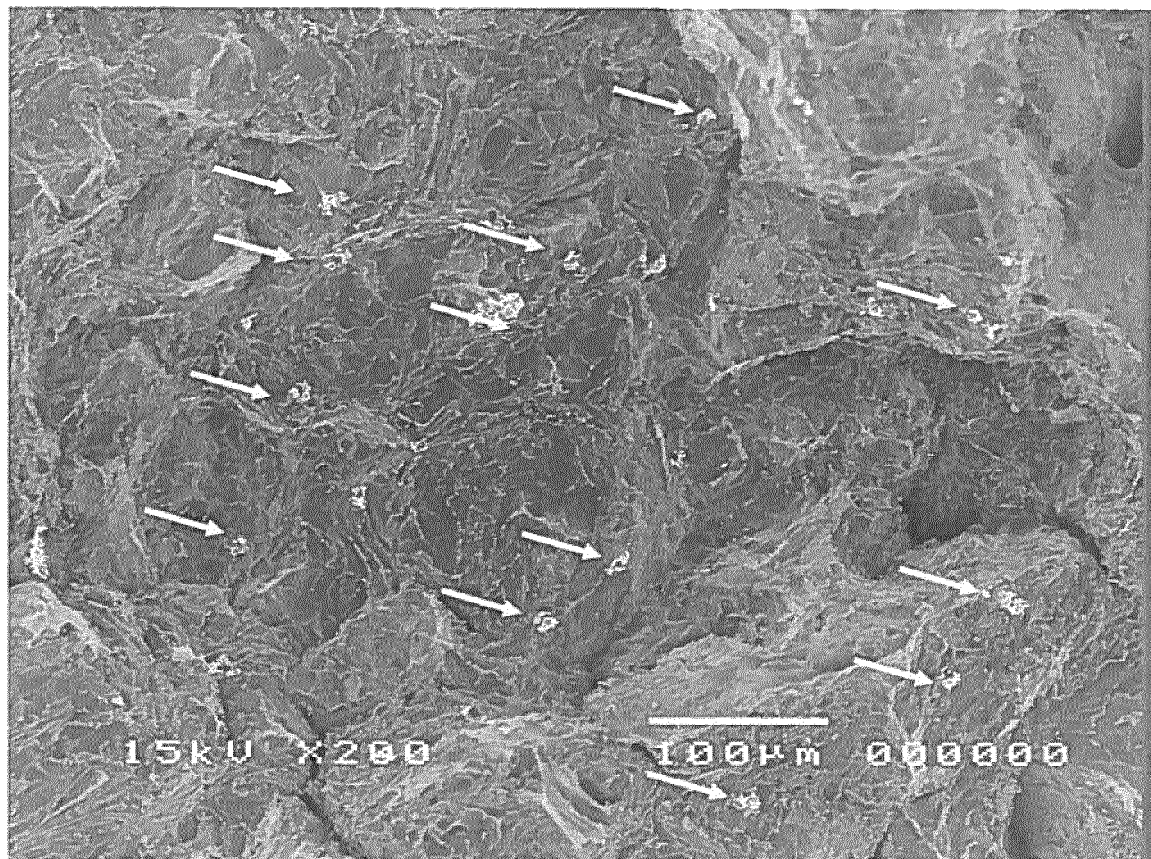


FIG. 3

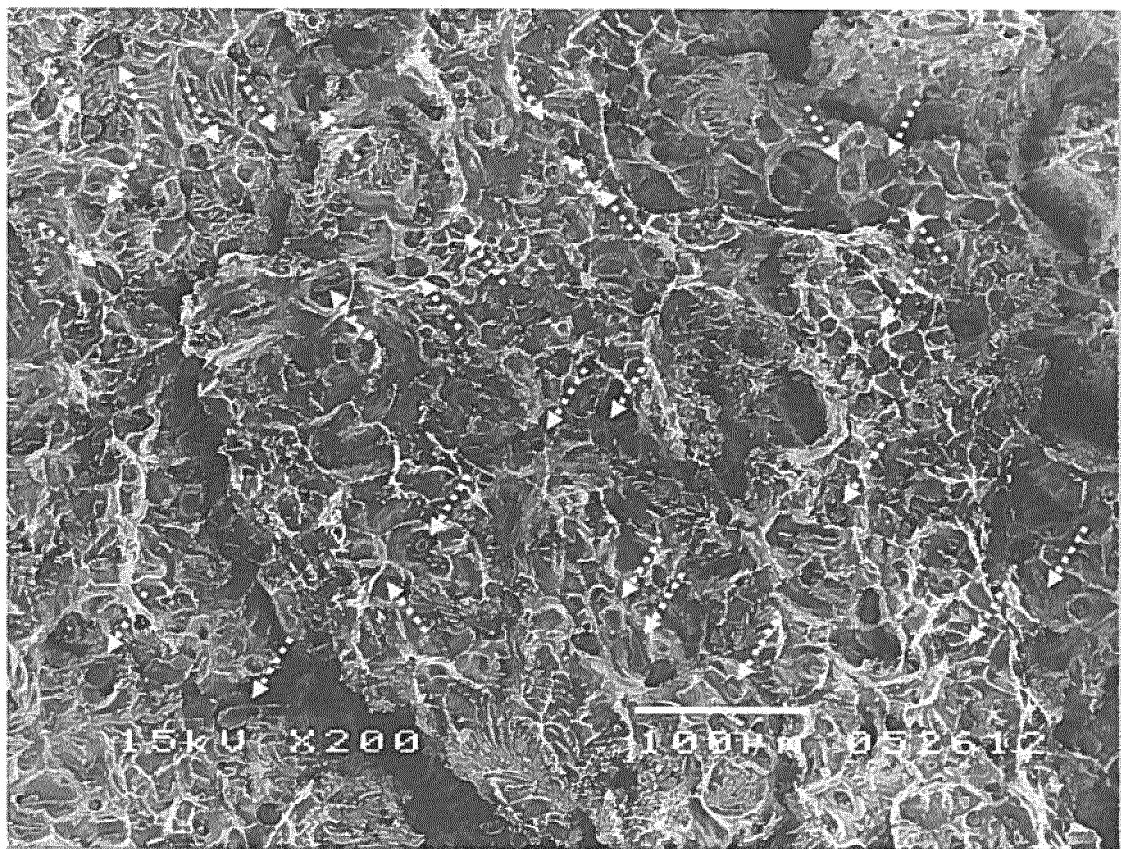


FIG. 4

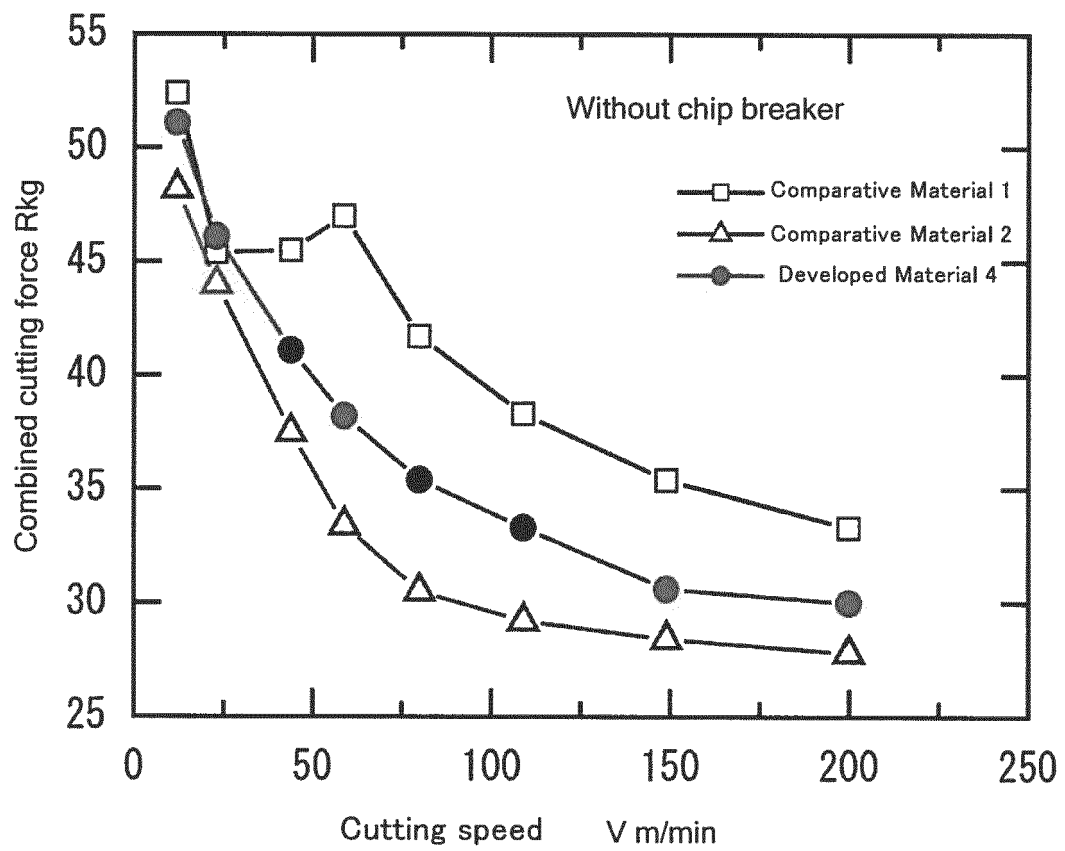


FIG. 5

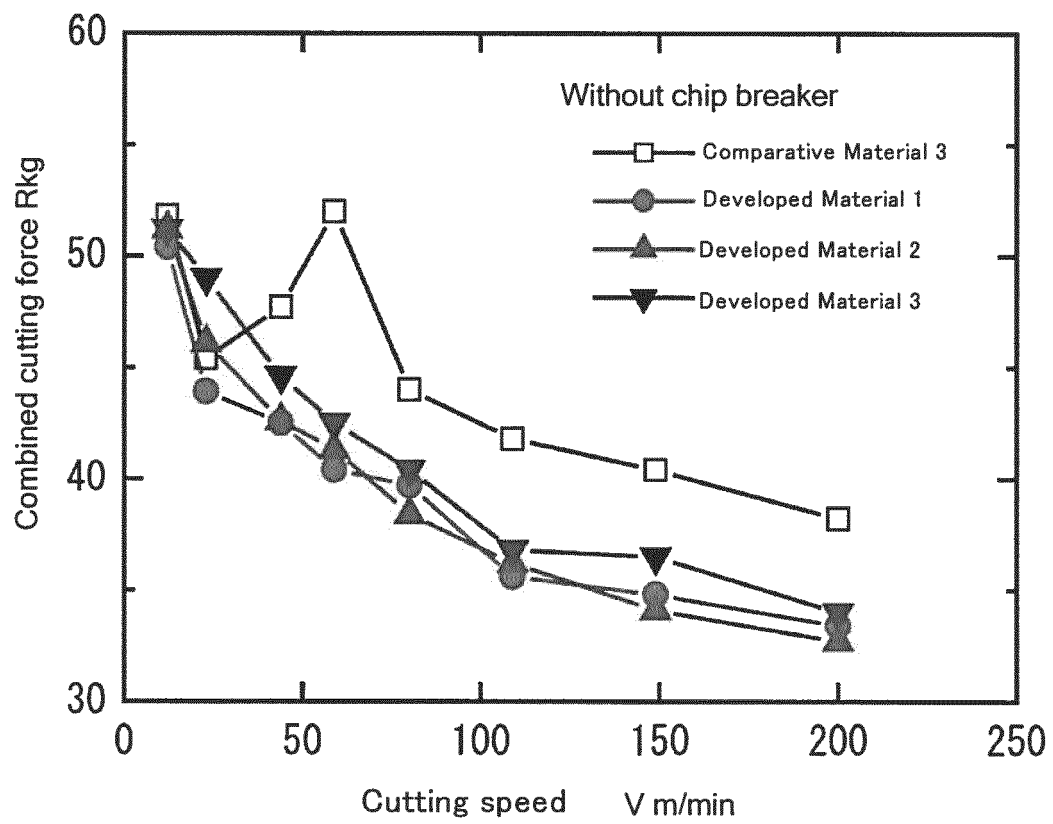
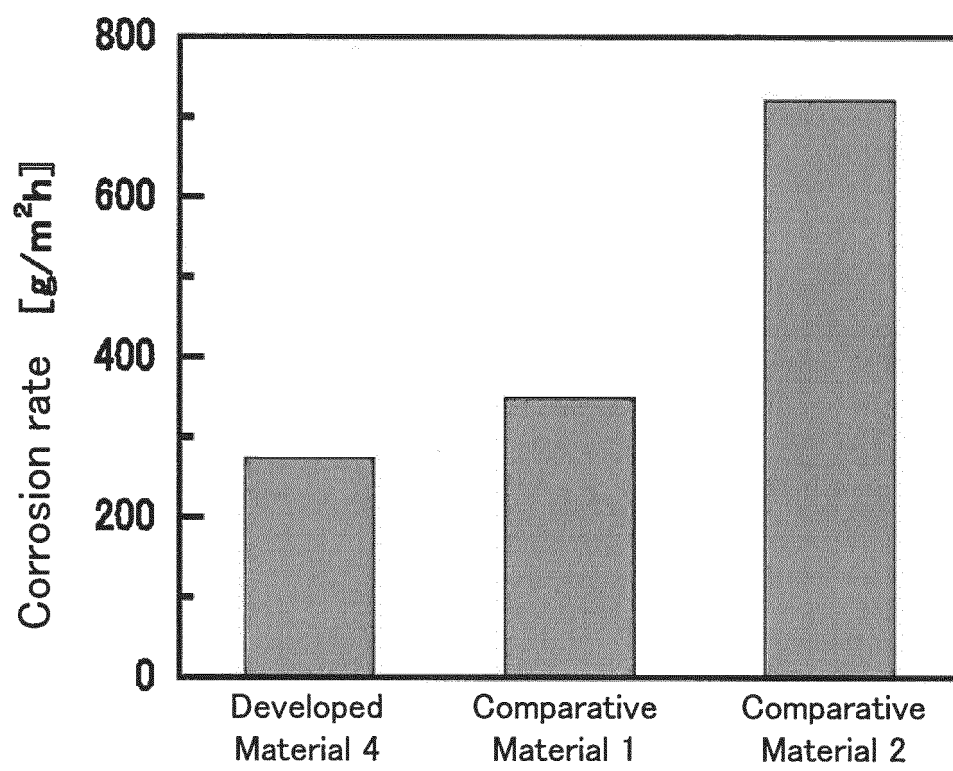


FIG. 6



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2011/059910

A. CLASSIFICATION OF SUBJECT MATTER

C22C38/00(2006.01) i, C21D6/00(2006.01) i, C22C33/04(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)

C22C38/00-38/60, C21D6/00, C22C33/04

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.
X A	WO 2008/016158 A1 (Independent Administrative Institution National Institute for Materials Science), 07 February 2008 (07.02.2008), entire text & EP 2048257 A1	1, 3, 5-7 2, 4
A	JP 2003-129191 A (Nisshin Steel Co., Ltd.), 08 May 2003 (08.05.2003), (Family: none)	1-7

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

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Date of the actual completion of the international search
08 July, 2011 (08.07.11)Date of mailing of the international search report
19 July, 2011 (19.07.11)Name and mailing address of the ISA/
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Patent documents cited in the description

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