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(71) Applicant: **Proterial, Ltd.**
Tokyo 135-0061 (JP)

(72) Inventors:
• **NAMITO, Tomonori**
Tokyo 135-0061 (JP)
• **KIMURA, Hirofumi**
Tokyo 135-0061 (JP)

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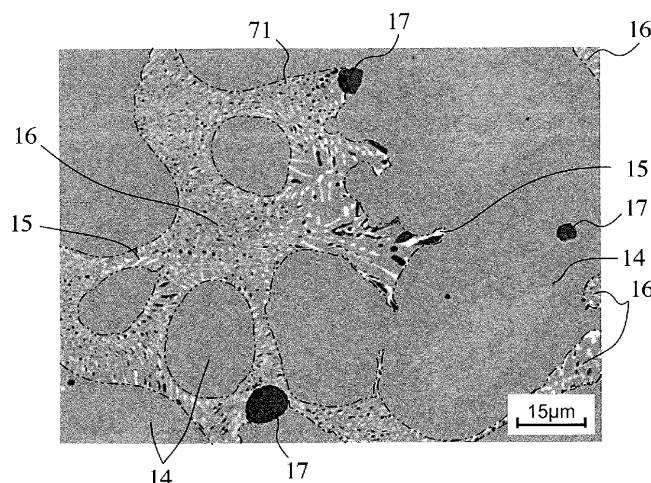
(74) Representative: **Diehl & Partner**
Patent- und Rechtsanwaltskanzlei mbB
Erika-Mann-Straße 9
80636 München (DE)

(54) **AUSTENITIC HEAT-RESISTANT CAST STEEL AND EXHAUST SYSTEM COMPONENT FORMED OF SAME**

(57) A heat-resistant, austenitic cast steel comprising by mass 0.30 to 0.50% of C, 0.50 to 2.0% of Si, 0.50 to 2.0% of Mn, 0.10 to 0.40% of S, 16.0 to 21.0% of Cr, 6.0 to

12.0% of Ni, 0.5 to 2.0% of Nb, and 0.80% or less of Cu, the balance being Fe and inevitable impurities.

Fig. 4B



Description

FIELD OF THE INVENTION

5 **[0001]** The present invention relates to a heat-resistant, austenitic cast steel having excellent shrinkage cracking resistance, cold cracking resistance and machinability, as well as good thermal fatigue properties and reduced content of expensive alloy elements, and an exhaust member made of the same.

BACKGROUND OF THE INVENTION

10 **[0002]** Exhaust members used in internal combustion engines typified by automobile engines, especially an exhaust manifold illustrated in Fig. 1, are manufactured using casting, which allows for a high degree of freedom in shape designing, because they are thin-walled and have complex shapes. Because they are exposed to high-temperature exhaust gases when an automobile is in operation, exhaust members should have excellent heat resistance and durability at high temperatures. Therefore, austenitic heat-resistant cast steel is mainly used as their constituent material. Various compositions have been proposed for austenitic heat-resistant cast steel.

15 **[0003]** For example, WO 2009/104792 proposes a heat-resistant, austenitic cast steel that is composed of, by mass, 0.3 to 0.6% of C, 1.1 to 2% of Si, 1.5% or less of Mn, 17.5 to 22.5% of Cr, 8 to 13% of Ni, 1.5 to 4% of W+2Mo (at least one of W and Mo), 1 to 4% of Nb, 0.01 to 0.3% of N, 0.01 to 0.5% of S, the balance being Fe and unavoidable impurities, and that satisfies the following formulas (1) to (4):

$$0.05 \leq (C - Nb/8) \leq 0.6 \dots (1)$$

25
$$17.5 \leq 17.5Si - (W + 2Mo) \dots (2)$$

$$5.6Si + (W + 2Mo) \leq 13.7 \dots (3)$$

30
$$0.08Si + (C - Nb/8) + 0.015Cr + 0.011Ni + 0.03W + 0.02Mo \leq 0.96 \dots (4)$$

[wherein the symbol of an element in each formula represents its content (% by mass)].

35 **[0004]** WO 2016/052750 proposes a heat-resistant, austenitic cast steel having excellent thermal fatigue properties that comprises, by mass, 0.3 to 0.6% of C, 0.5 to 3% of Si, 0.5 to 2% of Mn, 15 to 30% of Cr, 6 to 30% of Ni, 0.6 to 5% of Nb, 0.01 to 0.5% of N, and 0.01 to 0.5% of S, with a C/N ratio of 4 to 7, the balance being Fe and unavoidable impurities, wherein a ratio A/B of a Cr-carbide-forming index A to a Nb-carbide-forming index B is 0.6 to 1.7, wherein A and B are expressed by the following formulas (1) and (2):

40
$$A = 8.5C - Nb + 0.05Cr + 0.65Ni - 5 \dots (1)$$

$$B = 7.8Nb \dots (2)$$

45 [wherein the symbol of an element in each formula represents its content (% by mass)].

[0005] Although the heat-resistant, austenitic cast steels disclosed in WO 2009/104792 and WO 2016/052750 have excellent thermal fatigue life at temperatures of around 1000°C or higher, they contain a large amount of expensive alloy elements, resulting in poor cost performance. In addition, due to their low ductility at room temperature, thin-walled exhaust manifolds may suffer from cracking (cold cracking) during cooling after casting, which may reduce product acceptance rate.

50 **[0006]** JP 2011-219801 A proposes an iron (Fe)-based, heat-resistant, austenitic cast steel that, wherein the total is taken as 100% by mass (hereinafter simply referred to as "%"), contains 0.4 to 0.8% of carbon (C), 3.0% or less of silicon (Si), 0.5 to 2.0% of manganese (Mn), 0.05% or less of phosphorus (P), 0.03 to 0.2% of sulfur (S), 18 to 23% of chromium (Cr), 3.0 to 8.0% of nickel (Ni), and 0.05 to 0.4% of nitrogen (N), and the ratio of chromium (Cr) to carbon (C) is in the range of $22.5 \leq Cr/C \leq 57.5$. However, there is a concern that this heat-resistant, austenitic cast steel is prone to cracking caused by micro shrinkage cavities (hereinafter also referred to as shrinkage cracking) when cast into exhaust manifolds, which may result in a decrease in product acceptance rate.

55 **[0007]** In addition, SCH12, a type of austenitic heat-resistant steel specified in JIS G 5122, is not only prone to shrinkage

cracking, but also has difficulty in machinability compared to the materials disclosed in the above references, making it unsuitable for exhaust manifolds, which require machining during manufacturing.

OBJECT OF THE INVENTION

[0008] Accordingly, an object of the present invention is to provide a heat-resistant, austenitic cast steel which contains a small amount of expensive alloy elements, is resistant to shrinkage cracking during casting and cold cracking after casting, has good machinability after casting, and has predetermined thermal fatigue properties at around 800°C, and an exhaust member, particularly an exhaust manifold, made of the same.

SUMMARY OF THE INVENTION

[0009] Thus, the heat-resistant, austenitic cast steel of the present invention comprises by mass

0.30 to 0.50% of C,
0.50 to 2.0% of Si,
0.50 to 2.0% of Mn,
0.10 to 0.40% of S,
16.0 to 21.0% of Cr,
6.0 to 12.0% of Ni,
0.5 to 2.0% of Nb, and
0.80% or less of Cu,
the balance being Fe and inevitable impurities.

[0010] In the heat-resistant, austenitic cast steel of the present invention, the S content is preferably 0.15 to 0.37% by mass, and the Nb content is preferably 0.9 to 1.6% by mass, which not only further suppresses shrinkage cracking during casting and cold cracking after casting, but also provides a better balance between machinability and thermal fatigue properties.

[0011] In the heat-resistant, austenitic cast steel of the present invention, the number of manganese sulfides having equivalent circle diameters of 1 μm or more in an arbitrary cross section is preferably 350 to 2550 per mm², which improves machinability while ensuring oxidation resistance.

[0012] In the heat-resistant, austenitic cast steel of the present invention, an area ratio of niobium carbide in an arbitrary cross section is preferably 0.5 to 11.0%, which can suppress the occurrence of shrinkage cracking and provide a heat-resistant cast steel with good high-temperature strength and thermal fatigue properties.

[0013] The exhaust member of the present invention is made of the above heat-resistant, austenitic cast steel.

[0014] The exhaust member is preferably an exhaust manifold.

EFFECTS OF THE INVENTION

[0015] The heat-resistant, austenitic cast steel of the present invention is resistant to shrinkage cracking during casting and cold cracking after casting, has good workability after casting, has good thermal fatigue properties at around 800°C, and achieves low cost because the content of expensive alloy elements is suppressed. Such heat-resistant, austenitic cast steel is suitable for exhaust members, particularly an exhaust manifold, of internal combustion engines.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016]

Fig. 1 is a schematic front view showing an exhaust manifold of an example of an exhaust member.

Fig. 2A is a schematic plan view showing a casting from which a test piece for evaluating micro shrinkage cavities is taken.

Fig. 2B is a schematic side view showing a casting from which a test piece for evaluating micro shrinkage cavities is taken.

Fig. 3A is a schematic plan view showing a stepped casting from which a test piece for observing microstructure is taken.

Fig. 3B is a schematic side view showing a stepped casting from which a test piece for observing microstructure is taken.

Fig. 4A is a photograph showing the microstructure of the heat-resistant, austenitic cast steel of Example 4.

Fig. 4B is a photograph showing an expanded view of region A in Fig. 4A.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[1] Heat-resistant, austenitic cast steel

(A) Composition

[0017] The amount of each element described below is expressed on a mass basis unless otherwise mentioned.

(1) C (carbon): 0.30 to 0.50%

[0018] C improves the fluidity of a melt and increases castability, and after solidification, it is dissolved in the austenite matrix and strengthens the matrix (solid solution strengthening). It also forms thermally stable, hard carbides with alloy elements such as Cr (chromium) and Nb (niobium), which are dispersed in the austenite matrix and increase high-temperature strength. To exhibit such functions effectively, the C content should be 0.30% or more. On the other hand, excessive C also causes the amount of carbide precipitated to become excessive, which not only reduces ductility through embrittlement but also deteriorates machinability, so the C content should be 0.50% or less. Accordingly, the range of the C content is set to 0.30 to 0.50%. The lower limit of the C content is preferably 0.35%, and more preferably 0.37%. The upper limit of the C content is preferably 0.45%, and more preferably 0.44%.

(2) Si (silicon): 0.50 to 2.0%

[0019] Si improves oxidation resistance, resulting in improved thermal fatigue life, so the Si content should be 0.50% or more. However, excessive Si makes the austenite structure unstable and leads to deterioration of castability, so its upper limit is set at 2.0%. Accordingly, the range of the Si content is set to 0.50 to 2.0%. The lower limit of the Si content is preferably 0.80%, more preferably 0.90%, and most preferably 1.0%. The upper limit of the Si content is preferably 1.5%, more preferably 1.2%, and most preferably 1.1%.

(3) Mn (manganese): 0.50 to 2.0%

[0020] Mn is an element that not only stabilizes the austenite structure, but also forms sulfides (MnS) with S (sulfur) which are dispersed in the austenite matrix as free-cutting particles, thereby contributing to improved machinability. To obtain this effect, Mn should be 0.50% or more, but when it exceeds 2.0%, oxidation resistance deteriorates. Accordingly, the range of the Mn content is set to 0.50 to 2.0%. The lower limit of the Mn content is preferably 0.80%, and more preferably 0.90%. The upper limit of the Mn content is preferably 1.5%, more preferably 1.2%, and most preferably 1.1%.

(4) S (sulfur): 0.10 to 0.40%

[0021] S is combined with Mn and Cr to form MnS (sulfide) and (Mn, Cr)S (complex sulfide), which are dispersed in the austenite matrix. MnS and (Mn, Cr)S can be collectively called manganese sulfides. Manganese sulfides have a lubricating function, thereby contributing to improving the machinability of heat-resistant cast steel. To obtain this effect, the S content is set to 0.10% or more. However, when the S content exceeds 0.40%, the high-temperature strength and ductility have a stronger tendency to decrease, and the thermal fatigue properties also has a stronger tendency to decrease due to the excessive generation of manganese sulfides. Accordingly, the range of the S content is set to 0.10 to 0.40%. The lower limit of the S content is preferably 0.12%, more preferably 0.15%, and most preferably 0.16%. The upper limit of the S content is preferably 0.37%, and more preferably 0.34%.

(5) Cr (chromium): 16.0 to 21.0%

[0022] Cr is dissolved in the matrix to stabilize the austenite structure, and is combined with C to form thermally stable, hard carbides (Cr carbides), which are dispersed in the austenite matrix, increasing high-temperature strength. Cr is also combined with oxygen in the air to form strong oxides (passive film) on the casting surface, increasing oxidation resistance at high temperatures. To obtain such an effect, the Cr content should be 16.0% or more. However, when the Cr content exceeds 21.0%, the amount of Cr carbide dispersed in the austenite matrix becomes excessive, which promotes the propagation of cracks and actually reduces the thermal fatigue properties of the heat-resistant cast steel. Accordingly, the range of the Cr content is set to 16.0 to 21.0%. The lower limit of the Cr content is preferably 16.3%, more preferably 16.6%, and most preferably 17.0%. The upper limit of the Cr content is preferably 20.0%, more preferably 19.0%, and most

preferably 18.7%.

(6) Ni (nickel): 6.0 to 12.0%

[0023] Ni is dispersed in the matrix to stabilize the austenite structure like Cr, and increases the high-temperature strength and oxidation resistance of the heat-resistant cast steel. Ni also improves the casting formability of thin-walled, complex-shaped exhaust members such as exhaust manifolds. To obtain such an excellent effect, the Ni content is set to 6.0% or more. On the other hand, as the Ni content increases, the amount of Ni dissolved in the austenite matrix increases, but the limit of the solid solubility of C decreases and thus the formation of Cr carbide is promoted, which leads to a strong tendency to reduce the thermal fatigue properties of the heat-resistant cast steel. Therefore, from the viewpoint of suppressing the use of expensive Ni, it is preferable to set the upper limit of the Ni content to a level that ensures the desired thermal fatigue properties. The sufficient upper limit of the Ni content is 12.0% to ensure the necessary thermal fatigue strength at around 800°C. Accordingly, the range of the Ni content is set to 6.0 to 12.0%. The lower limit of the Ni content is preferably 6.2%, more preferably 6.3%, and most preferably 6.5%. The upper limit of the Ni content is preferably 10.0%, more preferably 9.0%, and most preferably 8.6%.

(7) Nb (niobium): 0.5 to 2.0%

[0024] Nb is combined with C more predominantly than Cr, to form fine Nb carbide (niobium carbide), thereby suppressing the formation of excess Cr carbide, and indirectly contributing to improving the high-temperature strength and thermal fatigue properties of the heat-resistant cast steel. In addition, Nb carbide is a eutectic carbide with austenite, and can exist as a molten liquid until just before the casting is completely solidified, making it resistant to micro shrinkage cavities. Therefore, Nb suppresses the occurrence of shrinkage cracking caused by shrinkage cavities, which is likely to occur when manufacturing thin-walled, complex-shaped castings such as exhaust manifolds. To obtain this effect, the Nb content is set to 0.5% or more. On the other hand, excessive Nb results in the formation of excessive Nb carbide, which actually reduces the high-temperature strength and thermal fatigue properties of the heat-resistant cast steel. Therefore, the upper limit of the Nb content is set to 2.0%. Accordingly, the range of the Nb content is 0.5 to 2.0%. The lower limit of the Nb content is preferably 0.9%, and more preferably 1.4%. The upper limit of the Nb content is preferably 1.8%, more preferably 1.6%, and most preferably 1.5%.

(8) Cu (copper): 0.80% or less

[0025] A small amount of Cu contributes to improving the ductility of the heat-resistant cast steel, and thus is expected to suppress cold cracking after casting. Therefore, the heat-resistant cast steel of the present invention contains Cu. However, when the Cu content exceeds 0.80%, the ductility of the heat-resistant cast steel decreases, so the upper limit of the Cu content is set to 0.80%. The upper limit of the Cu content is preferably 0.50%, more preferably 0.25%, and most preferably 0.20%. On the other hand, the lower limit of the Cu content is not particularly limited (but not including 0%), and may be 0.05% or 0.10%.

(9) Inevitable impurities

[0026] Impurities coming from starting materials and/or subsidiary materials (such as deoxidizers) are inevitably contained in the heat-resistant, austenitic cast steel of the present invention. Examples of such inevitable impurities include P (phosphorus), Al (aluminum), W (tungsten), Mo (molybdenum), etc., and it is preferable to suppress the content of these inevitable impurities as much as possible. For example, P significantly reduces the toughness of heat-resistant cast steel, so its content is preferably 0.06% or less. Al forms slug containing Al_2O_3 (alumina) during the melting process, which becomes contained in as an inclusion during casting, thereby causing casting defects. Al is also combined with N (nitrogen) in the air to produce hard and brittle AlN (aluminum nitride), which becomes contained in the product, thereby reducing the ductility and machinability thereof. Therefore, the content of Al is preferably 0.05% or less. In addition, W and Mo both form carbides with C, which not only reduces the ductility of the heat-resistant cast steel, but also is dissolved in the austenite matrix so as to reduce the amount of Cr dissolved in the matrix, thereby reducing the oxidation resistance of the matrix, and promotes the crystallization of Cr carbide so as to reduce the thermal fatigue properties. Accordingly, the content of W and Mo is preferably 0.60% or less each, and more preferably 0.60% or less in total.

(B) Microstructure

[0027] Fig. 4A is a photograph showing the microstructure of a cut section of the heat-resistant, austenitic cast steel of Example 4, which is an example of the present invention, and FIG. 4B is a photograph showing an expanded view of region

A in Fig. 4A. As shown in FIG. 4A, the structure of the heat-resistant, austenitic cast steel of the present invention is mainly composed of a gray-colored austenite phase (matrix) 14, a white-colored niobium carbide 15, a eutectic phase 16 of the niobium carbide 15 and the austenite phase 14, and a dark-gray-colored manganese sulfide 17. The eutectic phase 16 is distributed in a network shape so as to fill the gaps in the dendritic austenite phase 14.

[0028] In Fig. 4B, in order to make it more clear, the boundary between the austenite phase 14 and the eutectic phase 16 is indicated by a two-dot chain line. As described above, the eutectic phase 16 exists as a molten liquid until the final stage of solidification, and fills the small gaps in the dendritic austenite phase 14, which has already completely solidified, thereby suppressing the occurrence of the micro shrinkage cavities.

[0029] In the heat-resistant, austenitic cast steel of the present invention, the area ratio of the niobium carbide 15 in an arbitrary cross section is preferably 0.5 to 11.0%. When the area ratio is less than 0.5%, the effect of suppressing shrinkage cracking is insufficient. On the other hand, when the area ratio exceeds 11.0%, the high-temperature strength and thermal fatigue properties decrease, and machinability also decreases. The lower limit of the area ratio of the niobium carbide 15 is more preferably 1.0%, further preferably 1.8%, further more preferably 3.5%, and most preferably 5.0%. On the other hand, the upper limit of the area ratio of the niobium carbide 15 is more preferably 10.0%.

[0030] Referring to Fig. 4B, it can be seen that many manganese sulfide particles 17 are precipitated in the microstructure of the heat-resistant, austenitic cast steel of the present invention. Among these, manganese sulfide particles 17 that are relatively large with an equivalent circle diameter of 1 μm or more improve machinability, but extremely fine manganese sulfide particles 17 with an equivalent circle diameter of less than 1 μm do not contribute to improving machinability. The manganese sulfide particles 17 with an equivalent circle diameter of less than 1 μm often exist in the eutectic phase 16. Note that the "equivalent circle diameter" means the diameter of a circle having an area equal to that of each particle.

[0031] To improve machinability, it is better to have a large number of manganese sulfide particles 17 with an equivalent circular diameter of 1 μm or more. However, if there are too many manganese sulfide particles 17, the oxidation resistance of the heat-resistant, austenitic cast steel decreases. Therefore, the number of the manganese sulfide particles 17 with an equivalent circle diameter of 1 μm or more per mm^2 in an arbitrary cross section is preferably 350 to 2550. The lower limit of the number of the manganese sulfide particles 17 per mm^2 is more preferably 600, and its upper limit is more preferably 1600, and most preferably 1450.

[2] Exhaust member

[0032] The exhaust member of the present invention is made of the above-mentioned heat-resistant, austenitic cast steel. Preferred examples of the exhaust member are exhaust manifolds, turbine housings, integrally cast turbine housings/exhaust manifolds, catalyst cases, integrally cast catalyst cases/exhaust manifolds, and exhaust outlets, and thin-walled, complex-shaped manifolds are particularly preferred.

[0033] Fig. 1 shows an example of an exhaust manifold. An exhaust manifold 1 has a plurality of ports 2, a flange 3 connected to each port 2, a collection part 4 for the ports 2, and a flange 5 connected to the collection part 4.

[0034] The present invention will be explained in further detail by Examples below without intention of restricting the present invention thereto.

Examples 1 to 7 and Comparative Examples 1 and 2

[0035] 80 kg of starting materials, which were a mixture of steel scrap, return scrap, and ferroalloys containing predetermined amounts of constituent elements, were melted in the air using a high-frequency induction furnace (basic lining) with a melting capacity of 100 kg/charge, taken out of the furnace at 1650 to 1700°C, and then poured into a mold at temperatures of 1590 to 1610°C, to obtain sample materials for composition analysis of Examples 1 to 7 and Comparative Examples 1 and 2. A carbon/sulfur simultaneous analyzer (CS-444, available from LECO Corporation) was used for the analysis of C (carbon) and S (sulfur), an oxygen/nitrogen simultaneous analyzer (TC-436, available from LECO Corporation) was used for the analysis of N (nitrogen), and an optical emission spectrometer (PDA-8000, available from Shimadzu Corporation) was used for the analysis of other elements. The results are shown in Table 1.

[0036] Furthermore, to produce 1-inch Y-blocks for thermal fatigue life tests (described in JIS G 5502), test pieces 21 for evaluating micro shrinkage cavities shown in Figs. 2A and 2B, stepped castings 30 for observing microstructure shown in Figs. 3A and 3B, and cylindrical test pieces for tool life tests (not shown) having an outer diameter of 100 mm, an inner diameter of 60 mm, and a length of 60 mm, the melts of Examples 1 to 7 and Comparative Examples 1 and 2 were poured into respective molds for test pieces under the same conditions as above.

[0037] All of the molds used were CO_2 -cured alkaline phenolic molds, and were made by adding 3% by mass of resin (Kao Step C-840, manufactured by Kao-Quaker Company, Limited) to silica sand (Nikko silica sand $\alpha 6$) as aggregate.

Table 1

No.	Composition (% by mass)								
	C	Si	Mn	S	Cr	Ni	Nb	Cu	Fe ⁽¹⁾
Example 1	0.37	1.0	1.0	0.34	17.7	7.8	1.5	0.18	balance
Example 2	0.40	1.1	1.1	0.30	18.3	8.4	1.0	0.19	balance
Example 3	0.39	1.1	1.1	0.30	16.3	6.3	1.5	0.20	balance
Example 4	0.40	1.1	1.1	0.30	18.3	8.4	1.5	0.13	balance
Example 5	0.39	1.1	1.1	0.16	18.7	8.6	1.5	0.20	balance
Example 6	0.39	1.1	1.1	0.29	18.3	8.4	0.5	0.20	balance
Example 7	0.37	1.1	1.1	0.15	18.4	8.4	0.5	0.20	balance
Comp. Ex. 1	0.44	0.94	0.93	0.004	17.8	7.9	0.01	0.10	balance
Comp. Ex. 2	0.45	1.3	1.0	0.16	24.3	12.8	1.0	0.20	balance
Note: (1) Fe and inevitable impurities.									

(1) Evaluation of thermal fatigue properties (thermal fatigue life test)

[0038] To evaluate the thermal fatigue properties, the thermal fatigue life test TMF (Thermal Fatigue Test) described below was conducted. A smooth-surfaced, round rod test piece of 25 mm in gauge distance and 10 mm in diameter was cut out of each 1-inch Y-block, and attached to an electrohydraulic servo material tester ("Servopulser EHF-ED10TF-20L", available from Shimadzu Corporation) with a constraint ratio of 1.0. Each test piece was subjected to repeated heating/cooling cycles in the air, each cycle comprising a temperature elevation for 2 minutes, keeping the temperature for 1 minute, and cooling for 4 minutes, 7 minutes in total, with the lowest cooling temperature of 150°C, the highest heating temperature of 800°C, and a temperature amplitude of 650°C, thereby causing thermal fatigue while mechanically constraining elongation and shrinkage due to heating and cooling.

[0039] The degree of mechanical constraint is expressed by a constraint ratio η defined by [(elongation by free thermal expansion - elongation under mechanical constraint) / elongation by free thermal expansion]. For example, $\eta = 1.0$ means a mechanical constraint condition in which no elongation by free thermal expansion is permitted, and $\eta = 0.5$ means, for example, a mechanical constraint condition in which only elongation of 1 mm is permitted when elongation by free thermal expansion without mechanical constraint is 2 mm. In Examples 1 to 7 and Comparative Examples 1 and 2, the thermal fatigue life tests were carried out under a completely constraint condition ($\eta=1.0$) in which the test pieces were not allowed to elongate during either heating or cooling.

[0040] When heating/cooling cycles in TMF are repeated under the above mechanical constraint condition, the tensile load on the test pieces decreases due to thermal fatigue. Therefore, in the diagram of the number of heating/cooling cycles versus the tensile load, which records the change in load associated with heating/cooling cycles in TMF, when the maximum tensile load in the second cycle (corresponding to the tensile load at the lowest temperature of the cooling process) is taken as a reference (100%), the number of heating/cooling cycles until the maximum tensile load measured in each subsequent cycle fell to 75% of this reference (the maximum tensile load in the second cycle) was defined as the thermal fatigue life.

(2) Evaluation of machinability (tool life test)

[0041] The machinability was evaluated by a tool life test, which is widely used for testing machinability. In the process of cutting cylindrical test pieces (not shown) with an outer diameter of 100 mm, an inner diameter of 60 mm, and a length of 60 mm, while attached to an NC lathe, the tool life was defined as the time until the wear amount of the flank of the tool tip reached 0.2 mm, and the machinability of the test pieces was evaluated by the tool life. The NC lathe used was a model TAC-510×1000 manufactured by Takisawa Machine Tool Co., Ltd., and the tool was an insert (KCM25B VBMT160404LF or VBMT331LF, manufactured by Kennametal Inc.), which is made of a cemented carbide base material coated with a multilayered TiCN-Al₂O₃-TiOCN by CVD. Cutting was performed under wet conditions with an emulsion-based coolant (Castrol Superedge 6754, manufactured by Castrol Industrial North America Inc.), which was diluted to a concentration of 10 to 12%, at a tool peripheral speed of 128 m/min, a feed of 0.12 mm/tooth, and a cutting depth of 0.3 mm.

(3) Evaluation of shrinkage cracking resistance (measurement of volume ratio of micro shrinkage cavities)

[0042] Focusing on the fact that micro shrinkage cavities cause shrinkage cracking, the cross section of the test piece 21 for evaluating micro shrinkage cavities shown in Fig. 2 was photographed with X-ray, and the obtained image was analyzed to determine the volume ratio of the micro shrinkage cavities, from which shrinkage cracking resistance was evaluated.

[0043] Figs. 2A and 2B show a casting 20 from which the test piece 21 for evaluating micro shrinkage cavities is taken. The casting 20 is equipped with a test piece part 21 for evaluating micro shrinkage cavities where the poured melt is finally filled, an ingate 22 connected to the upstream side of the test piece part 21 for evaluating micro shrinkage cavities, a feeder 23 connected to the upstream side of the ingate 22, a runner 24 connected to the upstream side of the feeder 23, and a sprue (not shown) connected to the upstream side of the runner 24. The test piece part 21 for evaluating micro shrinkage cavities has an approximately flat plate shape with a width of 40 mm and a length of 100 mm in the surface direction, and has a tapered shape with a thickness of 13.2 mm at the front end and a thickness of 20 mm at the rear end in the thickness direction. The ingate 22 is 40 mm wide and 12 mm thick. The feeder 23 has a truncated cone shape with a diameter of 50 mm, tapering to a diameter of about 38.5 mm at a height of 66 mm, with a spherical base that projects downwards by about 20 mm. The runner 24 is 40 mm wide and 13 mm thick.

[0044] Melt with the same composition as the 1-inch Y-block was poured into a sand mold for producing the casting 20, and the mold was released after cooling to room temperature. The test piece 21 for evaluating micro shrinkage cavities was cut out of the obtained casting 20 and subjected to shot blasting treatment.

[0045] A cross section of the test piece 21 for evaluating micro shrinkage cavities was imaged using a CT scanner (XTH 450, manufactured by Nikon Corporation) at a tube voltage of 450 kV, and CT tomographic images of an approximately 1.4-mm-wide area at the center of test piece 21 for evaluating micro shrinkage cavities in the thickness direction were obtained at a pitch of 0.1 mm in the thickness direction using a 3D viewer (myVGL, manufactured by Volume Graphics Co., Ltd.). Each CT tomographic image was binarized into micro shrinkage cavities (dark areas) and other areas (light areas) using image processing software (Quick Grain Padplus, manufactured by Innotech Corporation), and the area of the micro shrinkage cavities (dark areas) per pitch (0.1 mm) was calculated. The volume of the micro shrinkage cavities (unit: mm³) was calculated by integrating them over the measurement range. The volume ratio of the micro shrinkage cavities was calculated by dividing the volume of the micro shrinkage cavities by the measured volume (75,000 mm³) of the test piece 21 for evaluating micro shrinkage cavities.

[0046] Table 2 shows the thermal fatigue life, tool life, and volume ratio of the micro shrinkage cavities in Examples 1 to 7 and Comparative Examples 1 and 2.

Table 2

No.	Thermal Fatigue Life TMF (Cycles)	Tool Life (min)	Volume Ratio of Micro Shrinkage Cavities ($\times 10^{-6}$)
Example 1	220	68	8.27
Example 2	175	75	740
Example 3	150	47	167
Example 4	190	91	14.1
Example 5	255	88	31.1
Example 6	150	138	359
Example 7	120	55	179
Comp. Ex. 1	225	26	1160
Comp. Ex. 2	195	61	89.1

[0047] The thermal fatigue life (TMF) of Examples 1 to 7 was 120 to 255 cycles, which was found to satisfy the standard required for an exhaust manifold at 800° C. In particular, Example 1 (220 cycles) and Example 5 (255 cycles) exhibited excellent thermal fatigue life compared to Comparative Example 2 (195 cycles). Example 5, which corresponds to the JIS alloy SCH12, exhibited a thermal fatigue life 1.1 times longer than that of Comparative Example 1.

[0048] The tool life of Examples 1 to 7 was 47 to 138 minutes, which was 1.8 to 5.3 times longer than that of Comparative Example 1, and was almost equal to or longer than 61 minutes of Comparative Example 2 (having a composition similar to that disclosed in WO 2016/052750), which has a relatively long life due to the high Cr and Ni content. In particular, Example 6 had a tool life of 138 minutes, which was 2.3 times longer than that of Comparative Example 2.

[0049] The volume ratios of the micro shrinkage cavities in Examples 1 to 7 were in the range of 8.27×10^{-6} to 740×10^{-6} , all of which were smaller than Comparative Example 1. Furthermore, even compared to Comparative Example 2, which had a relatively low volume ratio of the micro shrinkage cavities due to its high Cr and Ni content, Examples 1, 4, and 5 showed even lower volume ratios of the micro shrinkage cavities, and Examples 2, 3, 6, and 7 were inferior, but all of them were at a level that showed shrinkage cracking resistance usable for exhaust manifolds.

[0050] From the above comparison, it was found that (a) Examples 1 to 7 were superior to Comparative Example 1 in machinability (tool life) and shrinkage cracking resistance (represented by the volume ratio of micro shrinkage cavities), and (b) even though Examples 1 to 7 had low contents of expensive Ni and Cr, Examples 1 to 7 showed equal or better performance than Comparative Example 2, which is expensive because it contains approximately 1.5 to 2.0 times as much Ni content and approximately 1.3 to 1.5 times as much Cr content as Examples 1 to 7.

[0051] Accordingly, the heat-resistant, austenitic cast steel of the present invention satisfies the standard required for a material to be used for an exhaust manifold in terms of thermal fatigue life, has a relatively long tool life, thereby having good machinability, and has a small volume ratio of micro shrinkage cavities, thereby suppressing the occurrence of micro shrinkage cavities that cause shrinkage cracking. Therefore, it is not only a well-balanced material for use in exhaust members, especially exhaust manifolds, but also economically superior due to its low content of expensive alloy elements.

(4) Observation of microstructure

[0052] A sample cut out of a 10-mm-thick portion 31 of the stepped casting 30 shown in Figs. 3A and 3B was embedded in resin so that the cut section served as the observation surface, and then mirror-polished to obtain a sample for observing microstructure. The structure of the observation sample was observed using an electron-probe microanalyzer EPMA (EPMA-1720, manufactured by Shimadzu Corporation), and elemental mapping of C, Si, Mn, S, Cr, Ni, and Nb was performed. The structure was observed with the minimum beam diameter in an arbitrary 5 fields of view magnified 200 times under the conditions of an accelerating voltage of 15 kV, a beam current of 100 mA, a number of pixels of 640×480 , and an integration time of each pixel of 20 ms/point. Figs. 4A and 4B show a backscattered electron image (COMPO) of Example 4.

(a) Identification and number measurement of manganese sulfide particles

[0053] Since S is distributed in high concentrations throughout the entire manganese sulfide particle, manganese sulfide (MnS and (Mn, Cr)S) was identified by the S map in the microstructure observed at 200 times magnification with EMPA, and a mapping image was obtained in which only manganese sulfide was colored and the other areas were black. The colored areas corresponding to manganese sulfide had a gradation of 1500 to 100 levels according to brightness. Using image processing software (Quick Grain Padplus, manufactured by Innotech Corporation), the mapping image was binarized into areas with a brightness of 105 or more (light areas) and areas with a brightness of 104 or less (dark areas), and a color-inverted image was obtained in which the light areas were colored black and the dark areas were colored white. The number of black areas (corresponding to manganese sulfide) and the equivalent circle diameter of each black area were measured, and the number of black areas with an equivalent circle diameter of $1 \mu\text{m}$ or more per mm^2 was calculated.

(b) Measurement of the area ratio of niobium carbide

[0054] The Nb map was overlaid on the microstructure observed at 200 times magnification with an EPMA, and the occupied area ratio of Nb in the observed field was measured using the area ratio measurement function of the EPMA. Since almost all of Nb exists as NbC, the area ratio of Nb was considered to be equal to the area ratio of NbC.

[0055] The number of manganese sulfide particles and the area ratio of niobium carbide in Examples 1 to 7 are shown in Tables 3 and 4, respectively.

Table 3-1

No.	Number of Manganese Sulfide Particles(pieces/ mm^2)(1)							
	Field 1	Field 2	Field 3	Field 4	Field 5	Max	Min	Average
Example 1	959	955	905	838	733	959	733	878
Example 2	1156	888	812	808	1001	1156	808	933
Example 3	1399	1210	947	859	783	1399	783	1039
Example 4	1198	2525	1411	1554	997	2525	997	1537
Example 5	1060	1101	687	775	649	1101	649	854

(continued)

No.	Number of Manganese Sulfide Particles(pieces/mm ²)(¹)							
	Field 1	Field 2	Field 3	Field 4	Field 5	Max	Min	Average
Example 6	674	662	595	662	536	674	536	626
Example 7	498	503	482	461	419	503	419	472
Note: (1) The number of manganese sulfide particles with an equivalent circular diameter of 1 μm or more per unit area (1 mm ²).								

Table 3-2

No.	Maximum Equivalent Circular Diameter of Manganese Sulfide Particles (μm)						
	Field 1	Field 2	Field 3	Field 4	Field 5	Max	
Example 1	15.7	15.3	13.7	13.4	15.2	15.7	
Example 2	13.4	15.1	16.7	14.5	12.5	16.7	
Example 3	14.5	15.3	14.5	15.6	15.7	15.7	
Example 4	14.5	16.2	12.7	14.9	15.5	16.2	
Example 5	9.2	9.6	14.0	8.6	9.7	14.0	
Example 6	15.7	13.7	15.6	17.7	15.7	17.7	
Example 7	12.9	13.2	14.0	14.5	11.2	14.5	

[0056] As is clear from Table 3-1, the number of manganese sulfide particles per mm² observed in Examples 1 to 7 is in the range of 419 to 2525, with an average of 472 to 1537. In addition, as is clear from Table 3-2, the maximum equivalent circle diameter of the manganese sulfide particles observed in Examples 1 to 7 was in the range of 14.0 to 17.7 μm .

Table 4

No.	Occupied Area Ratio of Niobium Carbide (%)							
	Field 1	Field 2	Field 3	Field 4	Field 5	Max	Min	Average
Example 1	8.9	10.0	9.0	6.6	9.2	10.0	6.6	8.7
Example 2	3.9	5.1	5.3	5.2	3.9	5.3	3.9	4.7
Example 3	7.6	6.3	7.5	7.2	8.1	8.1	6.3	7.3
Example 4	6.8	5.0	6.9	5.3	6.5	6.9	5.0	6.1
Example 5	9.3	8.1	9.6	9.6	9.6	9.6	8.1	9.2
Example 6	1.7	1.0	1.7	1.5	1.3	1.7	1.0	1.4
Example 7	2.2	1.8	2.3	2.5	2.5	2.5	1.8	2.3

[0057] As is clear from Table 4, the area ratio of niobium carbide observed in Examples 1 to 7 was in the range of 1.0 to 10.0%, with an average of 1.4 to 9.2%.

Example 8

[0058] This example is the one in which the heat-resistant, austenitic cast steel of the present invention is used for an exhaust manifold (casting part) 1 shown in Fig. 1. Note that the dashed line in Fig. 1 indicates the inside of the casting part, and is not visible from the outside.

[0059] 4000 kg of starting materials, which were a mixture of steel scrap, return scrap, and ferroalloys containing predetermined amounts of constituent elements, were melted in the air using a high-frequency induction furnace (basic lining) with a melting capacity of 4800 kg/charge, taken out of the furnace at 1700 to 1750°C, and then poured into a mold which had a cavity in the shape of the exhaust manifold shown in Fig. 1 at a temperature of 1590 to 1640°C, to obtain the casting part shown in Fig. 1. The other manufacturing conditions are the same as in Example 1. The composition of this

casting part is shown in Table 5. The composition analysis method is the same as in Example 1.

Table 5

No.	Composition (mass%)								
	C	Si	Mn	S	Cr	Ni	Nb	Cu	Fe ⁽¹⁾
Example 8	0.42	1.1	1.1	0.29	19.5	8.8	1.5	0.19	balance
Note: (1) Fe and inevitable impurities.									

[0060] In the casting part manufactured in Example 8, cold cracking, which tends to occur particularly in thin-walled portions, and shrinkage cracking, which tends to occur during casting, were not observed.

INDUSTRIAL APPLICABILITY

[0061] The heat-resistant, austenitic cast steel of the present invention is particularly suitable for exhaust manifolds for internal combustion engines, but can also be used for other exhaust members, such as turbine housings, integrally cast turbine housings/exhaust manifolds, catalyst cases, integrally cast catalyst cases/exhaust manifolds, exhaust outlets, etc. In addition, it is not limited thereto, and can also be used for exhaust members joined to sheet metal or pipe-shaped members made of other materials. Of course, the use of the heat-resistant, austenitic cast steel of the present invention is not limited to these exhaust members.

DESCRIPTION OF REFERENCE NUMERALS

[0062]

- 1: Exhaust manifold
- 20: Casting from which a test piece for evaluating micro shrinkage cavities is taken
- 21: Test piece for evaluating micro shrinkage cavities
- 22: Ingate
- 23: Feeder
- 24: Runner
- 30: Stepped casting
- 31: 10-mm-thick portion
- 14: Austenite phase
- 15: Niobium carbide
- 16: Eutectic phase
- 17: Manganese sulfide particles
- 71: Fine manganese sulfide particles

Claims

1. A heat-resistant, austenitic cast steel comprising by mass

0.30 to 0.50% of C,
 0.50 to 2.0% of Si,
 0.50 to 2.0% of Mn,
 0.10 to 0.40% of S,
 16.0 to 21.0% of Cr,
 6.0 to 12.0% of Ni,
 0.5 to 2.0% of Nb, and
 0.80% or less of Cu,
 the balance being Fe and inevitable impurities.

2. The heat-resistant, austenitic cast steel according to claim 1, wherein the S content is 0.15 to 0.37% by mass, and the Nb content is 0.9 to 1.6% by mass.

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3. The heat-resistant, austenitic cast steel according to claim 1 or 2, wherein the number of sulfides having equivalent circle diameters of 1 μm or more in an arbitrary cross section is 350 to 2550 per mm^2 .
4. The heat-resistant, austenitic cast steel according to claim 1 or 2, wherein an area ratio of niobium carbide in an arbitrary cross section is 0.5 to 11.0%.
5. An exhaust member made of the heat-resistant, austenitic cast steel recited in any one of claims 1-4.
6. The exhaust member according to claim 5, which is an exhaust manifold.

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Fig. 1

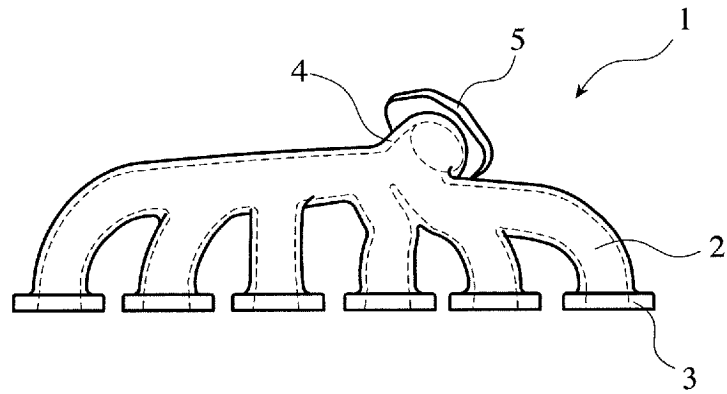


Fig. 2A

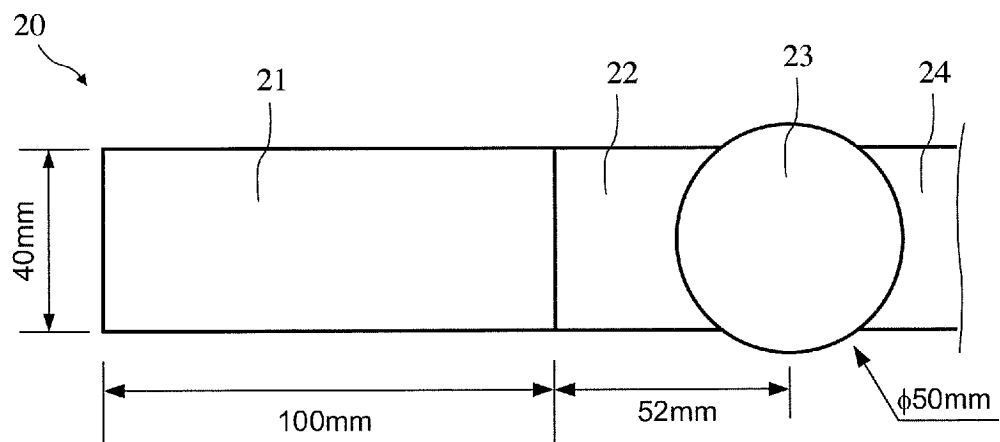


Fig. 2B

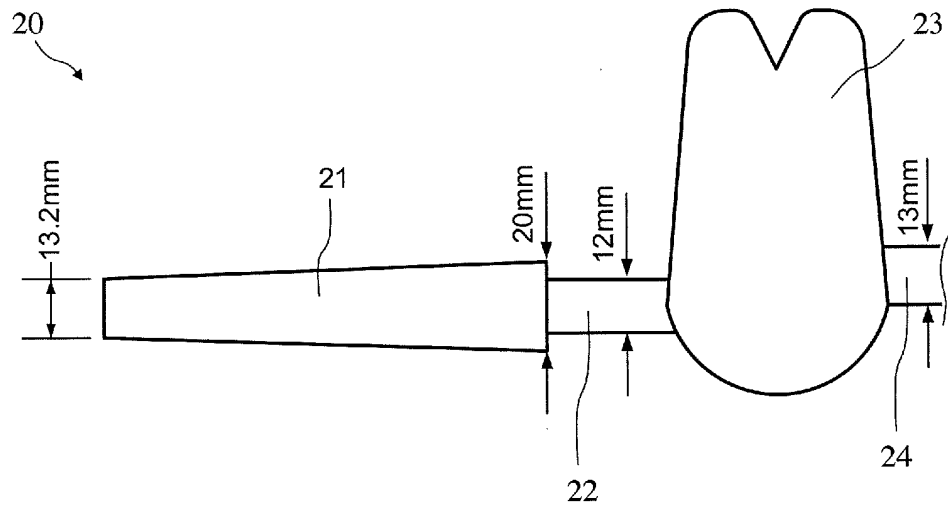


Fig. 3A

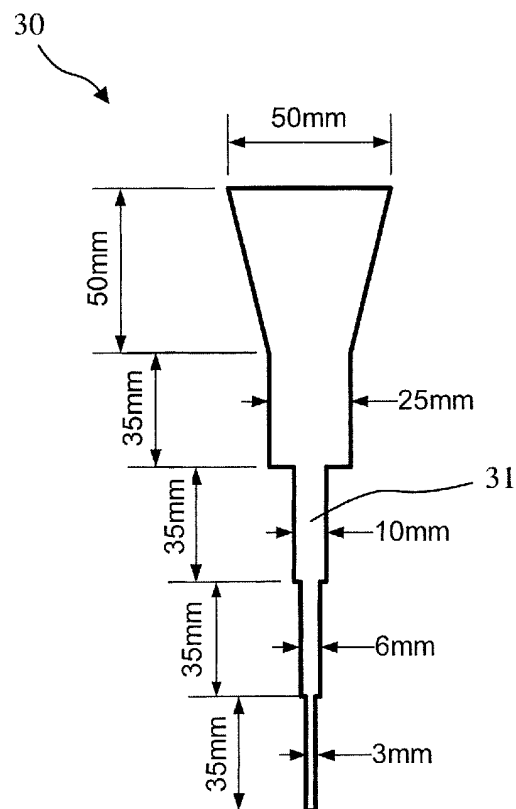


Fig. 3B

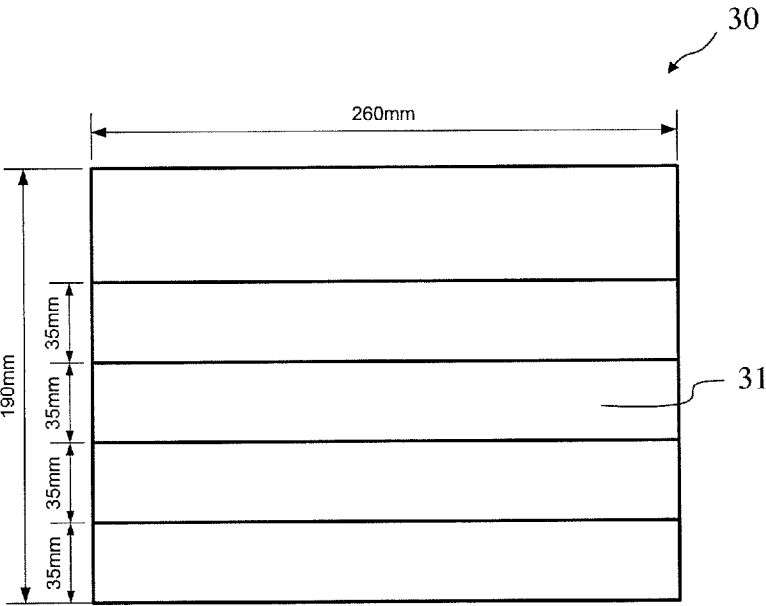


Fig. 4A

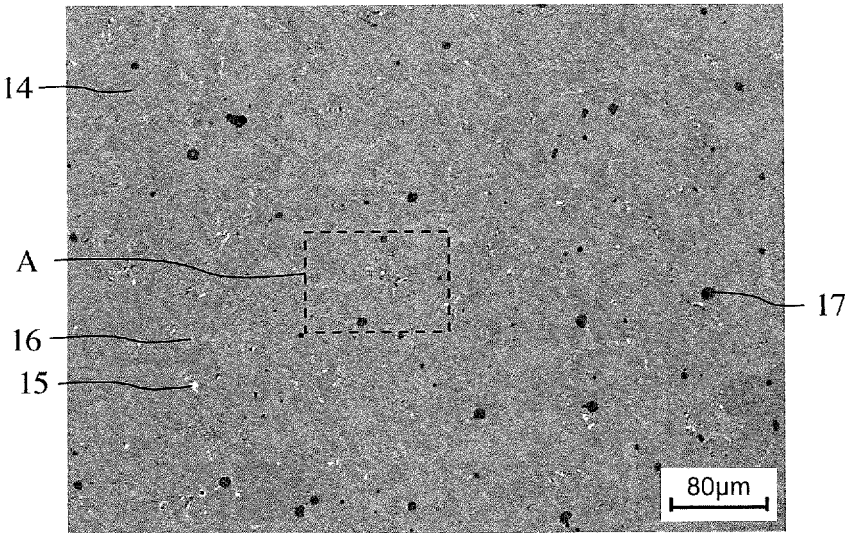
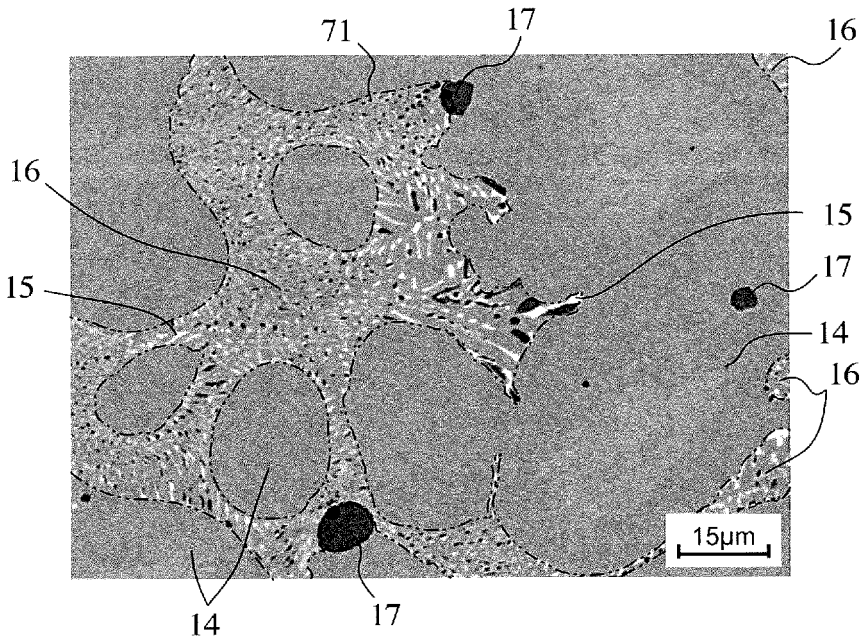


Fig. 4B



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2023/022479

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/00(2006.01)i; C22C 38/60(2006.01)i

FI: C22C38/00 302Z; C22C38/60

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

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

Published examined utility model applications of Japan 1922-1996

Published unexamined utility model applications of Japan 1971-2023

Registered utility model specifications of Japan 1996-2023

Published registered utility model applications of Japan 1994-2023

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.
A	JP 53-48916 A (TOYOTA MOTOR CO LTD) 02 May 1978 (1978-05-02) claims, table 1	1-6
A	JP 59-59865 A (UBE KOSAN KK) 05 April 1984 (1984-04-05) claims, table 1	1-6
A	JP 54-128922 A (HITACHI METALS LTD) 05 October 1979 (1979-10-05) claims, table 1	1-6
A	WO 2013/168770 A1 (HITACHI METALS LTD) 14 November 2013 (2013-11-14) claims, paragraph [0014], tables 1-1 to 2-2	1-6
A	JP 2003-193205 A (HITACHI METALS LTD) 09 July 2003 (2003-07-09) claims, tables 1-1 to 1-2	1-6
A	JP 2015-151573 A (TOYOTA MOTOR CORP) 24 August 2015 (2015-08-24) claims	1-6

☒ 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

23 August 2023

Date of mailing of the international search report

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Name and mailing address of the ISA/JP

Japan Patent Office (ISA/JP)
3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915
Japan

Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT

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PCT/JP2023/022479

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 101560633 A (WUXI YELONG PRECISION MACHINERY CO., LTD.) 21 October 2009 (2009-10-21) claims	1-6

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/JP2023/022479

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 53-48916 A	02 May 1978	(Family: none)	
JP 59-59865 A	05 April 1984	(Family: none)	
JP 54-128922 A	05 October 1979	(Family: none)	
WO 2013/168770 A1	14 November 2013	EP 2848710 A1 claims, paragraph [0014], tables 1-1 to 2-2	
		US 2015/0086412 A1	
		CN 104321453 A	
JP 2003-193205 A	09 July 2003	(Family: none)	
JP 2015-151573 A	24 August 2015	US 2015/0225823 A1 claims	
		CN 104846295 A	
CN 101560633 A	21 October 2009	(Family: none)	

Form PCT/ISA/210 (patent family annex) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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