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(54) FERRITIC STAINLESS STEEL

(57) A ferritic stainless steel having excellent creep resistance and thermal fatigue resistance is provided.

The ferritic stainless steel has a chemical composition containing, in mass%, C: 0.020% or less, Si: 0.1 to 1.0%, Mn: 0.05 to 0.60%, P: 0.050% or less, S: 0.008% or less, Ni: 0.02 to 0.60%, Al: 0.001 to 0.25%, Cr: 18.0 to 20.0%, Nb: 0.30 to 0.80%, Mo: 1.80 to 2.50%, N: 0.015% or less, and Sb: 0.002 to 0.50%, with the balance being Fe and inevitable impurities, and satisfying the following expression (1);

$$\text{Nb} + \text{Mo}: 2.3 \text{ to } 3.0\% \qquad (1)$$

where Nb and Mo in expression (1) represent the contents (mass%) of the respective elements.

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Description

Technical Field

[0001] The present invention relates to a ferritic stainless steel and particularly relates to a ferritic stainless steel that has excellent creep resistance and thermal fatigue resistance and that is suitable for use in exhaust system components used at high temperatures, such as automotive and motorcycle exhaust pipes and converter cases as well as exhaust ducts in thermal power generation plants.

Background Art

[0002] Excellent heat resistance is required for automotive exhaust system components, such as exhaust manifolds, exhaust pipes, converter cases, and mufflers/silencers. Heat resistance includes several properties, such as thermal fatigue resistance, high-temperature fatigue resistance, high-temperature strength (high-temperature proof stress), oxidation resistance, creep resistance, and hot salt corrosion resistance. Among these properties, Thermal fatigue resistance is one of the most important properties among these properties included in heat resistance. Exhaust system components are subjected to repeated heating and cooling as an engine is started and stopped. On such an occasion, thermal expansion and contraction of the exhaust system components is restrained due to peripheral parts connected thereto, thereby generating thermal strain in the materials per se. A low-cycle fatigue phenomenon in which repeated such thermal strain results in failure is referred to as thermal fatigue.

[0003] As a material for the above-mentioned components in which excellent thermal fatigue resistance are required, a ferritic stainless steel, such as Type 429, which contains Nb and Si (14%Cr-0.9%Si-0.4%Nb steel), is commonly used today. However, as the engine performance improves, an exhaust gas temperature has risen to a temperature exceeding 900°C. In such a case, Type 429 cannot fully satisfy, in particular, required thermal fatigue resistance.

[0004] As materials that can resolve this problem, for example, SUS444 (19%Cr-0.5%Nb-2%Mo) defined in JIS G 4305, which is a ferritic stainless steel having a high-temperature proof stress enhanced by addition of Nb and Mo; and a ferritic stainless steel added with Nb, Mo, and W have been developed (see, for example, Patent Literature 1)

Citation List

Patent Literature

[0005] PTL 1: Japanese Unexamined Patent Application Publication No. 2004-018921

Summary of Invention

Technical Problem

[0006] An exhaust gas temperature has a tendency to rise for the purpose of complying with tightening emission control regulations and/or improving fuel efficiency in these days. Consequently, even SUS444 or the like exhibits unsatisfactory heat resistance in some cases, in particular, thermal fatigue resistance. Moreover, stainless steel readily causes creep deformation when an exhaust gas temperature rises beyond 900°C and thus also needs creep resistance.

[0007] SUS444 has the highest level of heat resistance among ferritic stainless steels, but the heat resistance is not necessarily satisfactory when an exhaust gas temperature rises as a result of recent tightening of emission control regulations and/or improvements in fuel efficiency. As an exhaust gas temperature rises, an exhaust system component undergoes large thermal expansion upon heating. Consequently, further severe thermal strain is applied and a ferritic stainless steel used for the exhaust system component readily undergoes thermal fatigue failure. Further, a ferritic stainless steel tends to cause creep deformation when held for a prolonged time in a high-temperature range. Once creep deformation occurs, a portion thinned by creep deformation reaches fracture as it acts a starting point of fracture. Accordingly, it is also needed to improve creep resistance.

[0008] As described above, according to conventional techniques including SUS444, it was impossible to obtain a ferritic stainless steel that has satisfactory thermal fatigue resistance even when an exhaust gas temperature rises. Moreover, creep resistance, which are required particularly when an exhaust gas temperature exceeds 900°C, have not been evaluated sufficiently.

[0009] In view of the above, an object of the present invention is to resolve the above-mentioned problems and to provide a ferritic stainless steel having excellent creep resistance and thermal fatigue resistance.

[0010] In the present invention, the expression "excellent creep resistance" means that a rupture time is better than that of SUS444 when a creep test is performed at 900°C. Moreover, the expression "excellent thermal fatigue resistance" means that resistance better than SUS444 are exhibited, specifically, a thermal fatigue life is better than that of SUS444 when the temperature is elevated and lowered repeatedly between 200°C and 950°C.

Solution to Problem

[0011] For the purpose of developing a ferritic stainless steel that has better creep resistance and better thermal fatigue resistance than SUS444, the present inventors continued intensive studies on how various elements affect creep resistance and thermal fatigue resistance.

[0012] As a result, it was found that high-temperature strength increases in a wide temperature range and thermal fatigue resistance is improved by containing, in mass%, 0.30 to 0.80% of Nb and 1.80 to 2.50% of Mo in the total content of Nb and Mo of 2.3 to 3.0%. Further, it was also found that creep resistance is improved by containing Sb in a range of 0.002 to 0.50 mass%.

[0013] On the basis of the above findings, the present invention has been completed by satisfying a specific chemical composition that contains all of Cr, Nb, Mo, and Sb in appropriate amounts. Although the above-mentioned elements are important in the present invention, it is needed to adjust all the essential elements to predetermined contents in order to achieve the effects of the present invention.

[0014] The present invention is summarized as follows.

[1] A ferritic stainless steel having a chemical composition containing, in mass%, C: 0.020% or less, Si: 0.1 to 1.0%, Mn: 0.05 to 0.60%, P: 0.050% or less, S: 0.008% or less, Ni: 0.02 to 0.60%, Al: 0.001 to 0.25%, Cr: 18.0 to 20.0%, Nb: 0.30 to 0.80%, Mo: 1.80 to 2.50%, N: 0.015% or less, and Sb: 0.002 to 0.50%, with the balance being Fe and inevitable impurities, and satisfying the following expression (1);

$$\text{Nb} + \text{Mo: } 2.3 \text{ to } 3.0\% \qquad (1)$$

where Nb and Mo in expression (1) represent the contents (mass%) of the respective elements.

[2] The ferritic stainless steel according to [1], where the chemical composition further contains, in mass%, one or two or more selected from Ti: 0.01 to 0.16%, Zr: 0.01 to 0.50%, Co: 0.01 to 0.50%, B: 0.0002 to 0.0050%, V: 0.01 to 1.0%, W: 0.01 to 5.0%, Cu: 0.01 to 0.40%, and Sn: 0.001 to 0.005%.

[3] The ferritic stainless steel according to [1] or [2], where the chemical composition further contains, in mass%, one or two selected from Ca: 0.0002 to 0.0050% and Mg: 0.0002 to 0.0050%.

[4] The ferritic stainless steel according to any one of [1] to [3], where the ferritic stainless steel is used for an exhaust manifold whose temperature is elevated to 700°C or higher by an exhaust gas from an engine. Advantageous Effects of Invention

[0015] According to the present invention, it is possible to provide a ferritic stainless steel having better creep resistance and better thermal fatigue resistance than SUS444 (JIS G 4305). Accordingly, the ferritic stainless steel of the present invention can be suitably used for exhaust system components of automobiles and so forth.

Brief Description of Drawings

[0016]

[Fig. 1] Fig. 1 illustrates a creep test specimen.
[Fig. 2] Fig. 2 illustrates a thermal fatigue test specimen.
[Fig. 3] Fig. 3 illustrates the temperature and restraint conditions in a thermal fatigue test.

Description of Embodiments

[0017] Hereinafter, embodiments of the present invention will be described. However, the present invention is not limited to the following embodiments.

[0018] A ferritic stainless steel of the present invention contains, in mass%, C: 0.020% or less, Si: 0.1 to 1.0%, Mn: 0.05 to 0.60%, P: 0.050% or less, S: 0.008% or less, Ni: 0.02 to 0.60%, Al: 0.001 to 0.25%, Cr: 18.0 to 20.0%, Nb: 0.30 to 0.80%, Mo: 1.80 to 2.50%, N: 0.015% or less, and Sb: 0.002 to 0.50%, with the balance being Fe and inevitable impurities, and satisfies the following expression (1);

$$\text{Nb} + \text{Mo: } 2.3 \text{ to } 3.0\% \qquad (1)$$

where Nb and Mo in expression (1) represent the contents (mass%) of the respective elements.

[0019] In the present invention, the balance in the chemical composition is extremely important. By satisfying the above-described combinations of the chemical composition, it is possible to obtain a ferritic stainless steel having better creep resistance and better thermal fatigue resistance than SUS444. Meanwhile, even if one of the essential elements (C, Si, Mn, Ni, Al, Cr, Nb, Mo, N, Sb) in the chemical composition falls outside the above-mentioned content range, it is impossible to achieve expected creep resistance and thermal fatigue resistance.

[0020] Next, the chemical composition of the ferritic stainless steel of the present invention will be described. Hereinafter, the sign "%" as a unit denoting the content of each element means mass% unless otherwise stated.

C: 0.020% or less

[0021] C is an element effective for increasing the strength of steel, but toughness and formability remarkably deteriorate when C content exceeds 0.020%. Moreover, C combines with Nb, which is important in the present invention, and increases the amount of the resulting carbide. Consequently, the effect of improving thermal fatigue resistance and creep resistance by Nb described hereinafter diminishes. Accordingly, C content is set to 0.020% or less. From a viewpoint of ensuring formability, C content is set to preferably 0.010% or less and more preferably 0.008% or less. Meanwhile, from a viewpoint of ensuring the strength as an exhaust system component, C content is set to preferably 0.001% or more, more preferably 0.003% or more, and further preferably 0.004% or more.

Si: 0.1 to 1.0%

[0022] Si is an important element necessary for improving oxidation resistance. To ensure oxidation resistance in exhaust gases at elevated temperatures, Si content needs to be 0.1% or more. Meanwhile, excessive Si content beyond 1.0% deteriorates workability at room temperature. Accordingly, the upper limit of Si content is set to 1.0%. Si content is set to preferably 0.20% or more, more preferably 0.30% or more, and further preferably 0.40% or more. Meanwhile, Si content is set to preferably 0.90% or less and more preferably 0.60% or less.

Mn: 0.05 to 0.60%

[0023] Mn effectively improves thermal fatigue resistance due to improvement of spalling resistance of oxide scale. To obtain such an effect, Mn content needs to be 0.05% or more. Meanwhile, excessive Mn content beyond 0.60% deteriorates heat resistance due to the formation of γ phase at a high temperature. Accordingly, Mn content is set to 0.05% or more and 0.60% or less. Mn content is set to preferably 0.10% or more and more preferably 0.15% or more. Meanwhile, Mn content is set to preferably 0.50% or less and more preferably 0.40% or less.

P: 0.050% or less

[0024] P is a detrimental element that deteriorates toughness of steel and is thus desirably reduced as much as possible. Accordingly, P content is set to 0.050% or less. P content is preferably 0.040% or less, and more preferably 0.030% or less.

S: 0.008% or less

[0025] S reduces elongation and r-value, thereby adversely affecting formability. S is also a harmful element that deteriorates corrosion resistance, which is the basic properties of stainless steel, and is thus desirably reduced as much as possible. Accordingly, in the present invention, S content is set to 0.008% or less. S content is preferably 0.006% or less.

Ni: 0.02 to 0.60%

[0026] Ni is an element that improves toughness and oxidation resistance of steel. To obtain such an effect, Ni content is set to 0.02% or more. When oxidation resistance is insufficient, thermal fatigue resistance deteriorates due to reduction in a cross-sectional area of a material caused by an increased amount of oxide scale formed and/or spalling of oxide scale. Meanwhile, Ni is a powerful γ phase-forming element. Accordingly, excessive Ni content deteriorates oxidation resistance due to formation of γ phase at a high temperature and deteriorates thermal fatigue resistance due to increase in thermal expansion coefficient. Therefore, the upper limit of Ni content is set to 0.60%. Ni content is preferably 0.05% or more and more preferably 0.10% or more. Meanwhile, Ni content is preferably 0.40% or less and more preferably 0.30% or less.

Al: 0.001 to 0.25%

[0027] Al is an element that effectively improves oxidation resistance. To obtain such an effect, Al content needs to be 0.001% or more. Meanwhile, Al is also an element that increases a thermal expansion coefficient. A large thermal expansion coefficient results in deterioration in thermal fatigue resistance. Moreover, considerable hardening of steel deteriorates workability. Accordingly, Al content is set to 0.25% or less. Al content is preferably 0.005% or more, more preferably more than 0.010%, and further preferably more than 0.020%. Meanwhile, Al content is preferably less than 0.20% and more preferably less than 0.08%.

Cr: 18.0 to 20.0%

[0028] Cr is an important element that effectively improves corrosion resistance and oxidation resistance, which are the characteristics of stainless steel. However, when Cr content is less than 18.0%, satisfactory oxidation resistance cannot be achieved in a high-temperature range exceeding 900°C. When oxidation resistance is insufficient, the amount of oxide scale formed increases and consequently, thermal fatigue resistance also deteriorates due to reduction in a cross-sectional area of a material. Meanwhile, Cr is an element that hardens steel and reduces ductility due to solid solution strengthening of steel at room temperature. When Cr content exceeds 20.0%, the above-mentioned adverse effects predominate and thermal fatigue resistance rather deteriorates. Accordingly, the upper limit of Cr content is set to 20.0%. Preferably, Cr content is 18.5% or more. Meanwhile, Cr content is preferably 19.5% or less.

Nb: 0.30 to 0.80%

[0029] Nb is an element important to the present invention for increasing high-temperature strength, thereby improving thermal fatigue resistance and creep resistance. Such an effect is obtained when Nb content is 0.30% or more. When Nb content is less than 0.30%, excellent thermal fatigue resistance or creep resistance cannot be obtained due to insufficient strength at a high temperature. Meanwhile, when Nb content exceeds 0.80%, since a Laves phase (Fe_2Nb), which is an intermetallic compound, or the like tends to be precipitated, high-temperature strength is decreased. Consequently, not only thermal fatigue resistance and creep resistance deteriorate, but also embrittlement is promoted. Accordingly, Nb content is set to 0.30% or more and 0.80% or less. Nb content is preferably 0.40% or more, more preferably 0.45% or more, and further preferably more than 0.50%. Meanwhile, Nb content is preferably 0.70% or less and more preferably 0.60% or less.

Mo: 1.80 to 2.50%

[0030] Mo is an effective element that improves thermal fatigue resistance and creep resistance because it dissolves in steel and increase the high-temperature strength of steel. Such an effect is realized when Mo content is 1.80% or more. When Mo content is less than 1.80%, excellent thermal fatigue resistance or creep resistance cannot be obtained due to insufficient high-temperature strength. Meanwhile, excessive Mo content not only deteriorates workability due to hardening of steel, but also deteriorates thermal fatigue resistance because Mo precipitates as a Laves phase (Fe_2Mo) in a similar manner to Nb and the amount of Mo dissolved in steel is reduced. Moreover, Mo is precipitated, during a thermal fatigue test, since coarse σ phase that acts as a starting point of fracture, thermal fatigue resistance deteriorates. Accordingly, the upper limit of Mo content is set to 2.50%. Mo content is preferably 1.90% or more and more preferably more than 2.00%. Meanwhile, Mo content is preferably 2.30% or less and more preferably 2.10% or less.

N: 0.015% or less

[0031] N is an element that deteriorates toughness and formability of steel. When N content exceeds 0.015%, not only toughness and formability deteriorate considerably, but also creep resistance and thermal fatigue resistance deteriorate due to reduction in an amount of dissolved Nb through formation of Nb nitride. Accordingly, N content is set to 0.015% or less. From a viewpoint of ensuring toughness and formability, N is preferably reduced as much as possible, and N content is desirably set to less than 0.010%.

Sb: 0.002 to 0.50%

[0032] Sb is an important element for improving creep resistance in the present invention. Sb dissolves in steel and suppresses creep deformation of steel at a high temperature. Without being precipitated as a carbonitride or a Laves phase even in a high-temperature range, Sb remains dissolved in steel even after long-term use and suppresses creep deformation, thereby making it possible to improve creep resistance. Such an effect can be obtained when Sb content is 0.002% or more. Meanwhile, excessive Sb content deteriorates toughness and hot workability of steel. Consequently, not only does cracking readily occur during production, but also thermal fatigue resistance deteriorates due to reduced hot ductility. Accordingly, the upper limit of Sb content is set to 0.50%. Sb content is preferably 0.005% or more and more preferably 0.020% or more. Meanwhile, Sb content is preferably 0.30% or less and more preferably 0.10% or less.

Nb + Mo: 2.3 to 3.0% (1)

[0033] As in the foregoing, Nb and Mo are elements effective for improving thermal fatigue resistance and creep resistance. Such effects are obtained when the respective contents are 0.30% or more and 1.80% or more. However, to realize better thermal fatigue resistance and better creep resistance than SUS444 in terms of a thermal fatigue life when the temperature is elevated and lowered repeatedly between 200°C and 950°C to deal with elevated exhaust gas temperatures, it is required to contain both elements within the predetermined ranges and further to satisfy at least Nb + Mo $\geq$ 2.3%, in other words, to set the amount of Nb + Mo (total content of Nb and Mo) to 2.3% or more. When this condition is not satisfied, excellent creep resistance cannot be obtained even when a predetermined amount of Sb is contained. Preferably, the condition is Nb + Mo > 2.5%. Meanwhile, when the amount of Nb + Mo is excessively increased, excellent thermal fatigue resistance and creep resistance are not achieved due to embrittlement of steel. Accordingly, the upper limit of the mount of Nb + Mo is set to 3.0%. Preferably, the amount of Nb + Mo is 2.7% or less.

[0034] Here, Nb and Mo in the above expression (1) represent the contents (mass%) of the respective elements.

[0035] In the ferritic stainless steel of the present invention, the balance is Fe and inevitable impurities.

[0036] The ferritic stainless steel of the present invention may further contain, in addition to the above-described essential elements, one or two or more selected from Ti, Zr, Co, B, V, W, Cu, and Sn as optional elements within the following ranges.

Ti: 0.01 to 0.16%

[0037] Ti is an element that improves corrosion resistance and formability, and prevents intergranular corrosion of welds by stabilizing C and N. In the present invention, Ti may be contained as necessary. If contained, Ti preferentially combines with C and N compared with Nb. Consequently, it is possible to ensure the amount of Nb dissolved in steel, which is effective for improving high-temperature strength. Moreover, heat resistance is also effectively improved. Such effects can be obtained when Ti content is 0.01% or more. Meanwhile, excessive Ti content beyond 0.16% causes deterioration in toughness and adversely affects manufacturability, such as causing fracture through repeated bending and unbending in a hot-rolled sheet annealing line. Moreover, Nb carbonitride becomes readily precipitated by using Ti carbonitride as nuclei. Consequently, the amount of Nb dissolved in steel, which is effective for improving high-temperature strength, is rather reduced, thereby thermal fatigue resistance and creep resistance deteriorate. Accordingly, if contained, Ti content is set to 0.01 to 0.16%. Ti content is preferably 0.03% or more. Meanwhile, Ti content is preferably 0.12% or less, more preferably 0.08% or less, and further preferably 0.05% or less.

Zr: 0.01 to 0.50%

[0038] Zr is an element that improves oxidation resistance. In the present invention, Zr may be contained as necessary. The effect can be obtained when Zr content is 0.01% or more. Meanwhile, when Zr content exceeds 0.50%, a Zr intermetallic compound is precipitated, thereby embrittling steel. Accordingly, if contained, Zr content is set to 0.01 to 0.50%. Zr content is preferably 0.03% or more and more preferably 0.05% or more. Meanwhile, Zr content is preferably 0.30% or less and more preferably 0.10% or less.

Co: 0.01 to 0.50%

[0039] Co is known as an element effective for improving toughness of steel. The effect can be obtained when Co content is 0.01% or more. Meanwhile, since excessive Co content rather deteriorates toughness of steel, the upper limit of Co content is set to 0.50%. Accordingly, if contained, Co content is set to 0.01 to 0.50%. Co content is preferably 0.03% or more. Meanwhile, Co content is preferably 0.30% or less.

B: 0.0002 to 0.0050%

[0040] B is an element effective for improving workability, especially secondary workability, of steel. Such an effect can be obtained when B content is 0.0002% or more. Meanwhile, excessive B content deteriorates workability due to formation of BN. Accordingly, if contained, B content is set to 0.0002 to 0.0050%. B content is preferably 0.0005% or more and more preferably 0.0008% or more. Meanwhile, B content is 0.0030% or less and more preferably 0.0020%

or less.

V: 0.01 to 1.0%

[0041] V is an element effective for improving workability of steel as well as an element effective for improving oxidation resistance. These effects are remarkable when V content is 0.01% or more. Meanwhile, excessive V content beyond 1.0% deteriorates not only toughness but also surface quality due to precipitation of coarse V(C, N). Accordingly, if contained, V content is set to 0.01 to 1.0%. V content is preferably 0.03% or more and more preferably 0.05% or more. Meanwhile, V content is preferably 0.50% or less and more preferably 0.20% or less.

W: 0.01 to 5.0%

[0042] W is an element that significantly increases high-temperature strength through solid solution strengthening in a similar manner to Mo. The effect can be obtained when W content is 0.01% or more. Meanwhile, excessive W content not only hardens steel considerably but also makes descaling during pickling difficult due to formation of stable scale in an annealing step during production. Accordingly, if contained, W content is set to 0.01 to 5.0%. Preferably, W content is 0.05% or more. Meanwhile, W content is preferably 3.5% or less, more preferably 1.0% or less, and further preferably less than 0.30%.

Cu: 0.01 to 0.40%

[0043] Cu is an element that effectively improves corrosion resistance of steel and is contained when corrosion resistance is required. The effect can be obtained when Cu content is 0.01% or more. Meanwhile, when Cu content exceeds 0.40%, oxide scale easily spalls and cyclic oxidation resistance deteriorates. Accordingly, if contained, Cu content is set to 0.01 to 0.40%. Cu content is preferably 0.03% or more and more preferably 0.06% or more. Meanwhile, Cu content is preferably 0.20% or less and more preferably 0.10% or less.

Sn: 0.001 to 0.005%

[0044] Sn is an element effective for increasing high-temperature strength of steel. The effect can be obtained when Sn content is 0.001% or more. Meanwhile, excessive Sn content rather deteriorates thermal fatigue resistance due to embrittlement of steel. Accordingly, if contained, Sn content is set to 0.001 to 0.005%. Preferably, Sn content is 0.001% or more and 0.003% or less.

[0045] The ferritic stainless steel of the present invention may further contain one or two selected from Ca and Mg as optional elements within the following ranges.

Ca: 0.0002 to 0.0050%

[0046] Ca is an element effective for preventing clogging of nozzles that tend to occur during continuous casting due to precipitation of Ti-based inclusions. The effect can be obtained when Ca content is 0.0002% or more. Meanwhile, Ca content needs to be 0.0050% or less in order to obtain good surface quality without forming surface defects. Accordingly, if contained, Ca content is set to 0.0002 to 0.0050%. Ca content is preferably 0.0005% or more. Meanwhile, Ca content is preferably 0.0030% or less and more preferably 0.0020% or less.

Mg: 0.0002 to 0.0050%

[0047] Mg is an element effective for increasing the equiaxed crystal ratio of a slab and improving workability and toughness. In a steel containing Nb and Ti as in the present invention, Mg also effectively suppresses coarsening of Nb and/or Ti carbonitrides. Such effects can be obtained when Mg content is 0.0002% or more. Coarsened Ti carbonitride acts as a starting point of embrittlement cracking and thus considerably deteriorates toughness. When Nb carbonitride coarsens, the amount of Nb dissolved in steel decreases, thereby causing deterioration in thermal fatigue resistance. Meanwhile, when Mg content exceeds 0.0050%, surface quality of steel deteriorates. Accordingly, if contained, Mg content is set to 0.0002 to 0.0050%. Mg content is preferably 0.0003% or more and more preferably 0.0004% or more. Meanwhile, Mg content is preferably 0.0030% or less and more preferably 0.0020% or less.

[0048] The balance is Fe and inevitable impurities. When any of the above-described optional elements is contained at less than the above-mentioned lower limit, such an optional element is regarded as being contained as an inevitable impurity.

[0049] Next, a production method for a ferritic stainless steel of the present invention will be described.

[0050] The production method for a ferritic stainless steel of the present invention may suitably employ a common production method for a ferritic stainless steel and is not particularly limited.

[0051] A ferritic stainless steel of the present invention can be produced, for example, by a production process including: refining steel in a publicly known melting furnace, such as a converter or an electric furnace; alternatively or additionally subjecting to secondary refining, such as ladle refining or vacuum refining, to prepare steel having the above-described chemical composition of the present invention; forming into a slab by continuous casting or ingot casting and slabbing; and subsequently forming into a cold-rolled annealed sheet through steps of hot rolling, hot-rolled sheet annealing, pickling, cold rolling, finish annealing, pickling, and the like. The above-mentioned cold rolling may be performed once or twice or more via intermediate annealing. Moreover, each step of cold rolling, finish annealing, and pickling may be performed repeatedly. Further, the hot-rolled sheet annealing may be omitted, and when adjustment of the surface gloss or roughness of a steel sheet is required, skin-pass rolling may be performed after cold rolling or finish annealing.

[0052] Preferable production conditions in the above-described production method will be described.

[0053] In the steelmaking step for refining steel, steel melted in a converter, an electric furnace, or the like is preferably subjected to secondary refining through the VOD process, the AOD process, or the like to prepare steel containing the above-described essential elements and optional elements added as necessary. The resulting refined molten steel may be formed into a steel material by a publicly known method, but continuous casting is preferably employed in view of productivity and quality. The steel material is then heated to preferably 1,050°C to 1,250°C and hot rolled into a hot-rolled sheet having a desirable thickness. From a production viewpoint, the thickness of the hot-rolled sheet is desirably 5 mm or less. Naturally, it is also possible to form materials other than sheets through hot working. The hot-rolled sheet is preferably formed into a hot-rolled product by subjecting later, as necessary, to continuous annealing at a temperature of 900°C to 1,150°C or batch annealing at a temperature of 700°C to 900°C, followed by descaling through pickling, polishing, or the like. Here, as necessary, scale may be removed by shot blasting before pickling.

[0054] Further, the hot-rolled product (hot-rolled annealed sheet) may be formed into a cold-rolled product through steps of cold rolling and so forth. In this case, cold rolling may be performed once or twice or more via intermediate annealing in view of productivity and/or required quality. The total reduction in cold rolling that is performed once or twice or more is preferably 60% or more and more preferably 70% or more. The cold-rolled steel sheet is preferably formed into a cold-rolled product (cold-rolled annealed sheet) by subjecting later to continuous annealing (finish annealing) at a temperature of preferably 900°C to 1,200°C and further preferably 1,000°C to 1,150°C, followed by pickling or polishing. Here, finish annealing may be performed in a reducing atmosphere. In this case, pickling or polishing after finish annealing may be omitted. Further, depending on uses, the shape, surface roughness, and/or material properties of the steel sheet may be adjusted by subjecting to skin-pass rolling or the like after finish annealing.

[0055] The hot-rolled product or cold-rolled product obtained as described above is later subjected to processes, such as cutting, bending, bulging, and drawing, depending on the respective uses and formed, for example, into an automotive or a motorcycle exhaust pipe or converter case, an exhaust duct in a thermal power plant, or a fuel cell-related component, such as a separator, an interconnector, or a reformer. Among these uses, a ferritic stainless steel of the present invention is suitably used for exhaust system components, such as exhaust manifolds, exhaust pipes, converter cases, and mufflers. As one of its features, it is possible to obtain an exhaust manifold with excellent durability, in particular, even when the temperature in use is elevated to 700°C or higher by an exhaust gas from an engine.

[0056] A welding method for these components is not particularly limited and may employ common arc welding, such as metal inert gas (MIG), metal active gas (MAG), or tungsten inert gas (TIG) welding; electric resistance welding, such as spot welding or seam welding; high-frequency resistance welding, such as electro-seam welding; high-frequency induction welding, or the like.

EXAMPLES

[0057] Hereinafter, the present invention will be described in further detail by means of Examples.

[0058] Each steel having any of the chemical compositions of No. 1 to 41, 43, and 45 to 47 shown in Table 1 was refined in a vacuum melting furnace, cast into a 50 kg-ingot, heated at 1,170°C, and then hot-rolled into a 35 mm-thick sheet bar. The resulting sheet bar was divided into two. One of the sheet bar was heated to 1,100°C, then hot-rolled into a 5 mm-thick hot-rolled sheet, annealed in a temperature range of 1,000°C to 1,150°C, followed by grinding. Subsequently, the resulting hot-rolled annealed sheet was cold rolled at a reduction of 70%, finish annealed at a temperature of 1,000°C to 1,150°C, followed by descaling through pickling or polishing. The resulting 1.5 mm-thick cold-rolled annealed sheet was subjected to a creep test. As a reference, a cold-rolled annealed sheet was also prepared from SUS444 (Conventional Example No. 28) in the same manner as described above and subjected to a creep test. The annealing temperature was determined within the above-mentioned temperature ranges for each steel under observation of the microstructure.

<Creep Test>

[0059] A specimen having the shape illustrated in Fig. 1 was cut out from each cold-rolled annealed sheet obtained as described above and subjected to a creep test at 900°C and an applied stress of 15 MPa. The specimen was evaluated as follows on the basis of the time until rupture. The time until rupture was 5.5 hr for SUS444 (Conventional Example No. 28), which was tested by way of comparison.

⊙: rupture time ≥ 10 hr
○: 6 hr ≤ rupture time < 10 hr
×: rupture time < 6 hr

[0060] In the above evaluation, ⊙ and ○ were regarded as acceptable and × as unacceptable. The obtained results are shown in Table 1 (see creep at 900°C in Table 1).

[0061] Next, the other of the above-mentioned sheet bars after divided into two was heated to 1,100°C and then hot forged into a 30 mm-square bar. Subsequently, the bar was annealed at a temperature of 1,000°C to 1,150°C, then machined into a thermal fatigue test specimen having the shape and dimension illustrated in Fig. 2, and subjected to the following thermal fatigue test. The annealing temperature was set to a temperature at which recrystallization is completed under observation of the microstructure for every chemical composition. As a reference, a specimen was also prepared in the same manner as described above for steel having the chemical composition of SUS444 (Conventional Example No. 28) and subjected to the thermal fatigue test.

<Thermal Fatigue Test>

[0062] As illustrated in Fig. 3, a thermal fatigue test was performed under conditions that elevate and lower the temperature repeatedly between 200°C and 950°C while restraining the specimen at a restraint ratio of 0.5. On this occasion, the elevation rate of the temperature was set to 5°C/s and the lowering rate of the temperature to 2°C/s. Moreover, each holding time at 200°C and 950°C was set to 30 seconds. As illustrated in Fig. 3, the above-mentioned restraint ratio can be represented as restraint ratio $\eta = a/(a + b)$, where a is (free thermal expansion strain - controlled strain)/2 and b is (controlled strain)/2. Here, "free thermal expansion strain" means a strain when the temperature is elevated without applying any mechanical stress, and "controlled strain" means an absolute value of strain that is generated during the test. An actual restraint strain that is generated in the material due to restraint is (free thermal expansion strain - controlled strain).

[0063] Here, the thermal fatigue life was defined as the number of cycles when a stress value is reduced to 75% of the stress value in an early cycle (fifth cycle in which the test is stabilized), where the stress is calculated by dividing a load detected at 200°C by the cross-sectional area of a uniformly heated parallel portion (see Fig. 2) of the specimen, and evaluated as follows. The thermal fatigue life was 650 cycles for SUS444 (Conventional Example No. 28) tested by way of comparison.

⊙: 1,000 cycles or more (acceptable)
○: 800 cycles or more and less than 1,000 cycles (acceptable)
×: less than 800 cycles (unacceptable)

[0064] In the above evaluation, ⊙ and ○ were regarded as acceptable and × as unacceptable. The obtained results are shown in Table 1 (see thermal fatigue life at 950°C in Table 1).

[Table 1]

No.	Chemical composition (mass%)													Nb+Mo	Creep at 900°C	Thermal fatigue life at 950°C	Note
	C	Si	Mn	P	S	Al	Ni	Cr	Nb	Mo	Sb	N	Others				
1	0.005	0.44	0.59	0.032	0.001	0.031	0.25	19.6	0.57	2.08	0.036	0.006		2.65	○	○	Example
2	0.004	0.78	0.13	0.027	0.002	0.170	0.19	19.9	0.51	2.03	0.038	0.005	Ti:0.13	2.54	⊙	⊙	Example
3	0.004	0.22	0.08	0.025	0.002	0.089	0.11	18.8	0.35	2.50	0.070	0.005		2.85	○	○	Example
4	0.005	0.55	0.30	0.030	0.002	0.005	0.26	19.8	0.60	2.03	0.072	0.006	Ti:0.04	2.62	○	○	Example
5	0.005	0.71	0.15	0.029	0.002	0.087	0.30	18.4	0.53	2.10	0.080	0.005	Ti:0.15	2.63	○	○	Example
6	0.006	0.62	0.24	0.020	0.001	0.080	0.12	19.8	0.67	2.00	0.066	0.007		2.67	○	○	Example
7	0.004	0.60	0.49	0.036	0.003	0.088	0.55	19.5	0.50	2.09	0.037	0.006		2.59	○	○	Example
8	0.004	0.92	0.17	0.026	0.003	0.047	0.16	18.1	0.47	1.95	0.057	0.005		2.42	○	○	Example
9	0.006	0.44	0.34	0.027	0.002	0.083	0.13	18.6	0.58	2.15	0.054	0.006		2.73	⊙	⊙	Example
10	0.005	0.30	0.13	0.025	0.002	0.082	0.07	18.7	0.55	2.07	0.320	0.007		2.62	⊙	⊙	Example
11	0.004	0.31	0.16	0.029	0.002	0.020	0.28	19.1	0.56	2.00	0.020	0.007		2.56	○	○	Example
12	0.005	0.62	0.18	0.030	0.003	0.022	0.19	18.2	0.54	1.97	0.024	0.006	Cu:0.34	2.51	○	○	Example
13	0.004	0.32	0.19	0.028	0.001	0.023	0.14	18.8	0.50	2.00	0.085	0.005	Co:0.29	2.50	⊙	⊙	Example
14	0.004	0.53	0.34	0.039	0.003	0.039	0.27	19.0	0.55	2.06	0.051	0.007	W:0.07	2.61	⊙	⊙	Example
15	0.004	0.56	0.22	0.027	0.003	0.059	0.06	19.4	0.51	2.06	0.071	0.005	W:3.10	2.57	⊙	⊙	Example
16	0.005	0.60	0.16	0.039	0.003	0.043	0.15	19.9	0.52	1.99	0.075	0.005	V:0.21	2.51	○	○	Example
17	0.007	0.30	0.24	0.025	0.003	0.029	0.17	19.0	0.63	2.05	0.054	0.005	Zr:0.06	2.68	○	○	Example
18	0.004	0.65	0.33	0.024	0.001	0.045	0.27	18.7	0.58	2.05	0.026	0.007	B:0.0009	2.63	○	○	Example
19	0.006	021	0.28	0.028	0.002	0.090	0.18	19.6	0.56	1.88	0.039	0.008	Sn:0.003	2.44	○	○	Example
20	0.004	0.39	0.38	0.029	0.001	0.034	0.29	18.2	0.57	2.01	0.054	0.006	Ca: 0.0010	2.58	○	○	Example
21	0.005	0.38	0.34	0.023	0.002	0.067	0.34	18.6	0.59	2.02	0.046	0.007	Mg: 0.0011	2.61	○	○	Example

(continued)

22	0.005	0.78	0.25	0.036	0.003	0.065	0.30	19.2	0.53	1.99	0.041	0.005	Ca: 0.0008, Mg:0.009	2.52	○	○	Example
23	0.004	0.69	0.15	0.034	0.003	0.040	0.35	19.7	0.52	2.27	0.031	0.005	V:0.04, Cu:0.06	2.79	○	○	Example
24	0.004	0.78	0.16	0.024	0.003	0.058	0.16	19.4	0.59	1.85	0.020	0.006	Co;0.03, V:0.06	2.44	○	○	Example
25	0.004	0.30	0.18	0.028	0.001	0.081	0.08	19.9	0.51	2.46	0.074	0.005	Zr:0.08	2.97	○	○	Example
26	0.007	0.45	0.37	0.032	0.001	0.066	0.07	19.2	0.60	1.81	0.093	0.005	B:0.0008, Ca: 0.0006, Mg: 0.0007	2.41	○	○	Example
27	0.004	0.53	0.23	0.036	0.003	0.036	0.12	19.9	0.58	2.03	0.019	0.008	Co:0.02, B:0.0010, V:0.05, Cu:0.04, Ca: 0.0007, Mg: 0.0008	2.61	○	○	Example
28	0.006	0.28	0.19	0.023	0.003	0.020	0.14	18.2	0.37	1.80	-	0.008		2.17	×	×	Conventional Example SUS444
29	0.006	0.71	0.15	0.037	0.001	0.074	0.21	19.3	0.32	1.84	0.016	0.006		2.16	×	×	Comparative Example
30	0.004	0.47	0.31	0.022	0.003	0.042	0.81	18.8	0.59	2.11	0.095	0.007		2.70	○	×	Comparative Example
31	0.007	0.45	0.19	0.027	0.003	0.072	0.22	16.8	0.48	2.00	0.086	0.005		2.48	○	×	Comparative Example
32	0.007	0.63	0.33	0.029	0.001	0.039	0.34	19.4	0.63	1.60	0.026	0.008		2.23	×	×	Comparative Example

(continued)

33	0.004	0.42	0.26	0.024	0.003	0.085	0.09	18.6	<u>0.27</u>	2.04	0.065	0.009		2.31	×	×	Comparative Example
34	0.004	<u>0.04</u>	0.34	0.023	0.003	0.031	0.06	19.8	0.53	2.27	0.099	0.005		2.80	×	×	Comparative Example
35	0.007	0.25	0.20	0.035	0.001	0.057	0.17	19.3	0.57	2.07	0.076	0.007	Ti:<u>0.26</u>	2.64	×	×	Comparative Example
36	0.007	0.29	0.35	0.034	0.001	0.044	0.26	<u>23.4</u>	0.59	1.97	0.061	0.007		2.56	○	×	Comparative Example
37	0.005	0.72	<u>0.02</u>	0.037	0.001	0.049	0.10	18.3	0.56	2.06	0.026	0.006		2.62	○	×	Comparative Example
38	<u>0.024</u>	0.49	0.37	0.022	0.001	0.067	0.25	19.5	0.57	1.91	0.092	0.007		2.47	×	×	Comparative Example
39	0.007	0.62	0.26	0.037	0.002	0.033	0.08	20.0	0.57	2.21	0.040	0.018		2.78	×	×	Comparative Example
40	0.005	0.72	0.24	0.035	0.002	0.049	0.27	19.9	0.53	1.94	<u>0.860</u>	0.006		2.47	○	×	Comparative Example
41	0.005	0.23	0.17	0.025	0.002	0.062	0.08	18.0	0.60	<u>2.80</u>	0.088	0.007		<u>3.40</u>	<u>×</u>	×	Comparative Example
43	0.007	0.39	0.20	0.036	0.002	0.033	0.22	18.2	0.50	1.91	0.016	0.005	Sn:<u>0.06</u>	2.41	○	×	Comparative Example
45	0.005	0.31	0.22	0.033	0.001	0.025	0.18	19.4	0.57	2.05	<u>-</u>	0.008		2.62	×	×	Comparative Example
46	0.005	0.47	0.15	0.030	0.002	0.039	0.29	18.9	<u>0.91</u>	1.98	0.042	0.007		2.89	×	×	Comparative Example
47	0.006	0.56	0.31	0.029	0.002	0.044	0.22	19.1	0.77	2.47	0.051	0.008		<u>3.24</u>	×	×	Comparative Example

Note: Underlines indicate the outside of the scope of the present invention.

[0065] As shown in Table 1, all the ferritic stainless steels of Examples No. 1 to 27 (hereinafter, ferritic stainless steel is simply referred to as steel) exhibit better properties than SUS444 (Conventional Example No. 28) in the creep test and the thermal fatigue test.

[0066] In No. 29 steel having Nb + Mo content of less than 2.3 mass%, creep rupture time and thermal fatigue life were unacceptable. In No. 30 steel having Ni content of more than 0.60 mass%, thermal fatigue life was unacceptable. In No. 31 steel having Cr content of less than 18.0 mass%, thermal fatigue life was unacceptable. In No. 32 steel having Mo content of less than 1.80 mass%, creep rupture time and thermal fatigue life were unacceptable. In No. 33 steel having Nb content of less than 0.30 mass%, both creep rupture time and thermal fatigue life were unacceptable. In No. 34 steel having Si content of less than 0.1 mass%, oxidation was noticeably observed in both the creep test and the thermal fatigue test, and both creep rupture time and thermal fatigue life were unacceptable. In No. 35 steel having Ti content of more than 0.16 mass%, both creep rupture time and thermal fatigue life were unacceptable. In No. 36 steel having Cr content of more than 20.0 mass%, thermal fatigue life was unacceptable due to embrittlement of steel. In No. 37 steel having Mn content of less than 0.05 mass%, spalling of oxide scale occurred during the thermal fatigue test and thermal fatigue life was unacceptable. In No. 38 steel having C content of more than 0.020 mass%, both creep rupture time and thermal fatigue life were unacceptable due to a reduced amount of Nb in steel. In No. 39 steel having N content of more than 0.015 mass%, creep rupture time and thermal fatigue life were unacceptable due to a reduced amount of Nb in steel by precipitation of Nb nitride. In No. 40 steel having Sb content of more than 0.50 mass%, thermal fatigue life was unacceptable due to reduced hot ductility. In No. 41 steel having Mo content of more than 2.50 mass%, coarse σ phase (Fe-Cr-based intermetallic compound) precipitated during the thermal fatigue test and consequently, thermal fatigue life was unacceptable. In addition, creep rupture time was also unacceptable. In No. 43 steel having Sn content of more than 0.005 mass%, thermal fatigue life was unacceptable. In No. 45 steel without Sb, both creep rupture time and thermal fatigue life were unacceptable. In No. 46 steel having Nb content of more than 0.80 mass%, both creep rupture time and thermal fatigue life were unacceptable. In No. 47 steel having Nb + Mo content of more than 3.0%, both creep rupture time and thermal fatigue life were unacceptable.

Industrial Applicability

[0067] A ferritic stainless steel of the present invention is not only suitable for exhaust system components of automobiles and so forth but also well usable for exhaust system components in thermal power generation systems and for solid oxide fuel cell components, for both of which similar properties are required.

Claims

1. A ferritic stainless steel having a chemical composition containing, in mass%,
C: 0.020% or less,
Si: 0.1 to 1.0%,
Mn: 0.05 to 0.60%,
P: 0.050% or less,
S: 0.008% or less,
Ni: 0.02 to 0.60%,
Al: 0.001 to 0.25%,
Cr: 18.0 to 20.0%,
Nb: 0.30 to 0.80%,
Mo: 1.80 to 2.50%,
N: 0.015% or less, and
Sb: 0.002 to 0.50%,
with the balance being Fe and inevitable impurities, and satisfying the following expression (1);
Nb + Mo: 2.3 to 3.0% (1)
wherein Nb and Mo in expression (1) represent the contents (mass%) of the respective elements.

2. The ferritic stainless steel according to Claim 1, wherein the chemical composition further contains, in mass%, one or two or more selected from
Ti: 0.01 to 0.16%,
Zr: 0.01 to 0.50%,
Co: 0.01 to 0.50%,
B: 0.0002 to 0.0050%,
V: 0.01 to 1.0%,

W: 0.01 to 5.0%,
Cu: 0.01 to 0.40%, and
Sn: 0.001 to 0.005%.

3. The ferritic stainless steel according to Claim 1 or 2, wherein the chemical composition further contains, in mass%, one or two selected from
Ca: 0.0002 to 0.0050% and
Mg: 0.0002 to 0.0050%.

4. The ferritic stainless steel according to any one of Claims 1 to 3, wherein the ferritic stainless steel is used for an exhaust manifold whose temperature is elevated to 700°C or higher by an exhaust gas from an engine.

FIG. 1

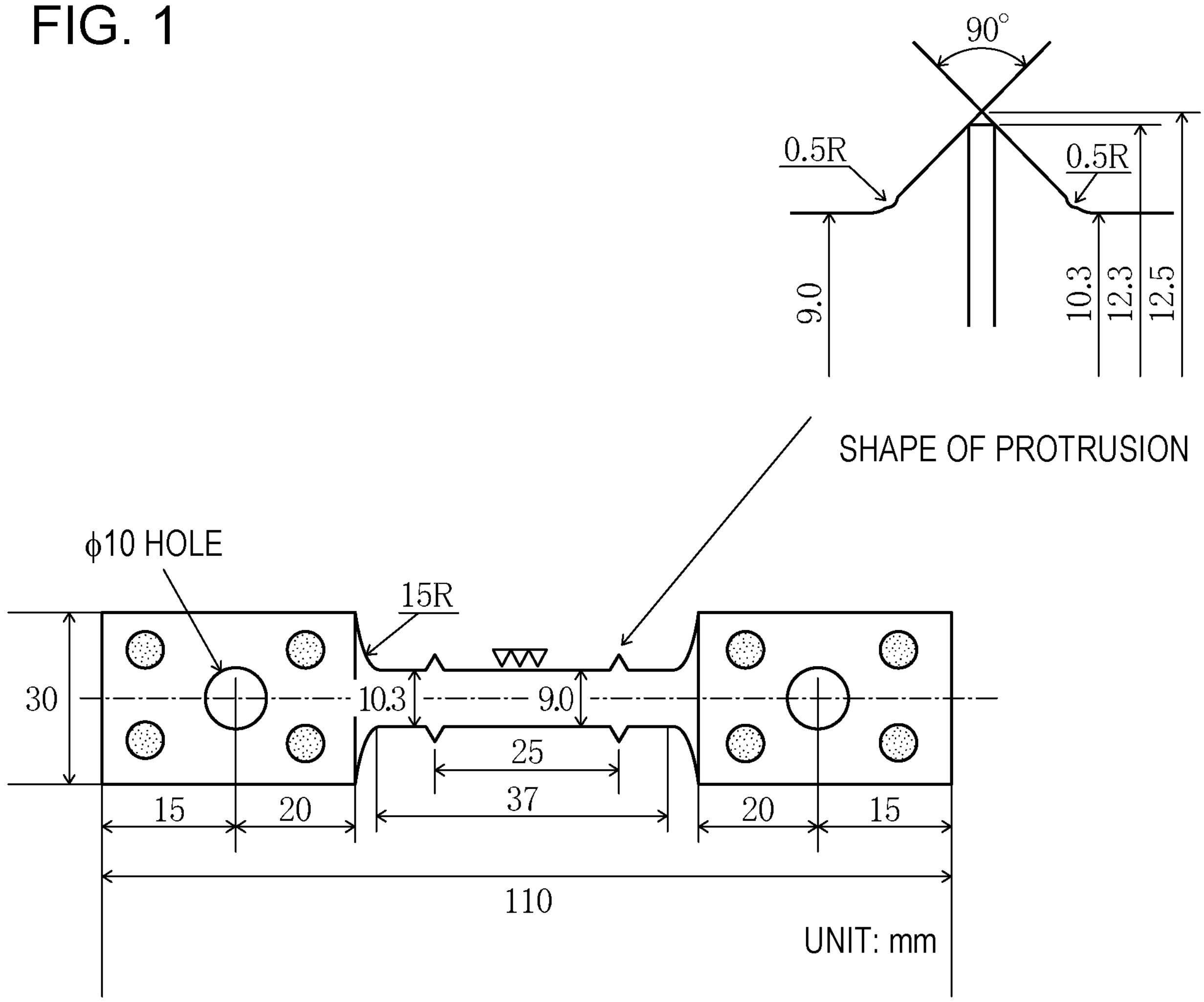

90°
0.5R
0.5R
9.0
10.3
12.3
12.5
SHAPE OF PROTRUSION
ϕ10 HOLE
15R
30
10.3
9.0
25
37
15
20
20
15
110
UNIT: mm

FIG. 2

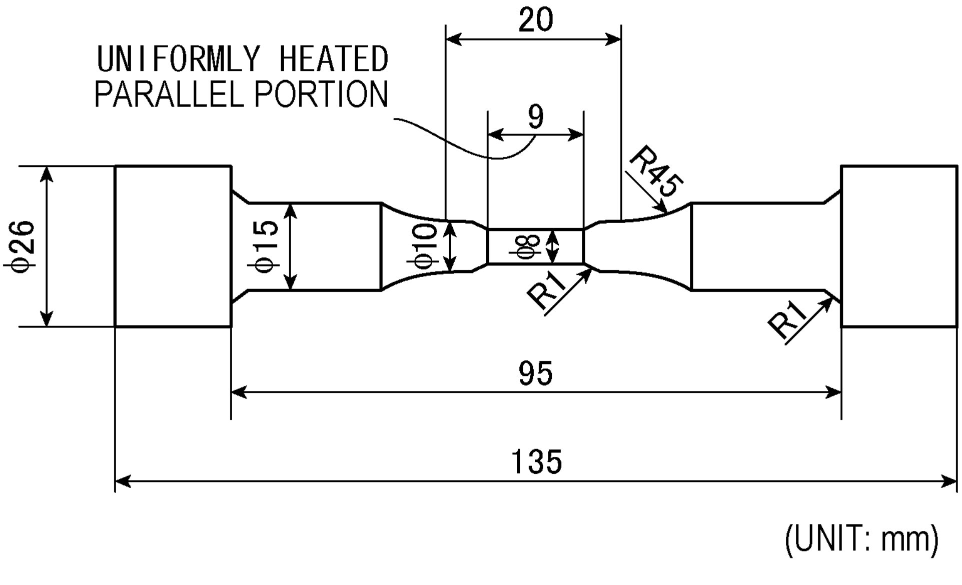
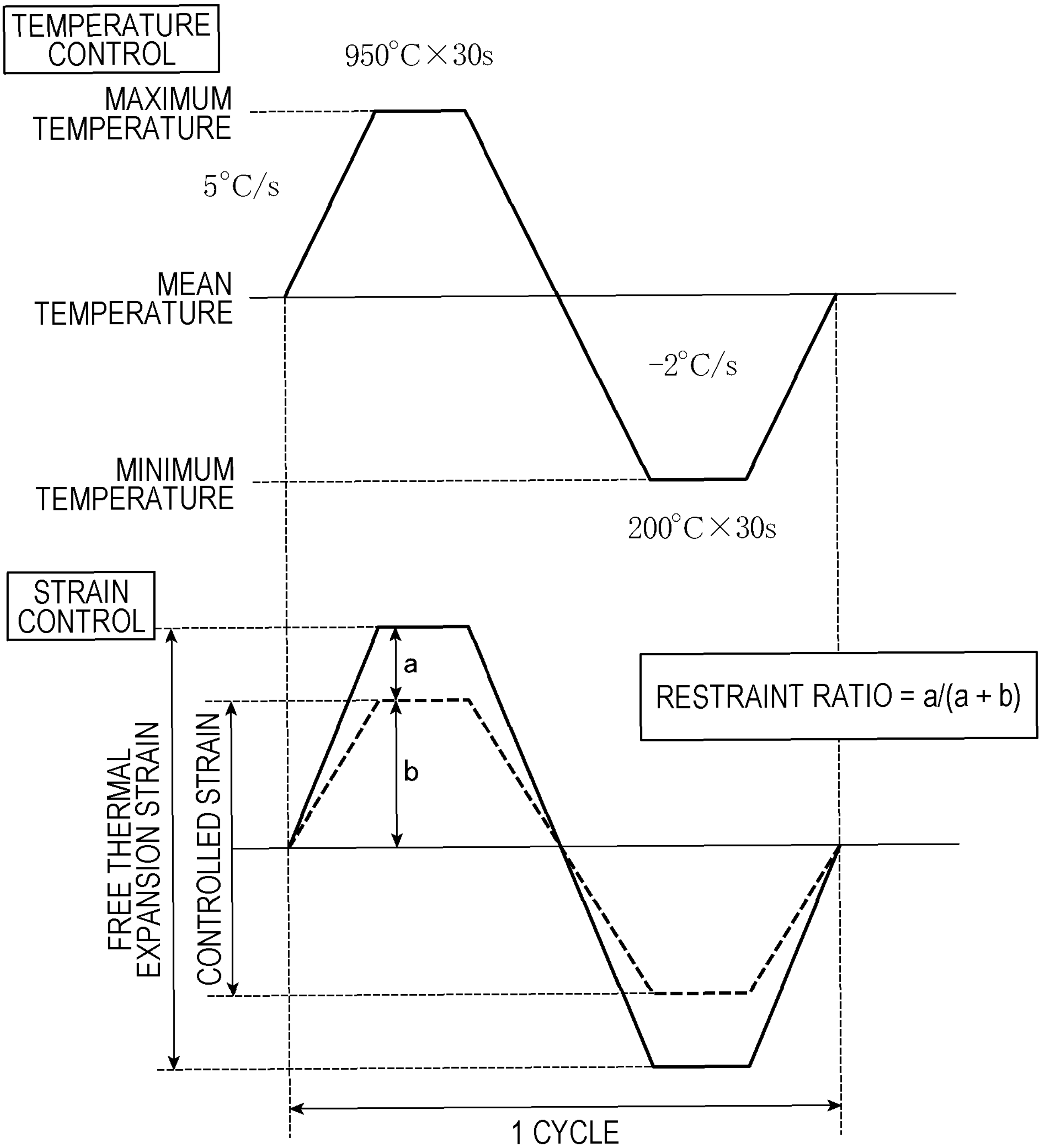

20
UNIFORMLY HEATED
PARALLEL PORTION
9
R45
ϕ26
ϕ15
ϕ10
ϕ8
R1
R1
95
135
(UNIT: mm)

FIG. 3


TEMPERATURE CONTROL
950°C×30s
MAXIMUM TEMPERATURE
5°C/s
MEAN TEMPERATURE
−2°C/s
MINIMUM TEMPERATURE
200°C×30s
STRAIN CONTROL
a
b
RESTRAINT RATIO = a/(a + b)
FREE THERMAL EXPANSION STRAIN
CONTROLLED STRAIN
1 CYCLE

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2019/002413

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. C22C38/00(2006.01)i, C22C38/60(2006.01)i, C21D9/46(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)
Int.Cl. C22C38/00, C22C38/60, C21D9/46

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	1971-2019
Registered utility model specifications of Japan	1996-2019
Published registered utility model applications of Japan	1994-2019

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	WO 2014/157104 A1 (NIPPON STEEL & SUMIKIN STAINLESS STEEL CORPORATION) 02 October 2014 & US 2016/0002760 A1 & EP 2980274 A1 & KR 10-2015-0110800 A & CN 105008590 A	1-4
A	WO 2014/119796 A1 (NIPPON STEEL & SUMIKIN STAINLESS STEEL CORPORATION) 07 August 2014 & US 2015/0376732 A1 & EP 2952602 A1 & CN 104968823 A & KR 10-2015-0100927 A & TW 201435098 A	1-4
A	WO 2016/117458 A1 (SHINNITTETSU STAINLESS KK) 28 July 2016 & US 2018/0016655 A1 & EP 3249067 A1 & CN 107208213 A & KR 10-2017-0101262 A & MX 2017009376 A	1-4

☒ 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
12 April 2019 (12.04.2019)

Date of mailing of the international search report
23 April 2019 (23.04.2019)

Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No. PCT/JP2019/002413

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X P, A	WO 2018/043309 A1 (JFE STEEL CORPORATION) 08 March 2018, claims 1-4, paragraphs [0015]-[0041], table 1 & JP 2018-87383 A & TW 201812050 A	2-4 1

Form PCT/ISA/210 (continuation of second sheet) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2004018921 A **[0005]**