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(54) **HEAT-RESISTANT AUSTENITIC STAINLESS STEEL HAVING EXCELLENT CYCLIC
OXIDATION RESISTANCE**

(57) A heat-resistant austenitic stainless steel comprising C: 0.05 to 0.2%, Si: 0.1 to 1%, Mn: 0.1 to 2.5%, Cu: 1 to 4%, Ni: 7 to 12%, Cr: 16 to 20%, Nb: 0.1 to 0.6%, Zr: 0.05 to 0.4%, Ce: 0.005 to 0.1%, Ti: 0.1 to 0.6%, B:

0.0005 to 0.005%, N: 0.001 to 0.15%, S: 0.005% or less (not including 0%), and P: 0.05% or less (not including 0%), with the balance of iron and unavoidable impurities.

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Description

Technical Field

5 **[0001]** The present invention concerns a heat-resistant austenitic stainless steel used preferably as materials of heat transfer tubes such as for boilers and it particularly relates to a heat-resistant austenitic stainless steel having excellent cyclic oxidation resistance.

Background Art

10 **[0002]** In recent years, for suppressing emission of carbon dioxide as greenhouse gas, improvement in the efficiency of coal-fired thermal power generation plants has been proceeded. For improving the power generation efficiency, it is effective to increase the temperature and the pressure of steam in boilers and, as the materials for heat transfer pipes of boilers, those having excellent high temperature strength and oxidation resistance are used. Further, austenitic stain-
 15 less steels are used generally as such materials having excellent properties.

20 **[0003]** The oxidation resistance required for the materials of heat transfer tubes include cyclic oxidation resistance. Since boilers are started and stopped repeatedly, oxides formed on the surface of the steel tubes (heat transfer tubes) are exposed to cyclic oxidation circumstance undergoing high temperature circumstance and low temperature circumstance alternately. In such a circumstance, oxides are peeled due to the difference of thermal expansion coefficient to the matrix to result in a problem of insufficiency of strength caused by further development of oxidation and weight loss (thinning) due to peeling off scale. The property less causing such phenomenon (referred to as "cyclic oxidation resistance" in the invention) even under such circumstance is required.

25 **[0004]** As heat-resistant materials having excellent oxidation resistance in a wide sense including those properties other than the cyclic oxidation resistance, 25Cr-20Ni austenitic stainless steel (SUS310S) has been known. However, since the stainless steel contains a great amount of expensive Ni, it takes a high cost. In view of the above, it is an important factor for the material of the heat transfer tubes of the boilers to use 18Cr-8Ni austenitic stainless steel (SUS304) containing lower amount of Ni content and having high temperature strength and satisfactory corrosion resistance as a basic component.

30 **[0005]** SUS321 system has been known as the composition similar to that of 18Cr-8Ni austenitic stainless steel and KA-SUS321J2HTB has been known as the stainless steel for boilers having a specification for thermal power station according to SUS321 system has been known. As a technology for improving the oxidation resistance in a wide sense includes (1) surface treatment such as shot peening or mechanical polishing, (2) addition of Al, Si and REM (rare earth metal) including Ce and La which are alloying elements for improving the corrosion resistance, and (3) refining of crystal grains. Technologies relating to austenitic stainless steels using Ti compounds as precipitation hardening mechanism
 35 have been proposed, for example, in Patent Literatures 1 and 2.

40 **[0006]** Among the technologies described above, the Patent Literature 1 discloses improvement of the oxidation resistance by the addition of Al that contributes to the improvement of the corrosion resistance and by the promotion of the formation of a Cr₂O₃ layer by surface polishing. Further, as a substitute for obtaining the same effect as the surface polishing treatment, the literature shows that the oxidation resistance can be improved also by increasing the total amount of Al and Si to 4% or more and, in addition, adding REM such as Ce, Y, and La, or Ca.

45 **[0007]** However, while the effect of retarding the growing rate of oxides formed on the surface of steel tubes can be expected, for example, by the addition of Al and Si or formation of the Cr₂O₃ layer, formation of the oxides cannot be prevented completely and provision of satisfactory cyclic oxidation resistance cannot be expected. Moreover, the steel containing Al also has a problem that surface defects tend to be caused during manufacture of tubes.

50 **[0008]** While the Patent Literature 2 discloses addition of Ce, La, and Hf for improving the oxidation resistance, it is expected that the cyclic oxidation resistance is low in the same manner as the technologies described above and the technology is not based on the recognition of the improvement for the cyclic oxidation resistance.

55 **[0009]** As the technology of improving the cyclic oxidation resistance, a technology as in the Patent Literature 3 has also been proposed. However, since a great amount of Al and Si is contained in this technology, this involves a problem of resulting surface defects of steel tubes or resulting in embrittlement after heat treatment for long time. In addition, while the literature shows that the addition of REM such as La and Ce including Y exhibits an effect of improving the scale adhesion, this effect is not enough and the technology is not intended for recognition for the improvement of the cyclic oxidation resistance.

60 **[0010]** On the other hand, as a technology of improving the oxidation resistance of the austenitic stainless steel for boilers, a technology as in the Patent Literature 4 has also been proposed. This technology concerns "KA-SUS304J1HTB" component systems containing Nb and N for precipitation and solution hardening. Also in this technology, about 0.002 to 0.05% of Ti is added with an aim of forming oxide type inclusions. However, in the steel using precipitation of a Ti compound as the hardening mechanism such as KA-SUS321J2HTB, it is expected that high temperature strength cannot

be ensured unless Ti is added by about 0.1 to 0.25%. Further, this technology is not intended for the improvement of the cyclic oxidation resistance and it is expected that the cyclic oxidation resistance is low.

[0011] In the technology of Patent Literature 5, oxidation resistance is improved by addition of REM and peening of blowing particles. However, peening results in another problem of increasing the cost due to increase in the manufacturing process and since the technology is not intended for the improvement of the cyclic oxidation resistance, it is expected that the cyclic oxidation resistance is low.

Citation List

Patent Literature

[0012]

[Patent Literature 1] JP-A No. 2004-43903
 [Patent Literature 2] JP-A No. Hei 9(1997)-165655
 [Patent Literature 3] JP-A No. Hei 8(1996)-337850
 [Patent Literature 4] JP-A No. 2003-268503
 [Patent Literature 2] JP-A No. Hei 6(1994)-322489

Summary of the Invention

Technical Problem

[0013] The present invention has been accomplished in view of such a situation and it intends to provide a heat-resistant austenitic stainless steel having excellent cyclic oxidation resistance, having a chemical composition comparable with that of 18Cr-8Ni austenitic stainless steels in view of Ni and Cr content, not depending on the addition of Al or Si and surface treatment, with less peeling off surface oxides in cyclic oxidation circumstance, and causing less weight loss.

Solution to Problem

[0014] A heat-resistant austenitic stainless steel of the invention capable of solving the problem described above comprises; C: 0.05 to 0.2% (means mass% for chemical composition here and hereinafter), Si: 0.1 to 1%, Mn: 0.1 to 2.5%, Cu: 1 to 4%, Ni: 7 to 12%, Cr: 16 to 20%, Nb: 0.1 to 0.6%, Zr: 0.05 to 0.4%, Ce: 0.005 to 0.1%, Ti: 0.1 to 0.6%, B: 0.0005 to 0.005%, N: 0.001 to 0.15%, S: 0.005% or less (not including 0%) and P: 0.05% or less (not including 0%) respectively, with the balance of iron and unavoidable impurities.

[0015] It is also useful that the heat-resistant austenitic stainless steel of the invention further includes optionally, Mo: 3% or less (not including 0%) and/or W: 5% or less (not including 0%), and the high temperature strength is further improved by containing of such elements.

[0016] In the heat-resistant austenitic stainless steel of the invention, the yield of Ce can be improved and the toughness can be improved by further addition optionally, Ca: 0.005% or less (not including 0%) and/or Mg: 0.005% or less (not including 0%).

[0017] The heat-resistant austenitic stainless steel improved the cyclic oxidation resistance can be obtained by controlling the chemical composition as described above. Further, higher cyclic oxidation resistance can be obtained and, in addition, the property can be provided stably by refining the crystal grain size of a metal structure to 6 or more and less than 12 in terms of the ASTM grain size number.

Advantageous Effects of Invention

[0018] In the heat-resistant austenitic stainless steel of the invention, since progress of oxidation due to peeling off scale and accompanying weight loss of the steel are less caused even in a cyclic oxidation circumstance, the power generation efficiency due to increase in the steam temperature can be improved by using the material as the heat transfer tube for coal-fired power plants and the service life of the heat transfer tube can be made longer compared with conventional materials, to reduce the maintenance cost. Further, when the material is used as the heat transfer tube, since less scale is peeled off, scattering of the scale in the inside can be suppressed to decrease damages of the turbine.

Description of Embodiments

[0019] The present inventors have made studies from various approaches in order to realize an austenitic stainless

steel improved for cyclic oxidation resistance while maintaining necessary high temperature strength. As a result, it has been found that an outstandingly excellent cyclic oxidation resistance can be provided by containing of a predetermined amount of Zr and Ce to stainless steel having a chemical composition comparable with that of 18Cr-8Ni austenitic stainless steel, in view of the content of Ni and Cr to accomplish the present invention.

[0020] The heat-resistant austenitic stainless steel of the invention has a feature of containing a predetermined amount of Zr and Ce to the chemical composition comparable with that of the 18Cr-8Ni austenitic stainless steel in view of the content of Ni and Cr, and the reason for defining the range of the content of Zr and Ce is as described below.

[0021] Zr and Ce exhibit an effect of suppressing peeling off oxides due to a synergistic effect of them. For providing such an effect, 0.05% or more of Zr has to be contained. However, if the Zr content is excessive, since coarse inclusions are formed to worsen the surface property and the toughness of the steel material (or steel tube), it is necessary to define the upper limit to 0.4% or less. Further, Ce has to be contained 0.005% or more for providing the effect. If the Ce content is excessive to exceed 0.1%, this increases cost from an economical point of view.

[0022] Since the addition of Zr and Ce increases the cost of the steel material, an appropriate content may be set while considering the balance between the effect obtained by containment and increase of the cost. From such a view point, a preferred lower limit of the Zr content is 0.10% or more (more preferably, 0.15% or more) and a preferred upper limit is 0.3% or less (more preferably, 0.25% or less). Further, a preferred lower limit of the Ce content is 0.01% or more (more preferably, 0.015% or more) and a preferred upper limit is 0.05% or less (more preferably 0.03% or less).

[0023] While pure Ce may be added as the Ce source, necessary Ce content can be added also by using a Ce-containing master alloy or a Ce-containing misch metal prepared. If La, Nd, Pr, etc. to be contained in the misch metal are contained in the steel at a concentration lower than that of Ce in the steel, they cause no problem, and handling during melting operation can be simplified by using the master alloy or misch metal compared with easily oxidizable pure Ce.

[0024] Among the prior art, the Patent Literatures 1, 3, and 5 disclose that adhesion of the oxides is improved by the addition of REM including Y, La, and Ce but each of such disclosures is based on the assumption of sole addition of REM and they do not disclose at all the synergistic effect obtained by addition of Ce together with Zr.

[0025] Further, the Patent Literature 2 also discloses that Zr and Ce can be contained in combination. However, each of them is not an essential alloy component in this technology and added optionally also including the case with no addition. Particularly, Zr is contained by a content less than the range defined in the invention while intending to strengthen the grain boundary and improve the creep ductility.

[0026] The heat-resistant austenitic stainless steel of the invention has a chemical composition comparable with that of 18Cr-8Ni austenitic stainless steel in view of the content of Ni and Cr. The chemical composition for each of the elements other than Zr and Ce (C, Si, Mn, Cu, Ni, Cr, Nb, Ti, B, N, S, and P) should also be controlled appropriately. The effect and the reason for defining the range of such elements are as described below.

[C: 0.05 to 0.2%]

[0027] C is an element of forming carbides in a high temperature service circumstance and having an effect of improving high temperature strength and creep strength necessary for the heat transfer tube, and it should be contained 0.05% or more in order to ensure the amount of carbide precipitates that works as hardening particles. However, when C is added excessively and its content is more than 0.2%, it goes beyond the solid solubility limit to form coarse carbides and no further hardening can be obtained. A preferred lower limit of the C content is 0.07% or more (more preferably, 0.09% or more) and a preferred upper limit is 0.18% or less (more preferably, 0.15% or less).

[Si: 0.1 to 1%]

[0028] Si is an element having a deoxidation effect in molten steels. Further, it acts effectively for the improvement of the oxidation resistance if it is contained even in a small amount. For providing such effects, it is necessary that the Si content is 0.1% or more. However, if Si is added excessively and its content is more than 1%, this results in formation of σ phase to embrittle the steel (σ embrittlement). A preferred lower limit of the Si content is 0.2% or more (more preferably, 0.3% or more) and a preferred upper limit is 0.9% or less (more preferably, 0.8% or less).

[Mn: 0.1 to 2.5%]

[0029] Mn is an element having a deoxidation effect in molten steels in the same manner as Si. Further, it has an effect of stabilizing austenite. For providing such effects, it is necessary that the Mn content is 0.1% or more. However, if Mn is added excessively and its content is more than 2.5%, this deteriorates hot workability. A preferred lower limit of the Mn content is 0.2% or more (more preferably, 0.3% or more) and a preferred upper limit is 2.0% or less (more preferably, 1.8% or less).

[Cu: 1 to 4%]

[0030] Cu is an element of forming coherent precipitates (precipitates in which the atomic arrangement is continuous with that of matrix) in steels and remarkably improving high temperature creep strength which is one of principal hardening mechanisms in stainless steels. In order to provide the effect, it is necessary that Cu content is 1% or more. However, if Cu is added excessively and its content is more than 4%, the effect is saturated. A preferred lower limit of the Cu content is 2.0% or more (more preferably, 2.5% or more) and a preferred upper limit is 3.7% or less (more preferably, 3.5% or less).

[Ni: 7 to 12%]

[0031] Ni has an effect of stabilizing austenite and it is necessary to be contained 7% or more in order to maintain an austenitic phase. However, if Ni is added excessively and its content is more than 12%, this increases the cost. A preferred lower limit of the Ni content is 7.5% or more (more preferably, 8.0% or more) and a preferred upper limit is 11.5% or less (more preferably, 11.0% or less).

[Cr: 16 to 20%]

[0032] Cr is an essential element for providing corrosion resistance as a stainless steel. For providing such an effect, it is necessary that Cr is contained 16% or more. However, if Cr is added excessively and its content is more than 20%, a ferrite phase which lowers the high temperature strength increases. A preferred lower limit of the Cr content is 16.5% or more (more preferably, 17.0% or more) and a preferred upper limit is 19.5% or less (more preferably, 19.0% or less).

[Nb: 0.1 to 0.6%]

[0033] Nb is an effective element to the improvement of the high temperature strength by precipitation of carbonitrides (carbides, nitrides, or carbonitrides) and, further, provides an effect of improving the corrosion resistance as a subsidiary effect by suppressing growing of the crystal grains and promoting diffusion of Cr by means of precipitates. In order to ensure a required precipitation amount, it is necessary that Nb is contained 0.1% or more. However, if Nb is added excessively and its content is more than 0.6%, precipitates become coarser to lower the toughness. A preferred limit of the Nb content is 0.12% or more (more preferably, 0.15% or more) and a preferred upper limit is 0.5% or less (more preferably, 0.3% or less).

[Ti: 0.1 to 0.6%]

[0034] Ti also provides the same effect as Nb and, when it is added with Nb and Zr, precipitates are further stabilized, which is also effective for maintaining high temperature strength for a long time. In order to provide such an effect effectively, it is necessary that the Ti content is 0.1% or more. However, if the Ti content becomes excessive, precipitates become coarser to lower the toughness in the same manner as Nb, so that the Ti content should be 0.6% or less. A preferred lower limit of the Ti content is 0.12% or more (more preferably, 0.15% or more) and a preferred upper limit is 0.5% or less (more preferably, 0.3% or less).

[B: 0.0005 to 0.005%]

[0035] B has an effect of promoting formation of $M_{23}C_6$ type carbides (M is carbide-forming elements) as one of principal hardening mechanisms by being solved into steel. In order to provide such an effect efficiently, it is necessary that the B content is 0.0005% or more. However, if the B content is excessive, since this deteriorates the hot workability and the weldability, it should be 0.005% or less. A preferred lower limit of the B content is 0.001% or more (more preferably, 0.0012% or more) and a preferred upper limit is 0.004% or less (more preferably, 0.003% or less).

[N: 0.001 to 0.15%]

[0036] N is an element having an effect of improving the high temperature strength through solid-solution hardening by being solved into steel, which is also effective for the improvement of the high temperature strength by forming nitrides with Cr or Nb under load at high temperature for a long time. In order to efficiently provide the effect, it is necessary that the N content is 0.001% or more. However, if N is added excessively and its content is more than 0.15%, this results in formation of coarse Ti nitrides or Nb nitrides to deteriorate the toughness. A preferred lower limit of the N content is 0.002% or more (more preferably, 0.003% or more) and a preferred upper limit is 0.10% or less (more preferably, 0.08%

or less, and, further preferably, 0.02% or less).

[S: 0.005% or less (not including 0%)]

- 5 **[0037]** S is an unavoidable impurity and, since hot workability is deteriorated as the content increases, it is necessary that the content is 0.005% or less. Further, since S fixes Ce as sulfides to decrease the effect obtained by the addition of Ce, it is preferably restricted to 0.002% or less (more preferably, 0.001% or less).

[P: 0.05% or less (not including 0%)]

- 10 **[0038]** P is an unavoidable impurity and, since the weldability is deteriorated as the content increases, it should be 0.05% or less. Preferably, it is restricted to 0.04% or less (more preferably, 0.03% or less)

- [0039]** The contained elements defined in the invention are described above and the balance is iron and unavoidable impurities. In addition to La, Nd, Pr, etc. which are contained at a concentration lower than Ce, respectively when adding a misch metal as a Ce source, intrusion of elements which are introduced depending on the raw materials, alloying source, and situations of production facilities, etc. are permissible. However, since impurity elements having low melting point such as Sn, Pb, Sb, As, and Zn derived from scrap materials lower the grain boundary strength during hot working and use at high temperature circumstance, it is preferred that they are kept to a low concentration in order to improve the hot workability and embrittlement cracks in long time use. Further, in the steel of the invention, Mo, W, Ca, and Mg, etc. may also be optionally contained and the properties of the steel are further improved in accordance with the kind of the elements to be contained.

[Mo: 3% or less (not including 0%) and/or W: 5% or less (not including 0%)]

- 25 **[0040]** Mo and W have an effect of improving the high temperature strength by solid solution hardening and can further increase the high temperature strength by optionally adding them. However, since the hot workability is deteriorated when the Mo content is excessive, it is preferably 3% or less. More preferably, it is 2.5% or less (further preferably, 2.0% or less). Further, since excessive W content forms coarse intermetallic compounds to lower the high temperature ductility, it is preferably less than 5% or less. More preferably, it is 4.5% or less (further preferably, 4.0% or less). A preferred lower limit for providing the effect efficiently described above is 0.1% or more (more preferably, 0.5% or more) for Mo and 0.1% or more (more preferably, 1.0% or more) for W. However, while the effect as described above can be provided by addition of such elements, since this increases the cost on the other hand, the content may be determined in accordance with the necessary hardening amount and an allowable cost.

- 35 [Ca: 0.005% or less (not including 0) and/or Mg: 0.005% or less (not including 0)]

- [0041]** Since Ca and Mg act as desulfurizing and deoxidizing elements, they can suppress formation of Ce sulfides and Ce oxides to improve the yield of Ce and suppress lowering of the toughness due to formation of inclusions. A preferred lower limit for providing such effect effectively is 0.0002% or more and, more preferably, 0.0005% or more for each of them. However, if the contents become excessive, since they impose restriction in view of operation such as occurrence of bumping of molten steel during melting operation, each of the upper limits is defined to 0.005% or less. More preferably, the content of each of them is 0.002% or less.

- [0042]** In the heat-resistant austenitic stainless steel of the invention, cyclic oxidation resistance can be improved by addition of a predetermined amount of Zr and Ce. For improving the property further, it is effective to control the crystal grain size of microstructure. From such a view point, the crystal grain size of the microstructure of the heat-resistant austenitic stainless steel is preferably defined as a fine structure of 6 or more and less than 12 in terms of the ASTM (American Society for Testing and Materials) grain size number. The grain size number (crystal grain size number) is defined by ASTM and means a grain size number calculated by a counting method (Planimetric method).

- [0043]** When the crystal grain size of the microstructure is less than 6 in terms of the ASTM grain size number, while the effect of improving the cyclic oxidation resistance per se by the addition of Zr and Ce can be obtained, the improving effect cannot be increased sufficiently. The grain size number is preferably 7 or more and, more preferably, 9 or more. On the other hand, in the tube production process by hot and cold working and heat treatment, since an extremely fine crystal grain structure cannot be manufactured substantially, an upper limit of the crystal grain size is preferably less than 12. In view of the manufacturing cost and the productivity, the upper limit is more preferably 10 or less.

- 55 **[0044]** The range of the crystal grain size as described above can be obtained by controlling the addition amount of the elements contributing to the pinning at the crystal grain boundary, conditions for hot and cold working such as drawing and extrusion in the tube production process, and heat treatment. The optimal condition for each of them changes depending on the three factors and, in order to refine the crystal grain size, it is necessary to increase the addition

amount of the precipitating elements, make the degree of strain higher, and lower the heat treatment temperature. Cold and hot working are applied for controlling the tube thickness and introducing strains and conditioning the crystal grain structure by heat treatment after working and usually performed at a reduction ratio of 30% or more. Further, the heat treatment is applied for removing strains and performed in a temperature range generally at 1,000°C or higher and lower than 1,300°C. For example, at the reduction ratio of about 35%, the defined range of the grain size can be obtained by setting the heat treatment temperature to 1,250°C or lower and, preferably, 1,225°C or lower and, particularly preferably, 1,150°C or lower, but the condition is not restricted depending on the balance for precipitating elements, working, and heat treatment.

[0045] When the heat transfer tubes of boilers are formed by using the heat-resistant austenitic stainless steel described above, they provide an excellent property under a cyclic oxidation circumstance.

[0046] The present invention is to be described more specifically with reference to examples. The invention is not restricted by the following examples and it is of course possible to practice the invention with appropriate modification within a range that can conform to the purport described above and to be described later, and each of them is included in the technical range of the invention.

[Example]

[Example 1]

[0047] 20 kg ingots prepared by melting various kinds of steels comprising chemical compositions shown in the following Table 1 in a vacuum melting furnace (VIF) were hot-forged each to 120 mm width x 20 mm thickness, applied with a heat treatment at 1250°C and processed by cold rolling to 13 mm thickness. Subsequently, a heat treatment at 1150°C for 5 min was performed again to provide a master material. A steel material of 20 mm x 30 mm x 2 mm was cut out from the master material by machining and the surface of the steel material was smoothed and mirror-finished by polishing using emery paper and by buff polishing using diamond abrasive grains to prepare specimens.

[0048] Among the steels shown in the following Table 1, specimens Nos. 1 to 10 are steels that satisfy the requirements defined in the invention (steel of the invention), and specimens Nos. 11 to 16 are steels out of the requirements defined in the invention (comparative steels), in which the specimens Nos. 14, 15, and 16 are "steels corresponding to KA-SUS304J1HTB", "steels corresponding to SUS304L", and "steels corresponding to SUS310S" which are conventional steels respectively. Further, the specimens Nos. 7 and 8 are steels with addition of Ce by using a misch metal and contain La, Pr, Nd, etc. as impurities. The specimens Nos. 9 and 10 are steels with addition of Mg and Ca respectively.

[0049] "Steel corresponding to KA-SUS304J1HTB" (specimen No. 14) described above belongs to 18Cr-8Ni austenitic stainless steel which is steel species used successfully as heat transfer tubes of boilers (for example, in "MATERIA", vol. 46, No. 2, 2007, pp. 99-101). Further, steel corresponding to SUS310S (specimen No. 16) belongs to 25Cr-20Ni austenitic stainless steel. While this is expensive since it contains more Ni than 18Cr-8Ni austenitic stainless steel, this is steel species more excellent in the corrosion resistance than 18Cr-8Ni austenitic stainless steel essentially in view of the chemical composition.

[Table 1]

Specimen No.	Chemical composition* (mass%)															Others (remarks)
	C	Si	Mn	P	S	Ni	Cr	Cu	Mo	Nb	Ti	Zr	Ce	B	N	
1	0.09	0.30	1.58	0.026	0.002	9.7	18.4	3.0	-	0.19	0.20	0.19	0.015	0.0020	0.009	
2	0.10	0.30	1.60	0.018	0.002	9.5	18.3	3.0	-	0.18	0.14	0.25	0.092	0.0020	0.005	
3	0.18	0.89	0.21	0.025	0.001	9.8	16.7	2.1	-	0.13	0.40	0.38	0.020	0.0048	0.130	
4	0.10	0.15	1.80	0.032	0.004	9.2	18.1	3.1	-	0.21	0.22	0.09	0.008	0.0021	0.004	
5	0.10	0.32	1.26	0.029	0.003	9.5	17.9	1.3	0.8	0.18	0.19	0.20	0.017	0.0019	0.080	
6	0.07	0.75	0.77	0.045	0.002	8.2	19.7	3.8	-	0.56	0.12	0.35	0.034	0.0005	0.008	
7	0.11	0.54	1.87	0.025	0.001	9.8	18.1	3.0	-	0.18	0.26	0.19	0.023	0.0018	0.010	Ce added in the form of misch metal
8	0.12	0.76	1.14	0.018	0.003	11.3	18.4	2.8	-	0.19	0.15	0.11	0.041	0.0019	0.019	Ce added in the form of misch metal
9	0.11	0.55	1.45	0.019	0.002	9.6	18.7	3.0	-	0.18	0.26	0.16	0.025	0.0018	0.003	Mg:0.0015
10	0.10	0.42	1.48	0.022	0.001	9.8	17.9	3.2	-	0.17	0.25	0.10	0.013	0.0021	0.005	Ca:0.0022
11	0.09	0.19	1.60	0.030	0.003	9.2	17.9	3.0	-	0.27	0.23	0.02	0.019	0.0018	0.050	
12	0.06	0.25	1.50	0.031	0.002	9.3	18.1	3.1	-	0.19	0.16	0.15	<0.001	0.0022	0.015	
13	0.11	0.29	1.48	0.031	0.002	9.3	18.1	3.0	-	0.21	0.19	0.01	0.003	0.0022	0.023	
14	0.10	0.19	0.73	0.030	0.003	9.2	18.0	3.1	-	0.38	-	-	-	0.0018	0.110	
15	0.05	0.40	1.82	0.032	0.002	8.4	18.5	0.3	0.21	-	-	-	-	-	0.059	
16	0.05	1.46	1.80	0.030	0.001	19.52	24.2	0.08	0.15	-	-	-	-	0.0012	0.058	
* Balance: Iron and unavoidable impurities other than P and S																

[0050] Each of the specimens obtained as described above was used and repeating oxidation tests were performed for evaluating a weight loss. In the cyclic oxidation test, specimens were carried into and out of a furnace at 1100°C in air at a cycle of furnace heating for 25 min and cooling for 5 min in air, and heating and cooling were repeated up to 20 cycles. After the cyclic oxidation test, weight change of the specimen was measured by an electronic balance and the weight loss ($\text{mg} \cdot \text{cm}^{-2}$) of the specimens was calculated. Further the surface roughness of the specimen after the cyclic oxidation test was observed visually.

[0051] The result of the measurement (weight loss, surface roughness) is shown in the following Table 2.

[Table 2]

Specimen No.	Weight loss ($\text{mg} \cdot \text{cm}^{-2}$)	Surface roughness
1	10.8	smooth
2	7.6	smooth
3	8.5	smooth
4	33.2	smooth
5	11.6	smooth
6	20.4	smooth
7	9.2	smooth
8	7.9	smooth
9	8.1	smooth
10	8.7	smooth
11	73.4	rough
12	76.9	rough
13	93.1	rough
14	80.5	rough
15	140.1	rough
16	0.4	smooth

[0052] In view of the result, it can be considered as below. The weight loss is decreased in the steels that satisfy the chemical composition defined in the invention (steel of invention: specimens Nos. 1 to 10) compared with conventional steels (specimens Nos. 14, 15) and comparative steels that are out of the chemical compositions defined in the invention (specimen Nos. 11 to 13), and it can be seen that less scales are peeled and the weight loss can be suppressed by compound addition of Zr and Ce.

[0053] Further, it can be seen that since the roughness at the scale surface is smoothed in the steel of the invention scale are not formed and peeled off. Further, the steel of the invention provides properties comparable with those of steels corresponding to conventional steels SUS310S of 25Cr-20Ni which contain higher Ni content and are considered to be excellent in the corrosion resistance (specimen No. 16), and the cyclic oxidation resistance can be improved to a level comparable with that of 25Cr-20Ni austenitic stainless steel although this is a 18Cr-8Ni austenitic stainless steel and inexpensive.

[Example 2]

[0054] For the steels of the invention of specimens Nos. 1 to 6 and the comparative steel of specimen No. 14 shown in Tables 1 and 2, the heat treatment temperature was changed in temperature range of 1125 to 1275°C after cold working at 35% reduction ratio to prepare specimens of the respective steels with crystal grain size numbers of 4.5 to 10.0. In the cyclic oxidation test, specimens were carried into and out of a furnace at 1100°C in air at a temperature cycle including furnace heating for 25 min and cooling for 5 min in air, and weight loss (reduction in thickness: $\text{mg} \cdot \text{cm}^{-2}$) was determined by comparing the mass of the specimen after 40 cycles with the mass of the specimen in the initial state.

[0055] For the number of cycles, since the weight loss was improved greatly in some steels with addition of Zr and Ce and the weight loss after 20 cycles was about at a level of an allowable error depending on the grain size, heating and cooling were repeated till 40 cycles. The crystal grain size number was calculated by observation for three view

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fields per one steel species.

[0056] The result of the measurement described above (weight loss) are shown together with the crystal grain size number in the following Table 3.

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[Table 3]

Specimen No.	1		2		3		4		5		6		14	
	Crystal grain size	Weight loss (mg·cm ²)	Crystal grain size	Weight loss (mg·cm ²)	Crystal grain size	Weight loss (mg·cm ²)	Crystal grain size	Weight loss (mg·cm ²)	Crystal grain size	Weight loss (mg·cm ²)	Crystal grain size	Weight loss (mg·cm ²)	Crystal grain size	Weight loss (mg·cm ²)
Heat treatment temperature (°C)														
1125	9.8	9.6	9.2	20.4	10.0	15.6	9.6	73.8	10.0	13.5	9.8	25.2	9.8	311.7
1150	8.8	22.2	9.1	15.6	9.6	17.4	8.9	68.1	8.8	23.7	10.0	42.0	9.4	295.8
1200	8.0	63.9	7.7	44.7	8.7	52.2	7.9	108.3	8.1	80.4	8.9	84.6	8.4	312.6
1225	6.5	101.1	6.1	67.2	6.9	85.8	6.4	125.7	6.3	100.5	7.0	101.4	6.7	303.6
1275	<u>5.0</u>	107.1	<u>5.1</u>	71.1	<u>5.3</u>	99.6	<u>4.9</u>	130.5	<u>5.1</u>	108.3	<u>5.1</u>	104.7	<u>4.5</u>	282.6

[0057] Based on the result, it can be considered as below. Specimens with a crystal grain size number of 6 or more are examples of the invention that satisfy the definition in the invention for the crystal grain size in addition to the chemical composition and specimens with the number of less than 6 are examples of the invention that satisfy the chemical composition but do not satisfy the crystal grain size (grain size numbers are underlined). As shown by the result of the comparative steel of the specimen No. 14, it can be seen that in the steel out of the chemical composition of the invention, weight loss does not change substantially even when the crystal grain size changes but, in the steel of the invention of specimens Nos. 1 to 6, the weight loss tends to be decreased as the crystal grain size number is larger. Further, since any of the steels of the invention of different crystal grain size can decrease the weight loss more than the conventional steel of specimen No. 14, it can be seen that the cyclic oxidation resistance is improved by the addition of Zr and Ce per se and that the property is further improved as the crystal grain size is smaller even when the chemical composition is within a range defined by the invention.

[0058] Referring to the grain size dependence of Nos. 1 to 6 as the steels of the invention, it can be seen that while there is a difference in the property in terms of the absolute value due to the content of Zr and Ce for each of the steel species, the cyclic oxidation resistance is higher when the crystal grain size number is 6 or more compared with the cases of less than 6 in any of the steel species and a remarkable improving effect is obtained, particularly, in the case of the grain size number of 7 or more and, further, 9 or more. That is, the cyclic oxidation resistance can be improved in the steels that satisfy the range of composition of the invention, and the effect can be increased further by controlling the crystal grain size, and excellent cyclic oxidation resistance can be obtained stably.

[0059] While the present invention has been described specifically with reference to the specific embodiments, it will be apparent to those skilled in the art that various modifications or changes can be adopted without departing the gist and the range of the invention.

[0060] The present application is based on Japanese patent application filed on May 11, 2011 (Japanese Patent Application No. 2011-106588), Japanese patent application filed on September 16, 2011 (Japanese Patent Application No. 2011-203604), and Japanese patent application filed on March 5, 2012 (Japanese Patent Application No. 2012-048357), the content of which is incorporated herein for reference.

Industrial Applicability

[0061] The heat-resistant austenitic stainless steel of the invention can be used suitably as the material for heat transfer tubes of boilers, etc.

Claims

1. A heat-resistant austenitic stainless steel having excellent cyclic oxidation resistance, comprising C: 0.05 to 0.2% (mass% for chemical composition here and hereinafter), Si: 0.1 to 1%, Mn: 0.1 to 2.5%, Cu: 1 to 4%, Ni: 7 to 12%, Cr: 16 to 20%, Nb: 0.1 to 0.6%, Zr: 0.05 to 0.4%, Ce: 0.005 to 0.1%, Ti: 0.1 to 0.6%, B: 0.0005 to 0.005%, N: 0.001 to 0.15%, S: 0.005% or less (not including 0%), and P: 0.05% or less (not including 0%) respectively, with the balance of iron and unavoidable impurities.
2. The heat-resistant austenitic stainless steel according to claim 1, comprising at least one of the following elements; Mo: 3% or less (not including 0%), W: 5% or less (not including 0%), Ca: 0.005% or less (not inclusive 0%), and Mg: 0.005% or less (not including 0%).
3. The heat-resistant austenitic stainless steel according to claim 1 or 2, wherein the crystal grain size number of a microstructure is 6 or more and less than 12 in terms of ASTM grain size number.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/062039

A. CLASSIFICATION OF SUBJECT MATTER

C22C38/00 (2006.01) i, C22C38/58 (2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C38/00-38/60

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

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Kokai Jitsuyo Shinan Koho 1971-2012 Toroku Jitsuyo Shinan Koho 1994-2012

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 9-165655 A (NKK Corp.), 24 June 1997 (24.06.1997), entire text; all drawings (Family: none)	1-3
A	JP 9-324246 A (NKK Corp.), 16 December 1997 (16.12.1997), entire text; all drawings (Family: none)	1-3
A	WO 2006/106944 A1 (Sumitomo Metal Industries, Ltd.), 12 October 2006 (12.10.2006), entire text & US 2008/0089803 A1 & EP 1867743 A1 & CA 2603681 A1 & KR 10-2007-0107166 A & CN 101151394 A	1-3

☒ 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
01 August, 2012 (01.08.12)Date of mailing of the international search report
14 August, 2012 (14.08.12)Name and mailing address of the ISA/
Japanese Patent Office

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/062039

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2003-268503 A (Sumitomo Metal Industries, Ltd.), 25 September 2003 (25.09.2003), entire text; all drawings & US 2003/0231976 A1 & EP 1342807 A2 & DE 60306226 T2 & CA 2420796 A1 & CN 1443867 A	1-3

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

REFERENCES CITED IN THE DESCRIPTION

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- JP HEI61994322489 A [0012]
- JP 2011106588 A [0060]
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- *MATERIA*, 2007, vol. 46 (2), 99-101 [0049]