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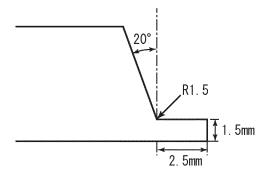
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(54) AUSTENITIC HEAT-RESISTANT ALLOY AND WELDED STRUCTURE

(57) An austenitic heat-resistant alloy is provided that provides good crack resistance and high-temperature strength in a stable manner. The austenitic heat-resistant alloy has a chemical composition of, in mass %: 0.04 to 0.14 % C; 0.05 to 1 % Si; 0.5 to 2.5 % Mn; up to 0.03 % P; less than 0.001 % S; 23 to 32 % Ni; 20 to 25 % Cr; 1 to 5 % W; 0.1 to 0.6 % Nb; 0.1 to 0.6 % V; 0.1 to 0.3 %

N; 0.0005 to 0.01 % B; 0.001 to 0.02 % Sn; up to 0.03 % Al; up to 0.02 % O; 0 to 0.5 % Ti; 0 to 2 % Co; 0 to 4 % Cu; 0 to 4 % Mo; 0 to 0.02 % Ca; 0 to 0.02 % Mg; 0 to 0.2 % REM; and the balance being Fe and impurities, the alloy having a microstructure with a grain size represented by a grain size number in accordance with ASTM E112 of 2.0 or more and less than 7.0.

Fig.1



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Description

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TECHNICAL FIELD

5 [0001] The present invention relates to an austenitic heat-resistant alloy and a welded structure including this alloy.

BACKGROUND ART

[0002] In recent years, worldwide efforts have been made to increase steam temperatures and pressures during the operation of thermal power boilers or the like to reduce loads to the environment. Materials used in superheater tubes or reheater tubes are required to have improved high-temperature strength and corrosion resistance.

[0003] To meet these requirements, various austenitic heat-resistant alloys containing large amounts of nitrogen have been disclosed.

[0004] For example, JP 2004-250783 A proposes an austenitic stainless steel with improved high-temperature strength and corrosion resistance, where the N content is 0.1 to 0.35 % and the Cr content is higher than 22 % and lower than 30 %, and a metallic microstructure is specified.

[0005] JP 2009-084606 A proposes an austenitic stainless steel with improved high-temperature strength and corrosion resistance, where the N content is 0.1 to 0.35 % and the Cr content is higher than 22 % and lower than 30 %, and impurity elements are specified.

[0006] JP 2012-1749 A discloses an austenitic heat-resistant steel with improved high-temperature strength and hot workability containing 0.09 to 0.30 % N and having large amounts of Mo and W in composite addition.

[0007] WO 2009/044796 A1 discloses a high-strength austenitic stainless steel containing 0.03 to 0.35 % N and one or more of Nb, V and Ti.

25 DISCLOSURE OF THE INVENTION

[0008] These austenitic heat-resistant alloys are usually welded for assembly and then used at high temperatures. However, when welded structures using austenitic heat-resistant alloys having high N contents are used at high temperatures for a prolonged period of time, cracks called strain-induced precipitation hardening (SIPH) cracks may occur in weld-heat-affected zones.

[0009] WO 2009/044796 A1discussed above states that limiting the amounts of the elements that cause embrittlement of the grain boundaries and the elements that strengthen the grain interiors to certain ranges prevents cracking that would occur during use for a prolonged period of time. Indeed, these materials prevent cracking under certain conditions. However, in recent years, the use of austenitic heat-resistant alloys with large amounts of W, Mo etc. added thereto to further improve properties such as high-temperature strength has become widespread. For some weld conditions, structure shapes and sizes, for example, these austenitic heat-resistant alloys may not prevent cracking in a stable manner. More specifically, they may not prevent cracking in a stable manner for high welding heat inputs, heavy plate thicknesses or high use temperatures such as above 650°C.

[0010] An object of the present invention is to provide an austenitic heat-resistant alloy that provides good crack resistance and high-temperature strength in a stable manner.

[0011] An austenitic heat-resistant alloy according to an embodiment of the present invention has a chemical composition of, in mass %: 0.04 to 0.14 % C; 0.05 to 1 % Si; 0.5 to 2.5 % Mn; up to 0.03 % P; less than 0.001 % S; 23 to 32 % Ni; 20 to 25 % Cr; 1 to 5 % W; 0.1 to 0.6 % Nb; 0.1 to 0.6 % V; 0.1 to 0.3 % N; 0.0005 to 0.01 % B; 0.001 to 0.02 % Sn; up to 0.03 % Al; up to 0.02 % O; 0 to 0.5 % Ti; 0 to 2 % Co; 0 to 4 % Cu; 0 to 4 % Mo; 0 to 0.02 % Ca; 0 to 0.02 % Mg; 0 to 0.2 % REM; and the balance being Fe and impurities, the alloy having a microstructure with a grain size represented by a grain size number in accordance with ASTM E112 of 2.0 or more and less than 7.0.

[0012] The present invention provides an austenitic heat-resistant alloy that provides good crack resistance and high-temperature strength in a stable manner.

50 BRIEF DESCRIPTION OF THE DRAWINGS

[0013] [FIG. 1] FIG. 1 is a cross-sectional view of a bevel produced for the Examples, showing the shape of the groove thereof.

55 EMBODIMENTS FOR CARRYING OUT THE INVENTION

[0014] The present inventors conducted a detailed investigation to solve the above-discussed problems, and revealed the following findings.

[0015] The inventors thoroughly investigated SIPH cracks occurring, during use, in welded joints using austenitic heat-resistant alloys with high N contents. They found that (1) cracks developed along grain boundaries in weld-heat-affected zones with coarse grains near the fusion lines, and (2) clear concentrating of S was detected on the fractured surfaces of cracks. They further found that (3) large amounts of nitrides and carbonitrides had precipitated within grains near the cracks. This was particularly significant for high Nb contents. In addition, they found that (4) the larger the initial grain size of the used austenitic heat-resistant alloy, the larger the grain size in weld-heat-affected zones became and the more likely cracking occurred.

[0016] From these finding, they assumed that SIPH cracks occurred because large amounts of nitrides and carbonitrides precipitate within grains during use at high temperatures and thus the grain interiors become less likely to be deformed, which leads to concentration of creep deformations on grain boundaries and finally to openings. S segregates on grain boundaries during welding or during use and thereby decreases the bonding force of the grain boundaries. Further, the larger the grain size, the smaller the area of grain boundaries per unit volume. Grain boundaries work as sites for producing nuclei for nitride and carbonitride particles. Thus, the smaller the grain boundaries, the larger the amounts of nitrides and carbonitrides that precipitate within grains. In addition, creep deformations that are caused by external forces applied during use, for example welding residual stress, are the more likely to be concentrated on certain grain boundaries. Thus, the inventors concluded that the larger the initial grain size of the base material, the more likely cracking occurs. Particularly, they concluded that, at high temperatures above 650 °C, precipitates precipitate in short periods of time and, in addition, grain-boundary segregation occurs at early stages, making the problems more apparent. [0017] To prevent such cracking, it is effective to reduce elements that increase the deformation resistance within the grains by using precipitation strengthening or solute strengthening. However, these elements are indispensable to provide sufficient creep strength at high temperatures. Thus, the prevention of cracks and the provision of sufficient creep strength at high temperatures are tradeoffs and are difficult to achieve at the same time.

[0018] After extended research, the inventors revealed that, in order to prevent SIPH cracking in an austenitic heat-resistant alloy containing 0.04 to 0.14 % C, 0.05 to 1 % Si, 0.5 to 2.5 % Mn, up to 0.03 % P, 23 to 32 % Ni, 20 to 25 % Cr, 1 to 5 % W, 0.1 to 0.3 % N, 0.0005 to 0.01 % B, up to 0.03 % Al, and up to 0.02 % O, it is effective to exactly control the Nb and S contents to be in the range of 0.1 to 0.6 % and below 0.001 %, respectively, and to have an initial grain size of the base material represented by a grain size number as defined by the American Society for Testing and Material (ASTM) of 2.0 or more. However, if the grain size is finer than necessary and the Nb content is limited, the creep strength of the base material does not reach a specified value. Thus, the inventors found that the grain size as represented by grain size number needs to be less than 7.0. In addition, they revealed that V, which has a lower precipitation strengthening property than Nb, in a content of 0.1 to 0.6 % is necessary to achieve a predetermined creep strength without impairing SIPH crack resistance.

[0019] While the inventors determined that these steps indeed prevent SIPH cracking, they found out during the research that another problem may arise.

[0020] As discussed above, austenitic heat-resistant alloys are generally welded for assembly. When they are welded, a filler material is usually used. However, for small parts with thin wall thicknesses, or even for components with heavy wall thickness for root running or tack welding, gas shield-arc welding may be performed without using a filler material. If the penetration depth is insufficient at this time, unwelded abutting surfaces remain as weld defects, and the strength required of a welded joint cannot be obtained. While S reduces SIPH crack resistance, S has the effect of increasing the penetration depth. Thus, the inventors found that the problem of insufficient penetration depth tends to be apparent if the S content is exactly controlled to be below 0.001 % to address the issue of SIPH crack resistance.

[0021] To prevent insufficient penetration depth, welding heat input may be simply increased. However, increasing welding heat input brings about grains coarsening in weld-heat-affected zones, and the inventors failed to prevent SIPH cracking even when the initial grain size of the base material had a grain size number of 2.0 or more.

[0022] After further research, the inventors found that, in order to prevent insufficient penetration depth in a stable manner, it is effective to have an Sn content in the range of 0.001 to 0.02 %. They concluded that this is because Sn can easily evaporate from the surface of the molten pool during welding and ionize in the arc to contribute to the formation of an electrifying path, thereby increasing the current density of the arc.

[0023] The present invention was made based on the above-discussed findings. An austenitic heat-resistant alloy according to an embodiment of the present invention will now be described in detail.

[Chemical Composition]

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[0024] The austenitic heat-resistant alloy according to the present embodiment has the chemical composition described below. In the following description, "%" in the content of an element means mass percent.

C: 0.04 to 0.14%

[0025] Carbon (C) stabilizes the austenite microstructure and forms fine carbide particles to improve creep strength during use at high temperatures. 0.04 % or more C needs to be contained in order that these effects are sufficiently present. However, if an excess amount of C is contained, large amounts of carbides precipitate, which reduces SIPH crack resistance. In view of this, the upper limit should be 0.14 %. The lower limit of C content is preferably 0.05 %, and more preferably 0.06 %. The upper limit of C content is preferably 0.13 %, and more preferably 0.12 %.

Si: 0.05 to 1 %

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[0026] Silicon (Si) has a deoxidizing effect, and is effective in improving the corrosion resistance and oxidation resistance at high temperatures. 0.05 % or more Si needs to be contained in order that these effects are sufficiently present. However, if an excess amount of Si is contained, the stability of the microstructure decreases, which decreases toughness and creep strength. In view of this, the upper limit should be 1 %. The lower limit of Si content is preferably 0.08 %, and more preferably 0.1 %. The upper limit of Si content is preferably 0.6 %, and more preferably 0.5 %.

Mn: 0.5 to 2.5 %

[0027] Similar to Si, manganese (Mn) has a deoxidizing effect. Mn also contributes to the stabilization of austenite microstructure. 0.5 % or more Mn needs to be contained in order that these effects are sufficiently present. However, if an excess amount of Mn is contained, this causes embrittlement of the alloy, and creep ductility decreases. In view of this, the upper limit should be 2.5 %. The lower limit of Mn content is preferably 0.6 %, and more preferably 0.7 %. The upper limit of Mn content is preferably 2 %, and more preferably 1.5 %.

P: up to 0.03 %

[0028] Phosphorus (P) is contained in the alloy in the form of an impurity, and, during welding, segregates on grain boundaries in weld-heat-affected zones, thereby increasing liquation cracking susceptibility. P also decreases creep ductility after use for a prolonged period of time. In view of this, an upper limit should be set for P content, which should be 0.03 % or lower. The upper limit of P content is preferably 0.028 %, and more preferably 0.025 %. It is preferable to minimize P content; however, reducing it excessively causes increased steel-manufacturing cost. In view of this, the lower limit of P content is preferably 0.0005 %, and more preferably 0.0008 %.

S: less than 0.001 %

[0029] Similar to P, sulfur (S) is contained in the alloy in the form of an impurity, and, during welding, segregates on grain boundaries in weld-heat-affected zones, thereby increasing liquation cracking susceptibility. S also segregates on grain boundaries during use for a prolonged period of time and causes embrittlement, which significantly reduces SIPH crack resistance. To prevent these effects within the limits of the chemical composition of the present embodiment, the S content needs to be less than 0.001 %. The upper limit of S content is preferably 0.0008 %, and more preferably 0.0005 %. It is preferable to minimize S content; however, reducing it excessively causes increased steel-manufacturing cost. In view of this, the lower limit of S content is preferably 0.0001 %, and more preferably 0.0002 %.

Ni: 23 to 32 %

[0030] Nickel (Ni) is an element indispensable for providing sufficient stability of the austenite phase during use for a prolonged period of time. 23 % or more Ni needs to be contained in order that this effect is sufficiently present within the limits of Cr and W contents of the present embodiment. However, Ni is an expensive element, and large amounts of Ni contained mean increased costs. In view of this, the upper limit should be 32 %. The lower limit of Ni content is preferably 25 %, and more preferably 25.5 %. The upper limit of Ni content is preferably 31.5 %, and more preferably 31 %.

Cr: 20 to 25 %

[0031] Chromium (Cr) is an element indispensable for providing sufficient oxidation resistance and corrosion resistance at high temperatures. Cr also forms fine carbide particles to contribute to the provision of sufficient creep strength, too. 20 % or more Cr needs to be contained in order that these effects are sufficiently present within the limits of Ni content of the present embodiment. However, if an excessive amount of Cr is contained, the microstructure stability of the austenite phase at high temperatures deteriorates, which decreases creep strength. In view of this, the upper limit should

be 25 %. The lower limit of Cr content is preferably 20.5 %, and more preferably 21 %. The upper limit of Cr content is preferably 24.5 %, and more preferably 24 %.

W: 1 to 5 %

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[0032] Tungsten (W) dissolves in the matrix, or forms fine intermetallic compounds to significantly contribute to the improvement of creep strength and tensile strength at high temperatures. 1 % or more W needs to be contained in order that these effects are sufficiently present. However, if an excess amount of W is contained, the deformation resistance with grains becomes high and SIPH crack resistance reduces, and creep strength may decrease. Further, W is an expensive element, and large amounts of W contained mean increased costs. In view of this, the upper limit should be 5 %. The lower limit of W content is preferably 1.2 %, and more preferably 1.5 %. The upper limit of W content is preferably 4.5 %, and more preferably 4 %.

Nb: 0.1 to 0.6 %

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[0033] Niobium (Nb) precipitates in the form of fine MX carbonitride particles, and, in addition, precipitates in the form of Z phase (CrNbN) within grains to significantly contribute to the improvement of creep strength and tensile strength at high temperatures. 0.1 % or more Nb needs to be contained in order that these effects are sufficiently present. However, if an excess amount of Nb is contained, the strengthening property of these precipitates is too high, which reduces SIPH crack resistance and causes a decrease in creep ductility and toughness. In view of this, the upper limit should be 0.6 %. The lower limit of Nb content is preferably 0.12 %, and more preferably 0.15 %. The upper limit of Nb content is preferably 0.55 %, and more preferably 0.5 %.

V: 0.1 to 0.6 %

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[0034] Vanadium (V) precipitates in the form of fine MX carbonitride particles within the grains to contribute to the improvement of creep strength and tensile strength at high temperatures. 0.1 % or more V needs to be contained in order that these effects are sufficiently present. However, if an excess amount of V is contained, large amounts of carbonitrides precipitate, which reduces SIPH crack resistance and causes a decrease in creep ductility and toughness. In view of this, the upper limit should be 0.6 %. The lower limit of V content is preferably 0.12 %, and more preferably 0.15 %. The upper limit of V content is preferably 0.55 %, and more preferably 0.5 %.

N: 0.1 to 0.3 %

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[0035] Nitrogen (N) stabilizes the austenite microstructure, and dissolves in the matrix or precipitates in the form of nitrides to contribute to the improvement of high-temperature strength. 0.1 % or more N needs to be contained in order that these effects are sufficiently present. However, if an excessive amount of N is contained, it dissolves during use for a short period of time, or large amounts of fine nitride particles precipitate within grains during use for a prolonged period of time, thereby increasing the deformation resistance within grains, which reduces SIPH crack resistance. Further, creep ductility and toughness decrease. In view of this, the upper limit should be 0.3 %. The lower limit of N content is preferably 0.12 %, and more preferably 0.14 %. The upper limit of N content is preferably 0.28 %, and more preferably 0.26 %.

B: 0.0005 to 0.01 %

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[0036] Boron (B) provides fine dispersed grain-boundary carbide particles to improve creep strength, and segregates on grain boundaries to strengthen grain boundaries. 0.0005 % or more B needs to be contained in order that these effects are sufficiently present. However, if an excess amount of B is contained, the weld thermal cycle during welding causes a large amount of B to segregate in weld heat affected zones near melt boundaries to decrease the melting point of grain boundaries, thereby increasing liquation cracking susceptibility. In view of this, the upper limit should be 0.01 %. The lower limit of B content is preferably 0.0008 %, and more preferably 0.001 %. The upper limit of B content is preferably 0.008 %, and more preferably 0.006 %.

Sn: 0.001 to 0.02 %

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[0037] Tin (Sn) has the effect of increasing the penetration depth during welding by evaporating from the molten pool to increase the current density of the arc. 0.001 % or more Sn needs to be contained in order that these effects are sufficiently present. However, if an excess amount of Sn is contained, the liquation cracking susceptibility in weld-heat-

affected zones during welding and the SIPH crack susceptibility during use become high. In view of this, the upper limit should be 0.02 %. The lower limit of Sn content is preferably 0.0015 %, and more preferably 0.002 %. The upper limit of Sn content is preferably 0.018 %, and more preferably 0.015 %.

⁵ Al: up to 0.03 %

[0038] Aluminum (AI) has a deoxidizing effect. However, if an excess amount of AI is contained, the cleanliness of the alloy deteriorates, which decreases hot workability. In view of this, the upper limit should be 0.03 %. The upper limit of AI content is preferably 0.025 %, and more preferably 0.02 %. No lower limit needs to be set; still, it should be noted that decreasing AI excessively causes an increase in steel-manufacturing cost.

In view of this, the lower limit of AI content is preferably 0.0005 %, and more preferably 0.001 %. AI as used herein means acid-soluble AI (sol. AI).

O: up to 0.02 %

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[0039] Oxygen (O) is contained in the alloy in the form of an impurity, and has the effect of increasing the penetration depth during welding. However, if an excess amount of O is contained, hot workability decreases and toughness and ductility deteriorate. In view of this, the upper limit should be 0.02 %. The upper limit of O content is preferably 0.018 %, and more preferably 0.015 %. No lower limit needs to be set; still, it should be noted that decreasing O excessively causes an increase in steel-manufacturing cost. In view of this, the lower limit of O content is preferably 0.0005 %, and more preferably 0.0008 %.

[0040] The balance of the chemical composition of the austenitic heat-resistant alloy in the present embodiment is Fe and impurities. Impurity as used herein means an element originating from ore or scrap used as raw material for the heat-resistant alloy being manufactured on an industrial basis or an element that has entered from the environment or the like during the manufacturing process.

[0041] In the chemical composition of the austenitic heat-resistant alloy in the present embodiment, some of the Fe may be replaced by one or more elements selected from one of the first to third groups provided below. All of the elements listed below are optional elements. That is, none of the elements listed below may be contained in the austenitic heat-resistant alloy of the present embodiment. Or, only one or some of them may be contained.

[0042] More specifically, for example, only one group may be selected from among the first to third groups and one or more elements may be selected from this group. In this case, it is not necessary to select all the elements belonging to the selected group. Further, a plurality of groups may be selected from among the first to third groups and one or more elements may be selected from each of these groups. Again, it is not necessary to select all the elements belonging to the selected groups.

First Group-Ti: 0 to 0.5 %

[0043] The element belonging to the first group is Ti. Ti improves the creep strength of the alloy through precipitation strengthening.

Ti: 0 to 0.5 %

[0044] Similar to Nb and V, Titanium (Ti) combines with carbon or nitrogen to form fine carbide or carbonitride particles, thereby contributing to the improvement of creep strength. These effects are present if a small amount of Ti is contained. On the other hand, if an excess amount of Ti is contained, large amounts of precipitates are produced, which reduces SIPH resistance and creep ductility. In view of this, the upper limit should be 0.5 %. The lower limit of Ti content is preferably 0.01 %, and more preferably 0.03 %. The upper limit of Ti content is preferably 0.45 %, and more preferably 0.4 %.

50 Second Group-Co: 0 to 2 %, Cu: 0 to 4 %, Mo: 0 to 4 %

[0045] The elements belonging to the second group are Co, Cu, and Mo. These elements improve the creep strength of the alloy.

55 Co: 0 to 2 %

[0046] Similar to Ni, cobalt (Co) is an austenite-forming element, and increases the stability of the austenite microstructure to contribute to the improvement of creep strength. These effects are present if a small amount of Co is

contained. However, Co is a very expensive element, and large amounts of Co contained mean increased costs. In view of this, the upper limit should be 2 %. The lower limit of Co content is preferably 0.01 %, and more preferably 0.03 %. The upper limit of Co content is preferably 1.8 %, and more preferably 1.5 %.

⁵ Cu: 0 to 4 %

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[0047] Similar to Ni and Co, copper (Cu) stabilizes the austenite microstructure, and precipitates in the form of fine particles during use to contribute to the improvement of creep strength. These effects are present if a small amount of Cu is contained. On the other hand, if an excessive amount of Cu is contained, this causes a decrease in hot workability. In view of this, the upper limit should be 4 %. The lower limit of Cu content is preferably 0.01 %, and more preferably 0.03 %. The upper limit of Cu content is preferably 3.8 %, and more preferably 3.5 %.

Mo: 0 to 4 %

[0048] Similar to W, molybdenum (Mo) dissolves in the matrix and contributes to the improvement of creep strength and tensile strength at high temperatures. These effects are present if a small amount of Mo is contained. On the other hand, if an excessive amount of Mo is contained, the deformation resistance within grains becomes high and SIPH crack resistance reduces, and creep strength may decrease. Further, Mo is an expensive element, and large amounts of Mo contained mean increased costs. In view of this, the upper limit should be 4 %. The lower limit of Mo content is preferably 0.01 %, and more preferably 0.03 %. The upper limit of Mo content is preferably 3.8 %, and more preferably 3.5 %.

Third Group-Ca: 0 to 0.02 %, Mg: 0 to 0.02 %, REM: 0 to 0.2 %

[0049] The elements belonging to the third group are Ca, Mg and REM. These elements improve hot workability of the alloy.

Ca: 0 to 0.02 %

[0050] Calcium (Ca) improves hot workability during manufacture. This effect is present if a small amount of Ca is contained. On the other hand, if an excessive amount of Ca is contained, it combines with oxygen to significantly decrease the cleanliness of the alloy, which decreases hot workability. In view of this, the upper limit should be 0.02 %. The lower limit of Ca content is preferably 0.0005 %, and more preferably 0.001 %. The upper limit of Ca content is preferably 0.01 %, and more preferably 0.005 %.

35 Mg: 0 to 0.02 %

[0051] Similar to Ca, magnesium (Mg) improves hot workability during manufacture. This effect is present if a small amount of Mg is contained. On the other hand, if an excess amount of Mg is contained, it combines with oxygen to significantly decrease the cleanliness of the alloy, which decreases hot workability. In view of this, the upper limit is 0.02 %. The lower limit of Mg content is preferably 0.005 %, and more preferably 0.001 %. The upper limit of Mg content is preferably 0.01 %, and more preferably 0.005 %.

REM: 0 to 0.2 %

- [0052] Similar to Ca and Mg, rare-earth metals (REMs) improve hot workability during manufacture. This effect is present if a small amount of REM is contained. On the other hand, if an excessive amount of REM is contained, it combines with oxygen to significantly decrease the cleanliness of the alloy, which decreases hot workability. In view of this, the upper limit should be 0.2 %. The lower limit of REM content is preferably 0.0005 %, and more preferably 0.001 %. The upper limit of REM content is preferably 0.15 %, and more preferably 0.1 %.
 - [0053] "REM" is a collective term for a total of 17 elements, i.e. Sc, Y and the lanthanoids, and "REM content" means the total content of one or more REM elements. REMs are usually contained in mischmetal. Thus, for example, mischmetal may be added to the alloy such that the REM content is in the above-indicated range.

[0054] Particularly, Nd has a strong affinity for S and P, and has the effect of reducing weld liquation cracking susceptibility by forming sulfides or phosphides, and thus it is more preferable to utilize Nd.

[Microstructure]

[0055] Grain Size Number: 2.0 or more and less than 7.0

[0056] The austenitic heat-resistant alloy according to the present embodiment has a microstructure having a grain size represented by a grain size number in accordance with ASTM E112 of 2.0 or more and less than 7.0.

[0057] In order to give sufficient SIPH crack resistance to the weld-heat-affected zones of a welded structure using the austenitic heat-resistant alloy of the present embodiment, the grains of the microstructure before welding need to be fine grains, i.e. their size as represented by grain size number in accordance with ASTM E112 needs to be 2.0 or more, in order to prevent the grains in the weld-heat-affected zones from becoming excessively coarse even after being affected by the heat cycle from the welding. On the other hand, if the grains are so fine as to have a grain size number of 7.0 or more, the required creep strength is not obtained. In view of this, the grain size number should be 2.0 or more and less than 7.0.

[0058] The microstructure having the above-specified grain size can be provided by performing a heat treatment on the alloy with the above-specified chemical composition under appropriate conditions. This microstructure may be achieved by, for example, shaping the alloy of the above-specified chemical composition into a predetermined shape by hot working or cold working before performing a solution heat treatment in which it is held at temperatures of 900 to 1250 °C for 3 to 60 minutes before water cooling. The higher the holding temperature of the solution heat treatment and the longer the holding time, the larger the grain size becomes (i.e. the smaller the grain size number becomes). More preferably, the solution heat treatment involves holding the alloy at temperatures of 1120 to 1220 °C for 3 to 45 minutes before water cooling, and yet more preferably holding the alloy at temperatures of 1140 to 1210 °C for 3 to 30 minutes before water cooling.

[0059] The austenitic heat-resistant alloy according to an embodiment of the present invention has been described. The present embodiment provides an austenitic heat-resistant alloy providing good crack resistance and high-temperature strength in a stable manner.

EXAMPLES

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²⁵ **[0060]** The present invention will be described in more detail below using examples. The present invention is not limited to these examples.

[0061] The materials labeled A to J having the chemical compositions shown in Table 1 were melted in a laboratory and ingots were cast, which were subjected to hot forging and hot rolling in the temperature range of 1000 to 1150 °C to provide plates with a thickness of 20 mm. These plates were further subjected to cold rolling to the thickness of 16 mm. The plates were subjected to a solution heat treatment in which they were held at 1200 °C for a predetermined period of time before water cooling. After the solution heat treatment, they were machined to plates with a thickness of 14 mm, a width of 50 mm and a length of 100 mm. From other plates subjected to the solution heat treatment, samples to be used for microstructure observation were taken and the grain size of the microstructure of each sample was measured in accordance with ASTM E 112. From material A, materials with different grain sizes were produced by changing the holding time of the solution heat treatment in the range of 3 to 30 minutes.

[Table 1]

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[0062]

TABLE 1

()						Ö	nemical	comp	osition ((in mass	%, balaı	Chemical composition (in mass %, balance being Fe and impurities)	Fe and i	mpurities		
<u> </u>	ပ	Si	Mn	۵	S	Z	Ö	>	g Q	>	z	В	A	0	Sn	Other
4	60.0	0.28	0.98	0.017	0.0008	30.2	21.8	3.3	0.25	0.21	0.197	0.0023	0.005	0.009	0.004	
В	0.08	0.32	1.02	0.008	9000'0	28.5	22.0	3.0	0.23	0.22	0.206	0.0017	900'0	0.008	0.012	Nd: 0.023
၁	0.10	0.25	1.10	0.016	9000'0	27.1	21.7	2.7	0.18	0.19	0.174	0.0018	0.005	600.0	0.001	Ti: 0.12, Ca: 0.002, Cu: 0.41, Mo: 0.03
۵	0.07	0.34	1.18	0.014	0.0004	30.6	22.3	2.9	0.21	0.19	0.185	0.0026	0.004	0.010	0.016	Nd: 0015 Co: 0.08, Mg; 0.001
Ш	0.07	0.29	0.82	0.017	0.0002	29.8	22.4	2.8	0.22	0.21	0.211	0.0024	0.012	0.004	*	
Ш	0.11	0.29	96'0	0.021	0.0021 *	30.5	21.9	3.1	0.38	0.31	0.198	0.0015	0.007	0.008	*	Ti: 0.18
g	60.0	0.30	86.0	0.023	0.0003	30.3	22.0	2.7	0.42	0.29	0.215	0.0044	0.003	0.009	0.033 *	Nd: 0.010
I	0.08	0.25	96'0	0.015	8000'0	22.4 *	24.6	2.5	0.45	0.21	0.221	0.0024	0.004	0.010	0.010	
_	0.08	0.25	1.04	0.015	2000'0	30.9	22.0	3.1	0.24	0.20	0.188	0.0019	0.004	0.008	0.003	REM: 0.018
ſ	0.07	0.26	0.85	0.015	9000'0	25.6	24.5	2.2	0.16	* 80.0	0.165	0.0018	0.006	0.009	0.004	
* indica	tes that	t the va	lue is o	utisde th	* indicates that the value is outisde the range specified by	ecified by	y the pro	esent i	the present invention.	'n.						

[Weldability]

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[0063] The groove shown in FIG. 1 was provided along the longitudinal direction of each plate produced as described above. With grooved plates abutting each other, two joints for each mark were subjected to butt welding using gastungsten arc welding to produce welded joints. The welding did not use filler material, and the amount of heat input was 5 k.l/cm

[0064] Those of the obtained welded joints that had back beads with a width of 2 mm or more across the entire length of the weld line for both joint parts were determined to have good weldability in fabrication and thus to have "passed" the test. Those that had a portion for either joint part in which no back bead was present were determined to have poor weldability in fabrication and thus to be "unacceptable".

[Weld Crack Resistance]

[0065] Each of the above-described welded joints, with only a first welded layer (i.e. root running), was placed on a commercial steel plate equivalent to the SM400B plate specified by JIS G 3106 (2008) (with a thickness of 30 mm, a width of 200 mm and a length of 200 mm), and restraint welding was performed on the four sides using a covered arc welding rod ENi 6625 specified by JIS Z 3224 (2010). Thereafter, a tig wire equivalent to the SNi 6625 wire specified by JIS Z 3334 (2011) was used to perform a multi-layer welding in the groove by TIG welding with a heat input of 10 to 15 kJ/cm, thereby producing welded joints, two for each mark.

[0066] Aging was performed on one of the welded-joint parts for each mark at 700 °C for 500 hours. Samples were taken from five points on each of the as-welded joints and welded joints after aging, with the observation surface represented by a transverse cross section of the joint (i.e. cross section perpendicular to the weld bead). Mirror polishing and etching were performed on these samples before inspection by optical microscopy to determine whether cracks were present in the weld-heat-affected zones. Welded joints where no cracks were found in any of the five samples were determined to be "good" and those where cracks were found in one sample were determined to be "acceptable", thus to have passed the test. Those welded joints where cracks were found in two or more samples were determined to be "unacceptable".

[Creep-Rupture Strength]

[0067] From those as-welded joints that have passed the weld crack resistance test, round-bar creep-rupture test specimens were taken such that the center of the parallel portion was made of welded metal. Creep-rupture testing was conducted at 700 °C and under 167 MPa, conditions that result in a target fracture time for the base material of about 1000 hours. The base material was fractured, and those joints where the fracture time was 90 % or more of the fracture time of the base material (i.e. 900 hours or longer) were determined to have "passed" the test.

[Performance Evaluation Results]

[0068] The performance evaluation results are shown in Table 2. Table 2 also shows the grain size number of the austenitic heat-resistant alloy for each mark.

[0069] [Table 2]

TARLE 2

		IA	BLE 2		
Mark	Grain size number	Weldability in Fabrication	Weld	crack	Creep-rupture test result
IVIAIK	Grain size number	Weldability in Fabrication	as-welded	aged	Creep-rupture test result
A-1	2.3	passed	good	good	passed
A-2	3.7	passed	good	good	passed
A-3	5.4	passed	good	good	passed
A-4	6.8	passed	good	good	passed
A-5	1.7 *	passed	acceptable	unacceptable	not tested
A-6	7.5 *	passed	good	good	not passed
В	3.5	passed	good	good	passed
С	3.4	passed	good	good	passed

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(continued)

Mark	Grain size number	Weldability in Fabrication	Weld	crack	Creep-rupture test result
IVIAIK	Grain size number	Weldability III Fabrication	as-welded	aged	Creep-rupture test result
D	3.6	passed	acceptable	acceptable	passed
Е	3.1	unacceptable	good	good	passed
F	3.6	passed	acceptable	unacceptable	not tested
G	3.4	passed	unacceptable	unacceptable	not tested
Н	3.8	passed	good	good	not passed
I	3.5	passed	good	good	passed
J	3.2	passed	good	good	not passed
* indica	ates that the value is	outisde the range specified b	y the present inv	rention.	

[0070] Each of the welded joints using the austenitic heat-resistant alloys with Marks A-1 to A-4, B to D and I as the base material had an appropriate chemical composition, where the initial grain size of the base material had a grain size of 2.0 or more and less than 7.0. Each of these welded joints had a back bead across the entire length after root running, and had good weldability in fabrication. Further, though the thickness of the base material was 14 mm, which is relatively large, no cracks were produced in weld-heat-affected zones even after aging, meaning good crack resistance. Further, the creep-rupture strength at high temperatures was sufficient.

[0071] In the welded joint using the austenite heat-resistant alloy with Mark A-5 as the base material, cracks that are believed to be SIPH cracks were produced after aging. This is presumably because the grain size of the austenitic heat-resistant alloy with Mark A-5 was too large.

[0072] The welded joint using the austenitic heat-resistant alloy with Mark A-6 as the base material had good crack resistance, but the creep-rupture time was below the target. This is presumably because the grain size of the austenitic heat-resistant alloy with Mark A-6 was too small.

[0073] In the welded joint using the austenitic heat-resistant alloy with Mark E as the base material, no back bead was present in some portions after root running. This is presumably because the Sn content of the austenitic heat-resistant alloy with Mark E was too low.

[0074] The welded joint using the austenitic heat-resistant alloy with Mark F as the base material contained no Sn but a large amount of S such that a sufficient back bead was produced. However, cracks that are believed to be SIPH cracks were produced after aging.

[0075] In the welded joint using the austenitic heat-resistant alloy with Mark G as the base material, directly after welding and after aging, cracks that are believed to be liquation cracks and SIPH cracks, respectively, were produced. This is presumably because the Sn content of the austenitic heat-resistant alloy with Mark G was too high.

[0076] In the welded joint using the austenitic heat-resistant alloy with Mark H as the base material, the weldability in fabrication and weld crack resistance were good but the required creep strength was not satisfied. This is presumably because the Ni content of the austenitic heat-resistant alloy with Mark H was too low, impairing phase stability.

[0077] In the welded joint using the austenitic heat-resistant alloy with Mark J as the base material, too, the required creep strength was not satisfied. This is presumably because the amount of V contained in the austenitic heat-resistant alloy with Mark J was lower than the lower limit.

INDUSTRIAL APPLICABILITY

[0078] The present invention can be suitably used as an austenitic heat-resistant alloy used as a high-temperature part such as a main steam tube or high-temperature reheating steam tube in a thermal power boiler.

Claims

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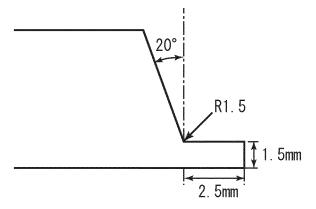
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1. An austenitic heat-resistant alloy having a chemical composition of, in mass %:

0.04 to 0.14 % C; 0.05 to 1 % Si;

		0.5 to 2.5 % Mn;
		up to 0.03 % P;
		less than 0.001 % S;
		23 to 32 % Ni;
5		20 to 25 % Cr;
		1 to 5 % W;
		0.1 to 0.6 % Nb;
		0.1 to 0.6 % V;
		0.1 to 0.3 % N;
10		0.0005 to 0.01 % B;
		0.001 to 0.02 % Sn;
		up to 0.03 % AI;
		up to 0.02 % O;
		0 to 0.5 % Ti;
15		0 to 2 % Co;
		0 to 4 % Cu;
		0 to 4 % Mo;
		0 to 0.02 % Ca;
		0 to 0.02 % Mg;
20		0 to 0.2 % REM; and
		the balance being Fe and impurities,
		the alloy having a microstructure with a grain size represented by a grain size number in accordance with ASTM
		E112 of 2.0 or more and less than 7.0.
25	2	The quetonitie heat resistant allow according to plain 1, wherein the chemical composition contains one or more
20	2.	The austenitic heat-resistant alloy according to claim 1, wherein the chemical composition contains one or more elements selected from one of the first to third groups provided below, in mass %:
		elements selected from one of the first to third groups provided below, in mass %.
		first group: 0.01 to 0.5 % Ti;
		second group: 0.01 to 2 % Co, 0.01 to 4 % Cu, and 0.01 to 4 % Mo; and
30		third group: 0.0005 to 0.02 % Ca; 0.0005 to 0.02 % Mg; and 0.0005 to 0.2 % REM.
	3.	A welded structure including the austenitic heat-resistant alloy according to claim 1 or 2.
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Fig.1



INTERNATIONAL SEARCH REPORT International application No. PCT/JP2016/066458 CLASSIFICATION OF SUBJECT MATTER C22C38/00(2006.01)i, C22C38/58(2006.01)i 5 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) 10 C22C38/00-38/60, C21D8/00-8/10 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2016 15 1971-2016 Toroku Jitsuyo Shinan Koho Kokai Jitsuyo Shinan Koho 1994-2016 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) 20 C. DOCUMENTS CONSIDERED TO BE RELEVANT Category* Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. JP 2014-047409 A (Nippon Steel & Sumitomo Α 1 - 3Metal Corp.), 17 March 2014 (17.03.2014), 25 (Family: none) Α JP 2006-307313 A (Sumitomo Metal Industries, 1-3 Ltd.), 09 November 2006 (09.11.2006), & US 2006/0057414 A1 & EP 1637785 A1 30 JP 2004-250783 A (Sumitomo Metal Industries, Α 1 - 309 September 2004 (09.09.2004), 35 X Further documents are listed in the continuation of Box C. See patent family annex. 40 Special categories of cited documents: later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "A" document defining the general state of the art which is not considered to "E" earlier application or patent but published on or after the international filing document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "L" document which may throw doubts on priority claim(s) or which is 45 cited to establish the publication date of another citation or other document of particular relevance; the claimed invention cannot be special reason (as specified) considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "O" document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 50 08 August 2016 (08.08.16) 16 August 2016 (16.08.16) Name and mailing address of the ISA/ Authorized officer Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, 55 Tokyo 100-8915, Japan Telephone No. Form PCT/ISA/210 (second sheet) (January 2015)

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5		. DOCUMENTS CONSIDERED TO BE RELEVANT		
	Category*	Citation of document, with indication, where appropriate, of the releva		Relevant to claim No.
10	A	<pre>JP 5-195127 A (Sumitomo Metal Industries Ltd.), 03 August 1993 (03.08.1993), & US 5378427 A</pre>	~, 	1-3
15	A	WO 2012/176586 A1 (Nippon Steel & Sumiton Metal Corp.), 27 December 2012 (27.12.2012), & US 2014/0127073 A1 & EP 2725112 A1	omo	1-3
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55		0 (continuation of second shoot) (January 2015)		

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Patent documents cited in the description

- JP 2004250783 A [0004]
- JP 2009084606 A **[0005]**

- JP 2012001749 A **[0006]**
- WO 2009044796 A1 [0007] [0009]