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(54) AUSTENITIC FE-NI-CR ALLOY HAVING EXCELLENT OXIDATION RESISTANCE AND METHOD FOR PRODUCING SAME

(57) An austenitic Fe-Ni-Cr alloy having superior oxidation resistance even under extreme high temperatures, the alloy consists of, in mass%: C: 0.004 to 0.13%, Si: 0.15 to 1.0%, Mn: 0.03 to 2.0%, P: ≤ 0.040%, S: ≤ 0.003%, Ni: 20.0 to 38.0%, Cr: 18.0 to 28.0%, Mo: ≤ 1.0%, Cu: ≤ 1.0%, N: ≤ 0.03%, B: ≤ 0.01%, Al: 0.10 to 1.0%, at least one of Ti: 0.10 to 1.0% and Zr: 0.01 to 0.6%, O: 0.0002 to 0.0030%, Ca: ≤ 0.002%, total weight of one or more kinds selected from La, Ce, and Y being rare earth metal elements (REMs): 0.001 to 0.010%, Fe as a remainder and inevitable impurities, and wherein the chemical composition satisfies the following formulae (1) and (2).

$$85 \geq 0.3\mathrm{x}Si + 1.5\mathrm{x}Ni + 1.3\mathrm{x}Cr + 5.8\mathrm{x}Al + 7.7\mathrm{x}Zr + 2.7\mathrm{x}Ti + 2173\mathrm{x}REM - 3582\mathrm{x}S - 32.9\mathrm{x}Mo - 2448\mathrm{x}B \geq 47 \quad (1)$$

$$40 \geq 0.6\mathrm{x}Si + 1.3\mathrm{x}Cr + 23.53\mathrm{x}Al + 5.88\ \mathrm{x}Ti + 3074\mathrm{x}REM - 5067\mathrm{x}S - 0.8\mathrm{x}Mn - 816\mathrm{x}N \geq 0 \quad (2)$$

and
each of element symbols in the formulae indicates content of the each element (mass%).

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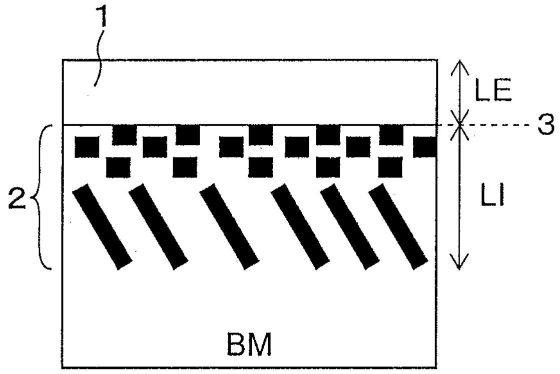
Fig. 1



Description

Technical Field

[0001] The present invention relates to austenitic Fe-Ni-Cr alloy, and relates to austenitic Fe-Ni-Cr alloy having superior oxidation resistance in high temperature environments.

Background Art

[0002] Since thermal power generating boilers, chemical plants, and reacting furnaces for purifying polysilicon are used under severe high temperature conditions at 700 to 900 °C, materials to be used should be superior in high temperature strength, high temperature corrosion resistance, and oxidation resistance. In particular, as one of the necessary properties regarding oxidation resistance, following properties can be mentioned in which surface protective oxidation scale which mainly contains Cr_2O_3 and which is formed on the material surface in such a high temperature environment is dense, and fit of the scale with respect to the material is high. As material used in an apparatus or the like used in such high temperature environments, Fe-Cr-Ni alloys are focused on. Among these alloys, since 18-8 stainless steels such as SUS304, SUS316 and SUS347 do not have sufficient properties in the above-mentioned use environment, SUS310S, NCF800 and the like in which content of Ni and Cr are increased are generally used.

[0003] As a technique to improve properties of materials used in such severe high temperature environments, for example, Patent Document 1 proposes austenitic stainless steel plate in which trace amounts of REMs (Rare Earth Metals) are added to stainless steel, and an upper limit of Mn content is defined according to Ni content and REM content so that rate of growth of Cr_2O_3 oxide film generated on the surface the steel plate is suppressed. Furthermore, Patent Document 2 proposes a heat resistant steel material for a reformer in which Si content is defined according to Cr and Ni contents in steel material so that fit of Cr_2O_3 generated on the surface of steel material is improved.

[0004] However, neither of the techniques disclosed in these Patent documents consider effects of S, which possibly forms compounds with REMs or Cr in the material, and they are insufficient to be used in high temperature environments in which superior oxidation resistance properties are required. Furthermore, although REMs include multiple elements, neither of the Patent documents disclose which element among them is effective, and the techniques are difficult to practice.

[0005] In addition, neither of the Patent documents consider the influence of an internal oxide layer affecting oxidation resistance properties, and they are insufficient as a technique to be used in severe high temperature environments.

[0006] Furthermore, in recent years, Ni-Cr-Fe alloys having superior creep strength and strain release cracking resistance properties by complex addition of Ti, Al, and REM is proposed (For example, see Patent document 3). However, the alloy is produced by adjusting compositions in a high frequency induction furnace, obtaining a slab, and performing hot rolling of the slab, in a laboratory scale. It is impossible to apply the technique for mass production such as a 60 t level or the like. Furthermore, although the technique mentions that all REMs are effective, on the contrary, only Nd is mainly added, and Ce, La, and Y are merely added in some of the alloys. Furthermore, as a major problem, the technique does not include a removing process of S and O, and therefore, the technique cannot be realized unless the raw materials are carefully selected. Then, in some cases, REM may be oxidized or sulfurized, it is not an industrially reliable proposal and cannot achieve the original purpose. Therefore, according to the technique, it is difficult to rapidly and accurately provide an alloy in which creep strength is improved by adding REM at an industrial level.

[0007] The Patent documents are as follows:

Patent document 1: Japanese Unexamined Patent Application Publication No. 2003-171745
Patent document 2: Japanese Unexamined Patent Application Publication No. 2002-256398
Patent document 3: WO2018-066579

Summary of Invention

[0008] The present invention has been completed in view of the above circumstances, and an object of the present invention is to provide austenitic Fe-Ni-Cr alloys having superior oxidation resistance even when exposed to severe high temperature environments.

[0009] The inventors have researched to overcome the above. So far, a fact is known in which fitting of the surface oxidation scale generated on the surface of alloy in high temperature environments can be improved by adding La, Ce, and Y among the REMs; however, regarding contribution to oxidation resistance which is evaluated by a cycle examination in which temperature is varied from room temperature to 700 to 900°C in a mixed gas atmosphere consisting of $7\%O_2$ -16% H_2O -$10\%CO_2$ -0.5%CO - 0.1%NO_2 -bal. N_2, sufficient knowledge has not been obtained yet. Then, correlation of La, Ce, Y and other contained elements contained in alloy was researched in detail. As a result, it became obvious that addition of

La, Ce, and Y was very effective to improve oxidation resistance, and that Si, Ni, Cr, Al, Ti, and Zr as another element were also effective. On the other hand, it became obvious that content of S, Mo, and B may interfere with improvement in oxidation resistance. According to this, the inventors found that it was necessary to control Si, Ni, Cr, Al, Ti, Zr, S, Mo, and B in order to sufficiently maintain action by REM addition.

[0010] In addition, an internal oxide layer consisting of oxides of Cr, Si, Mn, Al, Ti, La, Ce, and Y may be formed immediately below the protective oxidation scale formed on the surface in a high temperature environment, as a result of studying behavior of formation of the internal oxide layer in detail, the inventors found that there was a good correlation between area ratio of the internal oxide layer and weight reduction by oxidation in the high temperature oxidation test. Practically, in an area of 0.005 mm^2 in the internal oxide layer immediately below the surface oxidation scale, oxidation resistance was improved in a case in which the area ratio of the internal oxide occupied not less than 30%. As a result of study of the relationship between the formation behavior of the internal oxide layer and alloy elements, the inventors found that La, Ce, Y, Si, Cr, Al, and Ti were effective; on the other hand, containing of S, Mn, and N inhibited the formation behavior of the internal oxide layer. According to these results, the inventors found that it was necessary to control La, Ce, Y, Si, Cr, Al, Ti, S, Mn, and N in order to improve oxidation resistance by control of the internal oxide layer.

[0011] Furthermore, the inventors found that a value in which total weight (mass%) of one or more kinds selected from La, Ce, and Y being REMs as alloy element contained in alloy is divided by content (mass%) of S contained in the alloy had good correlation with weight reduction by oxidation in high temperature oxidation tests, and it became obvious that the characteristics formula obtained by them was $3.2 \leq REM/S$.

[0012] In addition, as a result of research focusing on structure of surface oxidation scale formed in high temperature environments, in a case in which surface oxidation scale is formed to have thickness of 10 to 100 μm in a cycle test in which temperature is repeatedly increased from room temperature to 700 to 900°C in a mixed gas atmosphere consisting of 7% O_2-16%H_2O-10%CO_2-0.5%CO-0.1%NO_2-bal.N_2, the surface oxidation scale was formed densely, had superior fit, and showed good results in weight reduction by oxidation after the test.

[0013] That is, the austenitic Fe-Ni-Cr Alloy of the present invention consists of, in mass%, C: 0.004 to 0.13%, Si: 0.15 to 1.0%, Mn: 0.03 to 2.0%, P: ≤0.040%, S: ≤0.003%, Ni: 20.0 to 38.0%, Cr: 18.0 to 28.0%, Mo: ≤1.0%, Cu: ≤1.0%, N: ≤0.03%, B: ≤0.01%, Al: 0.10 to 1.0%, at least one of Ti: 0.10 to 1.0% and Zr: 0.01 to 0.6%, O: 0.0002 to 0.0030%, Ca: ≤0.002%, total weight of one or more kinds selected from La, Ce, and Y being rare earth metal elements (REMs): 0.001 to 0.010%, Fe as the remainder and inevitable impurities, and satisfies the following formulae (1) and (2).

$$85 \geq 0.3xSi + 1.5xNi + 1.3xCr + 5.8xAl + 7.7xZr + 2.7xTi + 2173REM - 3582xS - 32.9xMo - 2448xB \geq 47 \quad (1)$$

$$40 \geq 0.6xSi + 1.3xCr + 23.53xAl + 5.88\,xTi + 3074xREM - 5067xS - 0.8xMn - 816xN \geq 0 \quad (2)$$

[0014] Furthermore, in the austenitic Fe-Ni-Cr alloy of the present invention, one or more kinds selected from La, Ce and Y being rare earth metal elements (REMs) satisfies the following formula (3).

$$3.2 \leq \mathrm{REM\ (La, Ce, Y)} / \mathrm{S} \cdots (3)$$

[0015] In the austenitic Fe-Ni-Cr alloy of the present invention, in addition to the above chemical compositions, composition of surface oxidation scale which is formed in a cycle test in which temperature is repeatedly increased from the room temperature to 700 to 900°C in a mixed gas atmosphere consisting of 7%O_2-16%H_2O-10%CO_2-0.5%CO-0.1% NO_2-bal.N_2 consists of, in mass%:
Cr: not less than 40%, Fe: 10 to 20%, Ni: 0 to 10%, O:10 to 40%, REM: 0.05 to 0.5%, and remainder Mn, Si, and Ti as an inevitable element, and the surface oxidation scale has thickness of 10 to 100 μm.

[0016] Furthermore, internal oxide layer which is formed immediately below the surface oxidation scale comprises internal oxide containing at least one kind of Cr, Si, Mn, Al, Ti, and REM, and at the same time, area ratio of the internal oxide layer occupies not less than 30% per 0.005 mm^2 immediately below the surface oxidation scale.

[0017] Furthermore, the present invention also proposes a method for production of the austenitic Fe-Ni-Cr alloy. That is, alloy compositions are adjusted by melting alloy raw materials and refining, in the refining process, decarburizing is performed by blowing mixed gas of oxygen and argon into melted alloy raw materials (fused alloy) so as to control nitrogen concentration the be not more than 0.03%, Cr reduction is performed, and then, aluminum, limestone and fluorite are added in the fused alloy so as to form CaO-SiO_2-Al_2O_3-MgO-F slag, oxygen concentration in the fused alloy is controlled to 0.0002 to 0.0030 mass%, and after that, raw material containing at least one of La, Ce, and Y is added so as to adjust compositions, the fused alloy is cast so as to obtain a slab, and the slab is subjected to hot-rolling processing so as to produce a coil.

Effect of Invention

[0018] According to the present invention, superior oxidation resistance can be imparted to an alloy in high temperature environments, and the alloy can greatly contribute to increased service life of a product.

Brief Description of Drawings

[0019] Fig. 1 is a schematic view explaining surface structure of Fe-Cr-Ni alloy plate in a high temperature oxidation test according to an embodiment of the present invention.

Embodiments of Invention

[0020] The chemical compositions which should be contained in the austenitic Fe-Ni-Cr alloy of the present invention are explained.

C: 0.004 to 0.13 mass%

[0021] C is an element which contributes to stabilizing an austenitic phase. However, if it is added excessively, carbides may be formed by combining Cr, Mo, and the like, amount of Cr solid-solved therearound may be decreased, and oxidation resistance may be deteriorated. On the other hand, since C also has an effect of increasing alloy strength by solid solution strengthening, the lower limit is set to be 0.004 mass%. Therefore, C is limited to 0.004 to 0.13 mass%. It is desirably 0.005 to 0.080 mass%, and more desirably 0.006 to 0.070 mass%.

Si: 0.15 to 1.0 mass%

[0022] Si is an element effective for improving oxidation resistance and avoidance of separating of oxide film. The effects can be obtained by addition of not less than 0.15 mass%. However, if it is added excessively, precipitation of intermetallic compound such as σ phase may be promoted and surface damage due to the intermetallic compounds may be generated, content is set to be 0.15 to 1.0 mass%. It is desirably 0.16 to 0.8 mass% and more desirably 0.17 to 0.6 mass%.

Mn: 0.03 to 2.0 mass%

[0023] Since Mn is an element which stabilizes an austenitic phase and has action of deoxidation, it is necessary to add not less than 0.03 mass% to obtain the effects. However, similar to Si, Mn may also cause precipitation of intermetallic compounds such as σ phase and deterioration of oxidation resistance, and it is not desirable to add more than the required amount. Therefore, it is necessary to limit it to 0.03 to 2.0 mass%. It is desirably 0.03 to 1.50 mass% and more desirably 0.03 to 1.00 mass%.

P: Not more than 0.040 mass%

[0024] P is an element inevitably contained as an impurity, and an element which degrades hot workability since it may segregate at crystalline grain boundaries as a phosphide. Therefore, it is desirable to be reduced as much as possible. However, production cost may increase by attempting to extremely reduce P content. Therefore, in the present invention, P is limited to not more than 0.040 mass%. It is desirably not more than 0.030 mass% and more desirably not more than 0.020 mass%.

S: Not more than 0.003 mass%

[0025] Similar to P, S is an element inevitably contained as an impurity. It may easily segregate at crystalline grain boundaries, and in particular, may extremely degrade hot workability. Furthermore, it may form compounds with Cr which contribute to oxidation resistance mentioned below so that Cr, which is necessary to form the surface oxidation scale, is consumed, fit between oxide film and parent material may be deteriorated so that the oxide film may separate, oxidation may be promoted, and it is a harmful element for oxidation resistance. Since the harmfulness is extremely exhibited if it is contained at more than 0.003 mass%, it is necessary to limit it to not more than 0.003 mass%. It is desirably not more than 0.002 mass%, and more desirably not more than 0.001 mass%. As mentioned below, S can be reduced by addition of Al and reaction with slag components.

Ni: 20.0 to 38.0 mass%

[0026] Ni is an element which stabilizes the austenitic phase, and it has an action to restrain precipitation of intermetallic compounds such as a σ phase. Furthermore, it also has an action to improve heat resistance and high temperature strength. In order to obtain the above effects sufficiently, it is added at not less than 20 mass%. On the other hand, excessive addition may cause deterioration of hot workability, increase in hot deformation resistance and increase in cost. Therefore, Ni content is set to be 20.0 to 38.0 mass%. It is desirably 21.0 to 36.0 mass% and more desirably 22.0 to 35.0 mass%.

Cr: 18.0 to 28.0 mass%

[0027] Cr is an element which contributes to preventing corrosion in high temperature environments, and also has effects of forming a protective oxide film on the surface of an alloy in high temperature environments and reducing high temperature oxidation. It is necessary to be contained at not less than 18.0 mass% in order to sufficiently obtain the above effects. However, if Cr is added excessively, surface oxidation scale may form excessively, and fit may be deteriorated and oxidation resistance may be deteriorated. In addition, since stability of austenitic phase may be decreased and thereby Ni may need to be added in large amounts, the content is set to be 18.0 to 28.0 mass%. It is desirably 19.0 to 26.0 mass% and more desirably 20.0 to 25.0 mass%.

Mo: Not more than 1.0 mass%

[0028] Mo has an effect of being solid-solved into an alloy and increasing high temperature strength even in a small amount of addition. However, in a material in which Mo is added in large amount, in a case in which surface oxygen potential is small and in high temperature environments, Mo may be preferentially oxidized and oxidation scale may separate, which are regarded as adverse effects. Therefore, from the viewpoint of maintaining fit of protective surface oxidation scale, Mo is limited to not more than 1.0 mass%. It is desirably not more than 0.8 mass% and more desirably not more than 0.6 mass%.

Cu: Not more than 1.0 mass%

[0029] Although there may be a case in which Cu is added as an element to improve corrosion resistance in wet environments, the effect is little exhibited in high temperature environments like in the present invention. On the other hand, if it is added excessively, an uneven film having mottled pattern may be formed on the surface of a material, thereby deteriorating corrosion resistance. Therefore, Cu content is limited to not more than 1.0 mass%. It is desirably not more than 0.8 mass% and more desirably not more than 0.6 mass%.

N: Not more than 0.03 mass%

[0030] N is an element which is inevitably contained as an impurity; however, since it is also an element which generates an austenitic phase, it contributes to stabilization of structure. However, in a case in which Al, Ti, Zr or the like is added like in the present invention, N may combine with these elements, thereby precipitating nitrides. Then, hot deformation resistance may be extremely increased and hot workability may be degraded. Furthermore, due to formation of the nitrides, since Al and Ti, which are constituent elements of internal oxide which is formed immediately below the surface oxidation scale are consumed, area ratio of the internal oxide layer may be decreased. Therefore, in the present invention, N content is set to be not more than 0.03 mass%. It is desirably not more than 0.02 mass% and more desirably not more than 0.01 mass%.

[0031] Oxygen is blown in during decarburization. During this, N moves to CO gas bubbles as nitrogen gas and is removed from the system, and thus, N can be controlled within the range of the present invention.

B: Not more than 0.01 mass%

[0032] B has an effect of helping an effect of rare earth metals (REMs) by grain boundary segregation, and is an element which contributes to high temperature strength. However, if it is added excessively, the surface oxidation scale may be porous, thereby deteriorating fit, welding property, and hot workability of an alloy. In the present invention, B content is set to be not more than 0.01 mass%. It is desirably not more than 0.008 mass% and more desirably not more than 0.006 mass%.

Al: 0.10 to 1.0 mass%

[0033] Al is an element which promotes formation of dense black film and improves oxidation resistance, and each of these effects can be obtained by addition of not less than 0.10 mass%. Furthermore, it is an element which is added as a deoxidizing agent, and is an important element in order to control oxygen concentration within the range of the present invention : 0.0002 to 0.0030 mass% according to the formula (a).

$$2\underline{\mathrm{Al}} + 3\underline{\mathrm{O}} = (\mathrm{Al_2O_3}) \quad \cdots(\mathrm{a})$$

[0034] Underlining indicates an element in melt steel and parentheses indicate composition in slag.

[0035] By using $CaO-SiO_2-Al_2O_3-MgO-F$ slag during refining of alloy of the present invention, Al_2O_3 which is generated is effectively absorbed, thereby enabling controlling oxygen concentration. Furthermore, by promoting deoxidation, S concentration in the melt steel may be also decreased according to the formula (b).

$$2\underline{\mathrm{Al}} + 3\underline{\mathrm{S}} + 3(\mathrm{CaO}) = 3(\mathrm{CaS}) + (\mathrm{Al_2O_3}) \quad \cdots(\mathrm{b})$$

[0036] According to the above, S concentration can be controlled within the range of the present invention at not more than 0.003 mass%. In order to satisfy this condition, it is necessary to contain Al at not less than 0.10 mass%. However, if it is added excessively, reaction may be extremely promoted toward the right-hand side of the formula (c), Ca concentration may be more than 0.002 mass%, excessive Ca-Al oxides inclusions may be formed, and Al in the alloy may be consumed there by deteriorating oxidation resistance.

$$3(\mathrm{CaO}) + 2\underline{\mathrm{Al}} = 3\underline{\mathrm{Ca}} + (\mathrm{Al_2O_3}) \quad \cdots(\mathrm{c})$$

[0037] According to the above, the upper limitation of Al is set to be 1.0 mass%. It is desirably 0.10 to 0.80 mass% and more desirably 0.10 to 0.60 mass%.

[0038] Similar to the above mentioned Al, since Ti and Zr act effectively to form a dense black film and to improve oxidation resistance, it is necessary to add at least one of them.

Ti: 0.10 to 1.0 mass%

[0039] Ti is an element which promotes formation of dense black film and improves oxidation resistance, and the effects can be obtained by addition of not less than 0.10 mass%. However, if it is added excessively, surface damage may occur due to formation of large amounts of carbonitrides (TiN, TiC, TiCN). Therefore, the upper limitation of Ti is set to be 1.0 mass%. It is desirably 0.10 to 0.80 mass% and more desirably 0.10 to 0.60 mass%. Furthermore, control of C and N concentrations within the range of the present invention as mentioned above is one means for restraining carbonitrides effectively.

Zr: 0.01 to 0.6 mass%

[0040] Zr is a homologous element of Ti, since it acts effectively to form a dense black film and to improve oxidation resistance similarly to Ti, it can be used as an alternative element of Ti. Since effect of Zr is superior to that of Ti, an effect can be obtained even by adding a small amount. If it is added excessively, large amounts of carbonitrides may be formed, thereby causing surface damage, and therefore, the upper limit is set to be 0.6 mass%. It is desirably 0.01 to 0.4 mass% and more desirably 0.05 to 0.3 mass%.

O: 0.0002 to 0.0030 mass%

[0041] O in alloy may combine with Al, Ti, Zr, Si, La, Ce, and Y in fused steel, thereby forming oxides thereof, which may cause impair desirable effects such as oxidation resistance of these elements. Furthermore, oxide type non-metallic inclusions of an alumina type may be excessively formed, they may adhere inside an immersed nozzle to pour melt steel from a tundish into a mold of a continuous casting apparatus, and they may fall off, causing surface damage. Therefore, it is desirable that oxygen concentration be lower as much as possible and be not more than 0.0030 mass%. In order to achieve the range, Al is controlled within the concentration range of the present invention as mentioned above to perform deoxidation. On the other hand, if O in an alloy is extremely reduced, according to the formula (c), Ca concentration may be higher than 0.002 mass%. Therefore, the lower limit is set to be 0.0002 mass%. It is desirably 0.0003 to 0.0027 mass% and more desirably 0.0005 to 0.0025 mass%.

Ca: Not more than 0.002 mass%

[0042] Ca is an element which is a contaminant from CaO in the slag, as mentioned above, in the alloy of the present invention. Since Ca forms large amounts of Ca-Al oxide inclusions and consumes Al in an alloy, thereby reducing oxidation resistance, it is necessary that Ca be reduced to a low level. Therefore, it is necessary that Al concentration be controlled 0.10 to 1.00 mass% and oxygen concentration be controlled 0.0002 to 0.0030 mass%. Therefore, it is necessary that Ca be not more than 0.002 mass%.

Total weight of at least one kind selected from La, Ce, and Y being rare earth metal (REM): 0.001 to 0.010 mass%

[0043] REM (La, Ce and Y) has effects in which hot workability of alloy, fit of surface oxidation scale and a parent material surface and oxidation resistance are improved, and noticeable effects can be obtained by using even a small amount thereof. Furthermore, by forming compounds with S which is solid-solved in the alloy, effects can be expected in which Cr being a constituent element of surface oxidation scale and S are restrained from forming compounds, and that local reduction in amount of Cr is prevented. In addition, a REM is used as a raw material in a form of misch metal which is an alloy generally containing multiple REMs, and there may be a case in which Fe-Ni alloy containing one kind of REM is used. However, if it is added excessively, hot workability and welding property of alloys may be deteriorated and REM type inclusions may be excessively formed, thereby deteriorating fit of surface oxidation scale. Furthermore, an immersed nozzle may become blocked during continuous casting, and productivity may be extremely deteriorated. Therefore, in the present invention, REM content is set to be 0.001 to 0.010 mass%. It is desirably 0.002 to 0.009 mass% and more desirably 0.003 to 0.008 mass%.

$$85 \geq 0.3xSi + 1.5xNi + 1.3xCr + 5.8xAl + 7.7xZr + 2.7xTi + 2173xREM - 3582xS - 32.9xMo - 2448xB \geq 47 \quad (1)$$

[0044] With respect to the elements affecting surface oxidation scale formed on the surface of the alloy, the formula (1) indicates extent of the effect by multiple regression analysis as a formula in oxidation resistance of Fe-Cr-Ni alloy. Si, Ni, Cr, Al, Ti, Zr and REM (La, Ce and Y) improve oxidation resistance which is evaluated by cycle testing in which temperature is repeatedly increased from room temperature to about 700 to 900°C in a mixed gas atmosphere consisting of $7\%O_2$ -16% H_2O -10%CO_2 - 0.5%CO -0.1%NO_2 -bal.N_2. On the other hand, S deteriorates fit between oxide film and parent material, thereby oxide film separates, and promoting oxidation. In a case in which Mo content is large and oxygen potential on the surface is low in high temperature environments, Mo may be preferentially oxidized, and thereby causing separation of oxidation scale. Furthermore, in a case in which B content is large, since oxidation scale of an alloy may become porous, oxidation rate at high temperature may be increased, and enlargement and separation of scale may be promoted. In addition, it is not desirable that alloy elements contributing to improvement of oxidation resistance be excessively added since fit may decrease by excessive growth of surface oxidation scale and large amounts of inclusions causing surface damage may be generated. Therefore, the lower limit and the upper limit of these elements are set to be 47 and 85 respectively, based on the formula (1). It is desirably 48 to 84 and more desirably 50 to 83.

$$40 \geq 0.6xSi + 1.3xCr + 23.53xAl + 5.88\,xTi + 3074xREM - 5067xS - 0.8xMn - 816xN \geq 0 \quad (2)$$

[0045] With respect to the elements affecting behavior in formation of the internal oxide layer formed immediately below the surface oxidation scale, the formula (2) shows the extent of the effect by multiple regression analysis as a formula in oxidation resistance of Fe-Cr-Ni alloy. In the internal oxide layer formed immediately below the oxidation scale formed on the surface of alloy in the cycle testing in which temperature is repeatedly increased from room temperature to about 700 to 900°C in a mixed gas atmosphere consisting of $7\%O_2$ -16%H_2O -10%CO_2 -0.5%CO - 0.1%NO_2 -bal.N_2, each of REMs, Si, Cr, Al, and Ti densely forms internal oxides, reduces oxidizing rate by restraint of internal diffusion of oxygen and improves oxidation resistance. On the other hand, by forming compounds of S and Cr, necessary Cr may be consumed during forming the internal oxide and forming surface oxidation scale of which the internal oxide transits. Furthermore, Mn also forms internal oxide similarly, oxidation resistance may be rather deteriorated if it is contained excessively. N forms AlN and TiN with Al and Ti respectively which contribute to improving oxidation resistance, thereby reducing effect of Al and Ti. Furthermore, it is not desirable to excessively add alloy elements contributing to improving oxidation resistance because large amounts of inclusions causing surface damage may be formed. Therefore, the lower limit and the upper limit of these elements are set to be 0 and 40 respectively based on the formula (2). It is desirably 10 to 39 and more desirably 20 to 38.

$$\underline{3.2 \leq \mathrm{REM\ (La,\ Ce,\ Y)\ /\ S} \cdots (3)}$$

[0046] As an index to sufficiently obtain effects improving hot workability and oxidation resistance of alloy, if the relationship of content of rare earth metals (REMs) and content of S forming compounds therewith satisfies 3.2 ≤ REM/S, REM content sufficient for fixing S as inclusions can be contained, thereby obtaining the above effects. On the other hand, if the relationship is less than 3.2, it is not desirable since effects by REMs cannot be obtained sufficiently.

Definition of surface oxidation scale and internal oxide layer formed immediately below the scale

[0047] As shown in Fig. 1, the Fe-Cr-Ni alloy plate according to one embodiment of the present invention has Fe-Cr-Ni-alloy containing compositions satisfying the above formulae (1) to (3) as a basis material BM. In the cycle test in which temperature is repeatedly increased from room temperature to about 700 to 900°C in a mixed gas atmosphere consisting of 7%O_2 -16%H_2O -10%CO_2 -0.5%CO -0.1%NO_2 -bal.N_2, oxidation scale mainly containing Cr oxide is formed on the surface of Fe-Cr-Ni alloy parent material of the present invention, and internal oxide layer containing at least one kind selected from Cr, Si, Mn, Al, Ti and REM is formed immediately below an interface between the scale and the alloy. During this, in Fig. 1, thickness of the surface oxidation scale corresponds to region LE which is from the outermost layer of the surface oxidation scale to the interface of the scale and the alloy in the observation of cross-sectional microstructure after the test, and thickness of the internal oxide layer corresponds to region LI which is to a position at which oxygen intensity of GDS analysis is 1/4 of intensity peak at the interface of the scale and the alloy. Furthermore, a range of measurement of area ratio of the internal oxide layer mentioned below is a range of 0.005 mm^2 which is surrounded by 0.05 mm of interface direction and 0.1 mm of depth direction when the scale and the alloy interface is regarded as the upper end, and the area ratio of the internal oxide containing at least one kind selected from Cr, Si, Mn, Al, Ti, and REM in the range of 0.005 mm^2 is measured.

The surface oxidation scale which is formed in the cycle test in which temperature is repeatedly increased from room temperature to 700 to 900°C in a mixed gas atmosphere consisting of 7%O_2 -16%H_2O -10%CO_2 - 0.5%CO -0.1% NO_2-bal.N_2, has a thickness of 10 to 100 μm

[0048] In the Fe-Cr-Ni alloy of the present invention, the oxidation scale mainly containing Cr oxide is formed on the surface of alloy parent material in the cycle testing in which temperature is repeatedly increased from room temperature to 700 to 900°C in a mixture gas atmosphere consisting of 7%O_2 -16%H_2O -10%CO_2 -0.5%CO -0.1%NO_2 -bal.N_2, and oxidation resistance in high temperature environments is obtained. During this time, sufficient oxidation resistance cannot be obtained in a case in which thickness of the surface oxidation scale is less than 10 μm; on the other hand, if the thickness is greater than 100 μm, separating property of the surface oxidation scale is increased, thereby reducing fit between the surface oxidation scale and surface of parent material. Therefore, it is necessary that thickness of the protective surface oxidation scale formed in the above high temperature environment be 10 to 100 μm. It is desirably 12 to 90 μm and more desirably 12 to 80 μm.

[Area ratio of internal oxide layer immediately below surface oxidation scale]: ≥ 30%/0.005 mm^2

[0049] When an alloy is exposed to high temperature environments, surface oxidation scale having a layered structure is formed on the surface of the alloy, and an internal oxide layer is formed immediately below interface of the scale and the alloy. The internal oxide layer includes Cr type oxide which is before transiting to the surface oxidation scale being an outer layer and an oxide which contains at least one kind selected from Si, Mn, Al, Ti, and REMs. When oxygen is present in high temperature environments, it diffuses to the inside of an alloy in oxidation reactions, and in a case in which oxygen passes through internal oxide is slower than in a case in which oxygen passes through alloy parent material.

[0050] Therefore, if an area ratio of an internal oxide layer is sufficiently maintained, oxygen can be restrained from diffusing inside. In the present invention, the above effect can be sufficiently obtained if the area ratio of the internal oxide in 0.005 mm^2 of the internal oxide layer is not less than 30%. On the other hand, it is not desirable if the above effect cannot be sufficiently obtained if the area ratio is less than 30%

[0051] The above limitation formula (1) is determined as follows.

[0052] Kinds of alloys all having Fe-30%Ni-20%Cr-0.8%Mn as a basic composition and each having varied contents of Si, Ni, Cr, Al, Ti, Zr, La, Ce, Y, B, Mo, and S were melted in a vacuum melting furnace, hot forged, and made into a hot forged plate of 8 mmt x 80 mmw. Each of the obtained hot forged plates was processed in solution heat treatment under conditions of 1200°C x 10 minutes, the surface thereof was ground, cold-rolled so as to be 2 mmt, and processed in solution heat treatment under conditions of 1150°C x 1 minute. After that, it was cut into 20 mm x 30 mm pieces and polished on the surface thereof by wet polishing of #320 so as to obtain test pieces. Each of the obtained test pieces was provided to a repeating oxidation test of900°C x 10 minutes, 700°C x 10 minutes, 900°C x 10 minutes, and room temperature x 20 minutes were one cycle in a mixed gas atmosphere consisting of $7\%O_2$ -$16\%H_2O$ -$10\%CO_2$ -0.5%CO - $0.1\%NO_2$ -bal.N_2. With respect to each of the test pieces after 200 cycles, evaluation was performed based on a value in which weight change excluding weight of separated scale was divided by surface area before the test.

[0053] According to the above test results, degree of influence of an element added affecting oxidation resistance of Fe-Cr-Ni alloy was obvious, and the relational formula of composition shown by the formula (1) was determined by multiple regression analysis. It was obvious that the alloy had sufficient oxidation resistance if the formula is 47 to 85.

[0054] The limitation formula (2) was determined as follows.

[0055] Kinds of alloys all having Fe-30%Ni-20%Cr-0.2%Zr as a basic composition and each having varied contents of Si, Cr, Al, Ti, La, Ce, Y, N, Mn, and S were melted in a vacuum melting furnace, hot forged, and made into hot forged plates of 8 mmt x 80 mmw. Each of the obtained hot forged plates was processed in solution heat treatment under the conditions of 1200°C x 10 minutes, the surface thereof was ground, cold-rolled so as to be 2 mmt, and processed in solution heat treatment under the conditions of 1150°C x 1 minute. After that, it was cut into 20 mm x 30 mm pieces and polished on the surface thereof by wet polishing using #320 so as to obtain test pieces. Each of the obtained test pieces was provided to a repeating oxidation test in which 900°C x 20 minutes, 700°C x 10 minutes, 900°C x 10 minutes and room temperature x 20 minutes are one cycle in a mixed gas atmosphere consisting of $7\%O_2$ -$16\%H_2O$ -$10\%CO_2$ -0.5%CO - $0.1\%NO_2$ -bal.N_2. Each of the test pieces after 200 cycles was cut and processed by Cu plating to observe a cross section thereof. Embedded samples were prepared, polished in wet conditions and finished by buff polishing at the end to make a mirror surface to allow observations to be made. Microstructures of cross section were observed by FE-SEM, and oxides were identified and area ratio of the internal oxide layer was measured by auxiliary EDS. The area ratio was a measured SEM image which was observed in 0.005 mm^2 of the internal oxide layer immediately below the surface oxidation scale at 2,000 times magnification. In a case of bulk oxide, length of two edges were measured and approximated a circle, and the area of the circle was calculated. In a case of a linear oxide, lengths of a longer edge and a shorter edge were measured and approximated as a rectangle, and the area of the rectangle was calculated. According to the areas, area ratio of the internal oxide layer of observation area 0.005 mm^2 immediately below the surface oxidation scale was evaluated. It is desirable that the area ratio be not less than 30%.

[0056] According to the above test results, in oxidation resistance of Fe-Cr-Ni alloy, degree of influence by added elements with respect to formation behavior of the internal oxide layer became obvious, and the relational formula of composition indicated by the formula (2) was calculated by multiple depression analysis. It is clear from the formula that sufficient oxidation resistance can be obtained by being 0 to 40.

[0057] Next, a method for production of austenitic Fe-Cr-Ni alloy of the present invention is explained.

[0058] In the method for production of austenitic Fe-Cr-Ni alloy of the present invention, raw material such as iron scrap, stainless steel scrap, ferronickel, ferrochromium and the like were melted in an electric furnace, a mixed gas of oxygen and a noble gas was blown in n AOD (Argon oxygen decarburization) furnace or a VOD (Vacuum oxygen decarburization) furnace so as to decarburize and refine, Cr oxides in the slag were reduced by adding calcined lime, Fe-Si alloy, Al or the like, $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}MgO\text{-}F$ slag was formed by adding fluorite so as to deoxidize and desulfurize, and Ni base alloy containing at least one selected from La, Ce, and Y was added. Reason for using $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}MgO\text{-}F$ slag is that, as mentioned above, deoxidizing and desulfurizing can be effectively promoted, and furthermore, REMs can be effectively added without being oxidized or sulfurized during addition of REM. During this, it is desirable that CaO concentration in the slag be in a range of 40 to 80%. That is, the above desulfurizing reaction may not be promoted if the content is less than 40%. Ca may be more than 0.002% in melt steel if the content is more than 80%. Furthermore, it is desirable that Al_2O_3 concentration be not more than 50%. The reason is that deoxidizing may be difficult to promote unless activity of alumina in slag is low, and therefore, desulfurizing may be also difficult. After refining, a slab was produced by a continuous casting apparatus, and it is desirable that the slab be hot-rolled, and further cold-rolled, if necessary, so as to obtain kinds of steel materials such as thin steel plate, thick steel plate, shaped steel, bar steel, wire material and the like. The production method is not limited to continuous casting, and an ingot casting-cogging rolling method can be employed to produce a slab.

Examples

[0059] A raw material in which scrap, ferrochromium, ferronickel, stainless steel scrap or the like are adjusted in a certain ratio was melted in an electric furnace of a scale of 70 t, and mixed gas of oxygen and a noble gas was blown in a melt metal in an AOD furnace or a VOD furnace so as to perform decarburization refining. After that, calcined lime, Fe-Si alloy, Al, and the like were added so as to reduce Cr oxides in the slag, and $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}MgO\text{-}F$ slag was formed by adding fluorite so as to deoxidize and desulfurize. After that, at least one selected from Ni-20%La, Ni-20%Ce, and Ni-20%Y was added at predetermined amount, and a casted slab was obtained by a continuous casting method. Each slab was obtained by adjusting chemical compositions as shown in Table 1 and then continuously casting. Each of compositions shown in Table 1 was measured as follows.

(1) C and S compositions were measured by using carbon-sulfur simultaneously analyzing apparatus (combustion in oxygen gas flow-infrared absorption method).
(2) N composition was analyzed by using oxygen-nitrogen simultaneously analyzing apparatus (inert gas-impulse heating melting method).
(3) Compositions other than C, S and N, and slag composition were analyzed by standard curve method using fluorescent X ray analysis.

Table 1

		C	Si	Mn	P	S	Ni	Cr	Mo	Cu	N	B	Al	Ti	Zr	O	Ca	REM			
																			La	Y	Ce
Examples	1	0.011	0.25	0.86	0.018	0.0002	27.76	19.74	0.82	0.06	0.0020	0.0017	0.540	0.420	0.430	0.0010	0.0009	0.0029	○		
	2	0.078	0.21	0.9	0.017	0.0002	32.33	20.11	0.06	0.08	0.0012	0.0060	0.443	0.454	0.050	0.0007	0.0007	0.0032	○		
	3	0.066	0.27	0.89	0.019	0.0001	33.59	20.05	0.36	0.06	0.0019	0.0090	0.239	0.000	0.020	0.0014	0.0002	0.0041		○	
	4	0.033	0.62	0.41	0.011	0.0002	30.44	21.22	0.55	0.86	0.0014	0.0055	0.312	0.341	0.000	0.0006	0.0005	0.0031			○
	5	0.045	0.35	0.22	0.010	0.0004	32.10	20.88	0.40	0.72	0.0020	0.0070	0.405	0.000	0.010	0.0019	0.0002	0.0022		○	
	6	0.035	0.49	0.35	0.023	0.0003	31.11	18.22	0.88	0.04	0.0016	0.0021	0.668	0.411	0.030	0.0026	0.0007	0.0028	○		○
	7	0.025	0.79	0.87	0.017	0.0002	37.92	19.86	0.51	0.04	0.0016	0.0021	0.442	0.467	0.030	0.0006	0.0001	0.0081	○		○
	8	0.097	0.16	0.91	0.022	0.0008	33.56	23.49	0.05	0.05	0.0018	0.0009	0.440	0.463	0.060	0.0009	0.0003	0.0026	○	○	
	9	0.065	0.51	0.9	0.021	0.0006	20.88	18.22	0.36	0.06	0.0011	0.0019	0.344	0.392	0.000	0.0005	0.0001	0.0064		○	○
	10	0.077	0.32	0.9	0.019	0.0007	20.41	23.98	0.22	0.07	0.0010	0.0022	0.270	0.280	0.000	0.0006	0.0008	0.0049		○	○
	11	0.061	0.23	1.01	0.015	0.0002	30.41	27.86	0.31	0.03	0.0018	0.0090	0.218	0.319	0.090	0.0029	0.0012	0.0076	○	○	○
	12	0.081	0.46	0.39	0.014	0.0002	23.55	20.35	0.23	0.04	0.0005	0.0055	0.469	0.460	0.020	0.0005	0.0006	0.0028			○
	13	0.028	0.41	0.68	0.011	0.0006	24.78	22.99	0.44	0.07	0.0220	0.0021	0.388	0.311	0.060	0.0007	0.0008	0.0081	○		
	14	0.066	0.54	1.62	0.020	0.0010	28.66	26.11	0.82	0.11	0.0130	0.0010	0.254	0.471	0.110	0.0008	0.0005	0.0036		○	
	15	0.044	0.70	0.97	0.017	0.0001	22.75	19.93	0.10	0.06	0.0008	0.0018	0.374	0.814	0.001	0.0006	0.0003	0.0028			○
	16	0.071	0.86	0.62	0.012	0.0005	34.26	22.88	0.09	0.07	0.0006	0.0034	0.469	0.460	0.030	0.0006	0.0002	0.0022	○		
	17	0.07	0.26	0.71	0.019	0.0006	37.70	20.20	0.04	0.07	0.0021	0.0023	0.264	0.271	0.040	0.0005	0.0004	0.0016	○		
Comparative Examples	18	(0.271)	0.25	0.8	0.019	0.0020	30.88	18.13	0.06	0.07	0.006	0.0015	(0.090)	0.258	0.050	(0.0077)	0.0001	0.0025		○	○
	19	0.062	(1.65)	(2.38)	0.019	0.0030	30.31	19.86	0.03	0.06	0.0080	0.0016	0.244	0.255	0.040	0.0005	0.0004	0.0016	○	○	○
	20	0.075	0.22	0.9	0.019	0.0030	(17.29)	19.79	0.12	0.06	0.003	0.0021	(1.136)	0.481	0.090	(0.0001)	(0.0032)	0.0022	○		
	21	0.075	0.22	0.9	0.019	0.0007	31.52	19.79	0.12	0.06	0.01	(0.0203)	0.443	0.481	0.090	(0.0037)	0.0005	0.0047		○	
	22	0.062	0.22	0.81	0.018	0.0020	30.34	(30.13)	0.05	0.05	0.005	0.0021	0.260	0.259	0.020	0.0006	0.0004	0.0068	○		○
	23	0.072	0.33	0.86	0.018	0.0002	31.41	22.85	0.07	0.04	0.013	0.0011	0.468	(1.128)	0.361	0.0008	0.0005	0.0065	○	○	
	24	0.072	0.24	0.87	0.020	0.0003	30.27	19.5	0.05	0.28	0.012	0.0022	0.461	0.463	0.052	0.0008	0.0004	(0.0009)	○		
	25	0.072	0.24	0.87	0.002	0.0003	30.27	25.87	0.05	0.28	0.0120	0.0022	0.420	0.463	(0.724)	0.0006	0.0002	0.0028	○		
	26	0.079	0.34	0.8	0.016	0.0003	30.47	18.14	(1.13)	0.05	0.09	0.0016	0.214	0.09	0.010	0.0007	0.0011	0.0031	○		
	27	0.079	0.34	0.8	0.030	0.0030	30.47	(17.88)	0.51	0.05	0.0200	0.0016	0.214	0.169	0.010	0.0005	0.0007	0.0015			○
	28	0.076	0.25	0.81	0.017	0.0005	30.31	20.02	0.07	0.06	0.007	0.0018	0.246	0.25	0.231	0.0011	0.0003	(0.0150)	○		
	29	0.059	0.25	0.91	0.030	(0.0040)	23.74	19.88	0.05	0.05	0.0113	0.0050	0.122	0.134	0.113	0.0014	0.0004	0.0014			○
	30	0.059	0.25	(0.02)	0.026	0.0010	(39.41)	21.88	0.05	0.05	0.0114	0.0010	0.234	0.238	0.113	0.0005	0.0003	0.0015	○		
	31	0.073	(0.11)	0.88	0.020	0.0010	20.22	18.11	0.25	0.04	0.0022	0.0013	0.161	0.182	0.009	0.0013	(0.0035)	0.0011		○	○
	32	0.073	0.26	0.88	0.020	0.0001	30.3	20.01	0.05	0.05	(0.0430)	0.0013	0.221	0.174	0.225	0.0026	0.0001	0.0023		○	
	33	0.066	0.33	0.35	0.021	0.0003	25.38	27.86	0.25	0.07	0.0132	0.0021	0.867	(1.241)	(0.738)	0.0006	0.0001	0.0081	○	○	○
	34	0.052	0.18	0.87	0.019	0.0006	21.85	20.35	0.51	0.03	0.0117	0.0009	0.218	(0.091)	(0.008)	0.0029	0.0003	0.0022			○
	35	0.073	0.26	1.28	0.020	0.0030	20.12	18.11	0.23	0.06	0.0300	0.0011	0.113	0.125	0.02	0.0012	0.0004	0.0020	○		○
	36	0.056	0.36	1.89	0.011	0.0029	20.12	19.57	0.01	0.03	0.0280	0.0010	0.385	0.225	0.58	0.0005	0.0005	0.0022	○	○	
	37	0.022	0.49	1.28	0.032	0.0027	20.12	20.18	0.98	0.02	0.0050	0.0090	0.129	0.131	0.31	0.0010	0.0005	0.0094		○	○

[0060] Next, the slab was hot rolled until it reached a thickness of 8 mm, and cold rolling, heat treatment, and acid washing were repeated to produce a cold-rolled coil having thickness of 2 to 3 mm. The final annealing temperature and time were 1150 °C and 1 minute, respectively. A piece for testing having a width of 20 mm, length of 30 mm, and thickness of 2 mm was collected from the plate.

<Test in oxidation at high temperature>

[0061] In order to evaluate oxidation resistance in high temperature environments, a surface of the test piece was polished using #320 emery paper under wet conditions and in a high vacuum atmosphere heat treatment furnace was a vacuum of 5.0 x 10^{-3} Pa. The inside was filled with mixed gas atmosphere consisting of 7%O_2 -16%H_2O -10%CO_2 - 0.5% CO -0.1%NO_2 -bal.N_2, and repeated oxidation testing was performed, in which 1 cycle of the testing was conducted in an atmosphere maintained at 900°C for 10 minutes, temperature was adjusted at a temperature decrease rate of 40 °C/min, atmosphere was maintained at 700°C for 10 minutes, temperature was adjusted at temperature increase rate of 40 °C/min, atmosphere was maintained at 900°C for 10 minutes, and then, the atmosphere was maintained at room temperature for 20 minutes. With respect to the test piece after 200 cycles, a value (mg/cm^2) in which change in weight, excluding weight of scale that separated, was divided by surface area before the test, was evaluated as a weight reduction by oxidation. A sample in which the weight reduction by oxidation was less than 50 mg/cm^2 and a sample in which it was not less than 50 mg/cm^2 were evaluated as superior oxidation resistance (o) and inferior oxidation resistance (x), respectively. In addition, microstructures in cross section was observed after the test, so that thickness of surface oxidation scale and area ratio of internal oxide layer formed immediately below the surface oxidation scale were measured.

Table 2

		Formula 1	Surface oxidation scale						Oxidation	Internal oxide layer		Formula 3	Remarks
			Thickness	Cr	Fe	Ni	O	REM	Resistance ○:	Formula 2	Area ratio		
Examples	1	49	35	50.6	12.6	5.8	23.5	0.06	○	21	53	14.3	
	2	68	41	56.9	16.7	2.9	16.4	0.14	○	20	31	16.0	
	3	53	53	42.5	14.2	11.4	22.4	0.20	○	16	54	41.0	
	4	51	53	49.2	13.2	8.5	24.6	0.48	○	17	48	15.5	
	5	51	53	58.2	10.6	2.3	21.0	0.09	○	13	32	5.5	
	6	47	9	40.2	18.6	19.3	21.0	0.22	○	24	42	9.3	
	7	82	37	45.1	12.9	19.7	18.5	0.06	○	36	47	40.5	
	8	84	58	53.6	11.4	7.6	23.1	0.05	○	15	36	3.3	
	9	53	45	48.9	21.8	3.2	24.7	0.44	○	26	42	10.7	
	10	60	29	45.7	15.7	0.4	29.8	0.17	○	18	38	7.0	
	11	68	87	50.8	18.6	9.4	18.9	0.25	○	27	57	38.0	
	12	50	65	61.2	18.1	2.7	13.5	0.10	○	21	33	14.0	
	13	66	65	63.5	16.0	1.3	11.8	0.36	○	14	30	13.5	
	14	55	65	57.4	17.8	6.9	15.0	0.12	○	3	37	3.6	
	15	62	65	46.3	18.1	21.1	13.5	0.19	○	21	32	28.0	
	16	78	17	46.2	13.9	16.3	21.4	0.06	○	17	39	4.4	
	17	80	73	39.5	15.7	18.5	25.3	0.23	○	8	45	2.7	
Comparative Examples	18	64	36	45.7	16.3	8.7	27.4	0.26	×	(−4)	23	1.3	Al_2O_3 concentration in slag 54%
	19	62	84	50.0	10.5	7.9	25.1	0.16	×	(−10)	32	0.5	
	20	(45)	71	49.9	19.2	0.2	21.7	0.22	×	18	77	0.7	CaO concentration in slag 85%
	21	(32)	71	49.9	19.2	0.2	21.7	0.48	×	16	49	6.7	In slag, Al_2O_3 concentration 52%, CaO concentration 28%. Alumina adhered in nozzle.
	22	(88)	103	52.8	11.4	8.4	17.9	0.69	×	14	40	3.4	
	23	(94)	66	57.6	16.3	4.6	18.5	0.66	×	25	50	32.5	
	24	69	8	49.1	15.6	13.1	15.3	0.09	×	5	43	3.1	
	25	(86)	29	52.0	18.1	6.9	15.3	0.29	×	9	35	9.3	
	26	(36)	21	45.7	11.7	19.4	21.2	0.32	×	5	40	10.3	
	27	(43)	94	38.4	10.3	16.2	31.3	0.15	×	(−21)	21	0.5	
	28	(100)	27	50.5	17.6	11.5	18.2	1.53	×	(45)	70	30.0	
	29	(38)	19	50.1	19.2	15.2	12.4	0.14	×	(−22)	19	0.4	CaO concentration in slag 35%
	30	(86)	19	55.1	11.4	21.3	11.9	0.15	×	(−3)	28	1.5	
	31	(43)	38	45.6	12.6	19.0	19.8	0.11	×	1	36	1.1	CaO concentration in slag 83%
	32	75	38	50.4	12.6	15.7	11.3	0.23	×	(−23)	17	23.0	
	33	(92)	44	45.1	12.9	19.7	18.5	0.06	×	40	47	27.0	
	34	(45)	72	63.5	16.0	1.3	11.8	0.36	×	(−1)	22	3.7	
	35	(38)	38	45.6	15.9	10.7	22.8	0.20	×	(−31)	15	0.7	
	36	55	38	49.3	13.3	10.7	26.1	0.22	×	(−22)	24	0.8	
	37	(17)	38	50.9	11.7	10.7	23.9	0.96	×	14	50	3.5	

[0062] Steel plates Nos. 1 to 17 shown in Tables 1 and 2 are Examples of the present invention, satisfied the conditions of the present invention, and exhibited superior oxidation resistance. On the other hand, steel plates Nos. 18 to 37 are Comparative Examples.

[0063] Since Al content was low, the steel plate of No. 18 did not satisfy the formula (2), and deoxidation was promoted weakly since alumina concentration in slag was high at 54%. As a result, oxygen concentration was high, elements effective for oxidation resistance formed oxides, and oxidation resistance was inferior. Furthermore, since C content was also high, inclusions which causes surface damage were formed, and surface quality was inferior.

[0064] Surface damage occurred due to intermetallic compounds such as a σ phase since Si content was high in the steel plate of No. 19. Furthermore, since Mn content was high, the steel plate of No. 19 did not satisfy the formula (2), and oxidation resistance was inferior.

[0065] Since Ni content was low, the steel plate of No. 20 did not satisfy the formula (1). Furthermore, since Al content was high, large amounts of carbonitrides causing surface damage formed, and surface quality was inferior. Furthermore, as a result of high CaO concentration in slag being 85% and too low oxygen concentration, Ca concentration was high, large amounts of Ca-Al oxides inclusions formed, and the effect of Al was lost.

[0066] Since the steel plate of No. 21 contained large amounts of B, the steel did not satisfy the formula (1) and had inferior oxidation resistance. Furthermore, since Al_2O_3 concentration in slag was high at 52% and CaO concentration was low at 28%, O content was high, alumina inclusions adhered to an immersed nozzle, and the inclusions that fell off seriously damaged the surface.

[0067] Since the steel plate of No. 22 had high Cr content, the steel did not satisfy the formula (1), surface oxidation scale grew excessively, thereby forming scale having poor fit, and oxidation resistance was rather deteriorated. Furthermore, since Cr nitride causing surface damage was generated, the steel had inferior surface quality.

[0068] Since Ti content was high, the steel plate of No. 23 did not satisfy the formula (1), carbonitrides causing surface damage were generated, and the surface quality was inferior.

[0069] Since the steel plate of No. 24 had low REM content, the steel did not satisfy the formula (3), and an effect in which oxidation resistance was improved and an effect in which S inhibiting oxidation resistance was fixed as inclusions could not obtained sufficiently.

[0070] Since the steel plate of No. 25 had high Zr content, the steel did not satisfy the formula (1), surface damage which was caused by formation of large amount of carbonitride was caused and the surface quality was inferior.

[0071] The steel plate of No. 26 did not satisfy the formula (1). Furthermore, since Mo content was high, fitting of scale was decreased thereby deteriorating oxidation resistance.

[0072] Since the steel plate of No. 27 had low Cr content and did not satisfy the formulae (1) and (2), oxidation resistance was inferior. Furthermore, since the steel did not satisfy the formula (3), an effect in which oxidation resistance was improved and an effect in which S inhibiting oxidation resistance was fixed as inclusions could not be sufficiently obtained.

[0073] Since the steel plate of No. 28 had high REM content, the steel did not satisfy the formulae (1) and (2). Furthermore, productivity was greatly deteriorated since hot workability and welding property were decreased and an immersed nozzle was blocked during continuous casting.

[0074] Since CaO concentration in slag was low at 35% in the steel plate of No. 29, desulfurization reaction was not promoted. Therefore, oxidation resistance was inferior since S content was high, the steel did not satisfy the formulae (1) and (2), large amounts of inclusions were formed, and Cr necessary for formation of surface oxidation scale was consumed.

[0075] Since Ni content was high, the steel plate of No. 30 did not satisfy the formula (1). Planned costs could not be accomplished since hot workability was deteriorated and hot deformation resistance was increased, thereby increasing production cost. Furthermore, since Mn content was low, effects of deoxidation action and stabilization of austenitic phase could not be sufficiently obtained. Furthermore, an effect in which oxidation resistance was improved and an effect in which S inhibiting oxidation resistance was fixed as inclusions could not be sufficiently obtained since the steel did not satisfy the formula (3).

[0076] Ca content was high since the steel plate of No. 31 did not satisfy the formula (1) and CaO concentration in slag was high at 83%. Large amounts of Ca-Al oxides inclusions were formed, Al in the alloy was consumed, and effective Al was decreased, thereby deteriorating oxidation resistance.

[0077] Since N content was high, the steel plate of No. 32 did not satisfy the formula (2), Cr, Al and Ti contributing to oxidation resistance were precipitated as nitrides and a sufficient internal oxide layer could not be formed, thereby deteriorating oxidation resistance.

[0078] Since Ti and Zr contents were high, the steel plate of No. 33 did not satisfy the formula (1), and large amounts of carbonitrides causing surface damage were formed, thereby deteriorating surface quality.

[0079] Since Ti and Zr contents were low, the steel plate of No. 34 did not satisfy the formulae (1) and (2), and an effect of Ti and Zr contributing to oxidation resistance could not be sufficiently obtained, thereby deteriorating oxidation resistance.

[0080] Although No. 35 satisfied the ranges of the composition of each of the elements, sufficient oxidation resistance was not exhibited since the formulae (1) to (3) were not satisfied.

[0081] Although No. 36 satisfied the ranges of the composition of each of the elements, sufficient oxidation resistance was not exhibited since the formulae (2) and (3) were not satisfied.

[0082] Although No. 37 satisfied the ranges of the compositions of each of the elements, sufficient oxidation resistance was not exhibited since the formula (1) was not satisfied.

Industrial Applicability

[0083] The austenitic Fe-Ni-Cr alloy of the present invention can be desirably used as in heat exchanger and combustion parts at high temperatures since the alloy has oxidation resistance in the above-mentioned high temperature environment and has heat resistance.

Explanation of Reference numerals

[0084] 1: Surface oxidation scale layer, 2: internal oxide layer, 3: interface

Claims

1. An austenitic Fe-Ni-Cr alloy consisting of, in mass%:

C: 0.004 to 0.13%,
Si: 0.15 to 1.0%,
Mn: 0.03 to 2.0%,
P: ≤ 0.040%,
S: ≤ 0.003%,
Ni: 20.0 to 38.0%,
Cr: 18.0 to 28.0%,
Mo: ≤ 1.0%,
Cu: ≤ 1.0%,
N: ≤ 0.03%,
B: ≤ 0.01%,

Al: 0.10 to 1.0%,
at least one of Ti: 0.10 to 1.0% and Zr: 0.01 to 0.6%,
O: 0.0002 to 0.0030%,
Ca: ≤ 0.002%,
total weight of one or more kinds selected from La, Ce, and Y being rare earth metal elements (REMs): 0.001 to 0.010%,
Fe as a remainder and
inevitable impurities, and
wherein the chemical composition satisfies the following formulae (1) and (2):

$$85 \geq 0.3xSi +1.5xNi +1.3xCr +5.8xAl +7.7xZr +2.7xTi +2173xREM -3582xS -32.9xMo -2448xB \geq 47 \quad (1)$$

$$40 \geq 0.6xSi +1.3xCr +23.53xAl +5.88\ xTi +3074xREM -5067xS - 0.8xMn -816xN \geq 0 \quad (2),$$

and
each of element symbols in the formulae indicates content of the each element (mass%).

2. The austenitic Fe-Ni-Cr alloy according to claim 1, wherein the total weight in mass% of one or more kinds selected from La, Ce, and Y being rare earth metal elements (REMs) that satisfy the following formula (3):

$$3.2 \leq \mathrm{REM}\ (\mathrm{La, Ce, Y}) / \mathrm{S} \cdots (3)$$

3. The austenitic Fe-Ni-Cr alloy according to claim 1, wherein composition of surface oxidation scale which is formed in a cycle test in which temperature is repeatedly increased from room temperature to 700 to 900°C in a mixed gas atmosphere consisting of 7%O_2-16%H_2O-10%CO_2-0.5%CO-0.1%NO_2-bal.N_2 consists of, in mass%:
Cr: not less than 40%, Fe: 10 to 20%, Ni: 0 to 10%, O:10 to 40%, REM: 0.05 to 0.5%, and remainder Mn, Si, and Ti as an inevitable impurity.

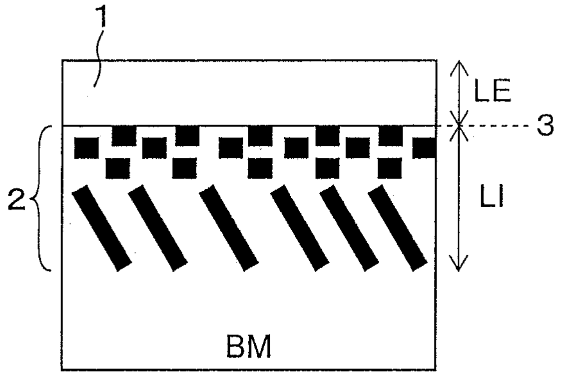
4. The austenitic Fe-Ni-Cr alloy according to claim 3, wherein the surface oxidation scale has a thickness of 10 to 100 μm.

5. The austenitic Fe-Ni-Cr alloy according to claim 3, wherein an internal oxide layer which is formed immediately below the surface oxidation scale comprises internal oxides containing at least one kind of Cr, Si, Mn, Al, Ti, and REM, and at the same time, an area ratio of the internal oxide layer occupies not less than 30% per 0.005 mm^2 immediately below the surface oxidation scale.

6. A method for production of the austenitic Fe-Ni-Cr alloy according to any one of claims 1 to 5, wherein

alloy compositions are adjusted by melting alloy raw materials and refining,
in the refining process, decarburizing is performed by blowing a mixed gas of oxygen and argon into melted alloy raw materials (fused alloy) so as to control nitrogen concentration to be not more than 0.03%, Cr reduction is performed, and then, aluminum, limestone and fluorite are added in the fused alloy so as to form CaO-SiO_2-Al_2O_3-MgO-F slag, oxygen concentration in the fused alloy is controlled to 0.0002 to 0.0030 mass%, and after that, raw material containing at least one of La, Ce, and Y is added, the fused alloy is casted so as to obtain a slab, and the slab is subjected to hot-rolling process.

Fig. 1



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2023/017180

A. CLASSIFICATION OF SUBJECT MATTER

C21C 7/00(2006.01)i; ***C21C 7/04***(2006.01)i; ***C22C 30/02***(2006.01)i; ***C22C 38/00***(2006.01)i; ***C22C 38/58***(2006.01)i; ***C23C 8/18***(2006.01)i
FI: C22C38/00 302Z; C22C38/58; C22C30/02; C23C8/18; C21C7/00 A; C21C7/04 D

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)

C21C7/00; C21C7/04; C22C30/02; C22C38/00; C22C38/58; C23C8/18

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

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2023
Registered utility model specifications of Japan 1996-2023
Published registered utility model applications of Japan 1994-2023

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2018/066579 A1 (NIPPON STEEL & SUMITOMO METAL CORP.) 12 April 2018 (2018-04-12)	1-6
A	JP 2014-031526 A (NIPPON STEEL & SUMITOMO METAL CORP.) 20 February 2014 (2014-02-20)	1-6
A	WO 2010/113843 A1 (SUMITOMO METAL INDUSTRIES, LTD.) 07 October 2010 (2010-10-07)	1-6

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

* Special categories of cited documents:	"T" 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 be of particular relevance	"X" 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
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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search **04 July 2023**	Date of mailing of the international search report **18 July 2023**
Name and mailing address of the ISA/JP **Japan Patent Office (ISA/JP)** **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2023/017180

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WO 2018/066579 A1	12 April 2018	US 2019/0284666 A1 EP 3524705 A1 CN 109790610 A KR 10-2019-0065352 A	
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- JP 2002256398 A **[0007]**
- WO 2018066579 A **[0007]**