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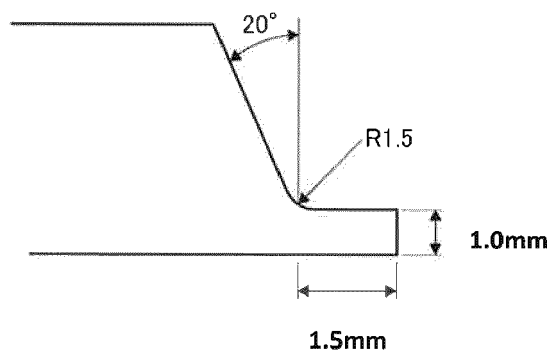
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(54) **NI-BASED ALLOY TUBE AND WELDED JOINT**

(57) A Ni-based alloy tube includes a chemical composition containing, in mass%, C: 0.005 to 0.080%, Si: 0.01 to 0.50%, Mn: 0.01 to 0.50%, P: 0.015% or less, S: 0.0001 to 0.0030%, Cr: 20.0 to 23.5%, Mo: 8.0 to 10.5%, Ti: 0.01 to 0.40%, N: 0.0010 to 0.0400%, Al: 0.01 to

0.40%, O: 0.0004 to 0.0100%, one or more elements selected from Nb and Ta, and Sn: 0 to 0.010%, with the balance: Ni and impurities, and satisfying $[0.0010 \leq S + 2O + 0.2Sn \leq 0.0180]$ and $[2.50 \leq Nb + Ta \leq 4.60]$.

Figure 1



Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to a Ni-based alloy tube and a welded joint.

BACKGROUND ART

10 **[0002]** In a chemical plant and a power plant, various kinds of plant equipment such as flue gas treatment equipment and seawater treatment equipment are installed. An inside of a plant is a harsh corrosive environment where substances accelerating corrosion, such as chlorides and hydrogen sulfide are present in a large amount. For this reason, materials used for plant equipment are required to have a strength as well as corrosion resistance. Therefore, as disclosed in Patent Documents 1 to 8, Ni-based alloys with enhanced corrosion resistance, which are assumed to be used for plant equipment, are developed.

LIST OF PRIOR ART DOCUMENTS

PATENT DOCUMENT

20 **[0003]**

Patent Document 1: JP54-110918A
 Patent Document 2: JP63-89637A
 Patent Document 3: JP2-156034A
 Patent Document 4: JP3-173732A
 Patent Document 5: JP5-271832A
 Patent Document 6: JP9-87786A
 Patent Document 7: JP10-30140A
 Patent Document 8: JP2012-72446A

SUMMARY OF INVENTION

TECHNICAL PROBLEM

35 **[0004]** Some kind of plant equipment is produced by constructing by welding. In such equipment, a weld bead shape may influence on corrosion behavior.

[0005] For example, some kind of heat exchanger consists of Ni-base alloy tubes serving as passage of coolant and constructed by butt-welding. When the heat exchanger is used, various kinds of corrosive fluid flow inside the tubes. At this point, if a height of an internal bead that is formed inside the tubes by welding, that is, a reinforcement of an internal bead is excessively high, the corrosive fluid accumulates and concentrates at a toe of weld, where a surface of the bead and a surface of a base metal intersect with each other. As a result, corrosion is liable to proceed at the toe of weld, which raises a problem.

[0006] On the other hand, if an amount of heat input during welding is reduced with an excessive decrease in a height of reinforcement intended, a butting surface between tubes is not melted completely, which makes it difficult to form a stable internal bead. As a result, a weld defect occurs, and corrosive fluid accumulates and concentrates in the weld defect, making corrosion liable to proceed, which raises a problem. However, Patent Documents 1 to 8 have no discussions about these problems.

[0007] Therefore, even when Ni-based alloy having high corrosion resistance is used as a material to produce tubes, it is difficult to form an internal bead having an appropriate shape during butt welding and making corrosion not liable to proceed between the tubes. In other words, a problem is that it is difficult to obtain a Ni-based alloy tube that allows an internal bead to be stably formed inside during welding and prevents a reinforcement with excessive height.

[0008] In view of the above, an objective of the present invention is to solve the problems described above and to provide a Ni-based alloy tube that allows an internal bead having good properties of its weldment to be formed stably, and a welded joint.

SOLUTION TO PROBLEM

[0009] The present invention is made to solve the above problems, and the gist of the present invention is the following

Ni-based alloy tube and welded joint.

(1) A Ni-based alloy tube having a chemical composition consisting of, in mass%:

C: 0.005 to 0.080%,
 Si: 0.01 to 0.50%,
 Mn: 0.01 to 0.50%,
 P: 0.015% or less,
 S: 0.0001 to 0.0030%,
 Cr: 20.0 to 23.5%,
 Mo: 8.0 to 10.5%,
 Ti: 0.01 to 0.40%,
 N: 0.0010 to 0.0400%,
 Al: 0.01 to 0.40%,
 O: 0.0004 to 0.0100%,
 one or more elements selected from Nb and Ta, and
 Sn: 0 to 0.010%, and

optionally,

Fe: 5.50% or less,
 Cu: 1.50% or less,
 Co: 1.50% or less,
 W: 1.00% or less,
 V: 0.40% or less,
 Ca: 0.0030% or less,
 Mg: 0.0030% or less,
 B: 0.0100% or less, and
 REM: 0.0100% or less,

with the balance: Ni and impurities, and
 satisfying Formulas (i) and (ii) below:

$$0.0010 \leq S + 2O + 0.2Sn \leq 0.0180 \quad (i)$$

$$2.50 \leq Nb + Ta \leq 4.60 \quad (ii)$$

where each symbol of an element in the formulas indicates a content of the element (mass%) contained in Ni-based alloy, and a content being zero means that the element is not contained.

(2) The Ni-based alloy tube according to (1) above, wherein on an internal surface of the Ni-based alloy tube, an arithmetic average roughness Ra of the tube in a longitudinal direction is 7.0 μm or less.

(3) The Ni-based alloy tube according to (1) or (2) above, wherein the chemical composition contains one or more elements selected from Cu and Co and satisfies Formula (iii) below:

$$0.01 \leq Cu + Co \leq 1.50 \quad (iii)$$

where each symbol of an element in the formulas indicates a content of the element (mass%) contained in Ni-based alloy, and a content being zero means that the element is not contained.

(4) A welded joint including the Ni-based alloy tube according to any one of (1) to (3) above.

ADVANTAGEOUS EFFECTS OF INVENTION

[0010] The present invention makes it possible to obtain a Ni-based alloy tube that allows an internal bead having good properties of a weldment to be formed stably.

BRIEF DESCRIPTION OF DRAWING

[0011] [Figure 1]

Figure 1 is a diagram illustrating a bevel shape in EXAMPLE.

DESCRIPTION OF EMBODIMENTS

[0012] The present inventors studied weldability of a Ni-based alloy tube and obtained the following findings (a) to (d).

(a) A shape of an internal bead of a Ni-based alloy tube formed during butt welding is influenced by contents of S and O contained in the tube. The present inventors revealed that, if the contents of S and O are small, the internal bead is not formed stably, and a butting surface partly remains unmelted.

On the other hand, if the contents of S and O are excessive, although the internal bead can be formed stably, a reinforcement of the internal bead becomes excessively high. Therefore, in this case, corrosive fluid accumulates in a vicinity of a bead, making corrosion liable to proceed. Hence, in order to allow an internal bead to be formed stably and prevent a reinforcement with excessive height, it is necessary to adjust the content of S and the content of O within their prescribed ranges.

(b) A possible reason that S and O have an influence on formation of a bead is as follows. S and O are surface-active elements and therefore strengthen inward convection in a molten pool during welding. As a result, welding heat is liable to be transmitted in a depth direction, which allows an internal bead to be formed stably. On the other hand, if S and O are contained excessively, a surface tension of molten metal is decreased excessively, which makes molten metal liable to suffer sagging. As a result, the internal bead is liable to have a convex shape where a shape of the internal bead excessively swells, (hereinafter, simply referred to as "convex shape"), and a height of reinforcement of the internal bead is liable to increase.

(c) Additionally, a shape of an internal bead is influenced by a surface roughness of an internal surface of the tube in a longitudinal direction. The present inventors revealed that, when a surface roughness is large, a height of reinforcement of an internal bead is increased, which makes an internal bead liable to have a convex shape. For this reason, it is desirable to control the surface roughness within a prescribed range. In particular, when a surface roughness of an internal surface of a tube in a longitudinal direction is large, molten metal is prevented from spreading in a width direction, which makes an internal bead have a convex shape, and a height of reinforcement of an internal bead is liable to increase.

(d) Moreover, the present inventors revealed that a shape of an internal bead is also influenced by a content of Sn. When Sn is contained, a penetration depth is increased, which allows an internal bead to be formed stably. On the other hand, if Sn is contained excessively, penetration becomes excessive, and an internal bead is liable to have a convex shape. A reason for this is considered that Sn vaporizes from a surface of a molten pool during welding and increases a degree of concentration of an arc. For this reason, when Sn is contained, it is necessary to control a content of Sn within a prescribed range and to make a relation among a content of S, a content of O, and the content of Sn satisfy a prescribed range so as to obtain an internal bead having an appropriate shape.

[0013] The present invention is made based on the findings described above. Requirements of the present invention will be described below in detail.

1. Chemical Composition of Alloy Tube

[0014] Reasons for limiting a content of each element are as follows. In the following description, a symbol "%" for each content means "mass%".

C: 0.005 to 0.080%

[0015] C has an effect of stabilizing a metal micro-structure. For this reason, a content of C is to be 0.005% or more. The content of C is to be preferably 0.008% or more, more preferably 0.010% or more, and still more preferably 0.012% or more. However, if C is contained excessively, C combines with Cr through weld thermal cycle to form carbide in grain boundaries in weld heat affected zone. As a result, Cr depleted zones are formed to develop in vicinities of the grain boundaries, decreasing corrosion resistance. For this reason, the content of C is set at 0.080% or less. The content of C is to be preferably 0.050% or less, more preferably 0.030% or less, and still more preferably 0.025% or less.

Si: 0.01 to 0.50%

[0016] Si has a deoxidation effect. For this reason, a content of Si is to be 0.01% or more. The content of Si is to be preferably 0.02% or more, and more preferably 0.03% or more. Still more preferably, the content of Si is to be 0.05% or more. However, if Si is contained excessively, a phase stability of the alloy is decreased, and a weld crack susceptibility of the alloy is increased. In addition, the excessive containing of Si may make it difficult for the internal bead to be formed stably. For this reason, the content of Si is to be 0.50% or less. The content of Si is to be preferably 0.48% or less, and more preferably 0.45% or less. Still more preferably, the content of Si is to be 0.43% or less.

Mn: 0.01 to 0.50%

[0017] As with Si, Mn has a deoxidation effect. In addition, Mn has an effect of increasing a phase stability of metal and makes no small contribution to stable formation of the internal bead. For this reason, a content of Mn is to be 0.01% or more. The content of Mn is to be preferably 0.03% or more, and more preferably 0.05% or more. Still more preferably, the content of Mn is to be 0.08% or more. However, if Mn is contained excessively, hot workability is decreased. For this reason, the content of Mn is to be 0.50% or less. The content of Mn is to be preferably 0.48% or less, and more preferably 0.45% or less. Still more preferably, the content of Mn is to be 0.40% or less.

P: 0.015% or less

[0018] P is contained in the Ni-based alloy as an impurity and significantly increases weld crack susceptibility. For this reason, a content of P is to be 0.015% or less. The content of P is to be preferably 0.013% or less, and more preferably 0.012% or less. The content of P is preferably reduced as much as possible, but an excessive reduction of the content of P increases production costs. For this reason, the content of P is to be preferably 0.001% or more, and more preferably 0.002% or more.

S: 0.0001 to 0.0030%

[0019] S is normally contained in the Ni-based alloy as an impurity, but in the alloy tube according to the present invention, S has an effect of increasing capability of forming the internal bead together with O during welding. For this reason, a content of S is to be 0.0001% or more. The content of S is to be preferably 0.0002% or more, and more preferably 0.0003% or more. However, if S is contained excessively, the internal bead is made to have a convex shape, and weld crack susceptibility is increased. For this reason, the content of S is to be 0.0030% or less. The content of S is to be preferably 0.0025% or less, and more preferably 0.0020% or less. Note that S is required to satisfy Formula (i) described below together with O and Sn.

Cr: 20.0 to 23.5%

[0020] Cr is an element that is essential in keeping corrosion resistance. In particular, Cr causes formation of a passivation film on a surface, increasing corrosion resistance under an acid environment of oxidative properties. For this reason, a content of Cr is to be 20.0% or more. The content of Cr is to be preferably 20.5% or more, more preferably 21.0% or more, and still more preferably 21.2% or more. However, if Cr is contained excessively, phase stability of metal is decreased. For this reason, the content of Cr is to be 23.5% or less. The content of Cr is to be preferably 23.3% or less, more preferably 23.0% or less, and still more preferably 22.8% or less.

Mo: 8.0 to 10.5%

[0021] Mo increases corrosion resistance under an environment where non-oxidizing acid and chloride are present. For this reason, a content of Mo is to be 8.0% or more. The content of Mo is to be preferably 8.2% or more, more preferably 8.5% or more, and still more preferably 8.7% or more. However, if Mo is contained excessively, phase stability of metal is decreased. Moreover, Mo is an expensive element, and thus production costs are increased. For this reason, the content of Mo is to be 10.5% or less. The content of Mo is to be preferably 10.3% or less, more preferably 10.0% or less, and still more preferably 9.8% or less.

Ti: 0.01 to 0.40%

[0022] Ti forms its carbide to contribute to strengthening and prevents or reduces formation of Cr carbide to mitigate deterioration in corrosion resistance of grain boundaries. For this reason, a content of Ti is to be 0.01% or more. The

content of Ti is to be preferably 0.05% or more, more preferably 0.08% or more, and still more preferably 0.10% or more. However, if Ti is contained excessively, carbide and carbo-nitride of Ti precipitate in a large quantity, decreasing ductility. For this reason, the content of Ti is to be 0.40% or less. The content of Ti is to be preferably 0.38% or less, more preferably 0.35% or less, and still more preferably 0.32% or less.

N: 0.0010 to 0.0400%

[0023] N contributes to phase stability of metal and has an effect of increasing pitting resistance. For this reason, a content of N is to be 0.0010% or more. The content of N is to be preferably 0.0020% or more, more preferably 0.0030% or more, and still more preferably 0.0040% or more. However, if N is contained excessively, nitride precipitates, decreasing ductility. For this reason, the content of N is to be 0.0400% or less. The content of N is to be preferably 0.0350% or less, and more preferably 0.0300% or less. Still more preferably, the content of N is to be 0.0250% or less.

Al: 0.01 to 0.40%

[0024] Al has a deoxidation effect. Al contributes to increase in oxidation resistance at high temperature. For this reason, a content of Al is to be 0.01% or more. The content of Al is to be preferably 0.02% or more, and more preferably 0.03% or more. Still more preferably, the content of Al is to be 0.05% or more. However, if Al is contained excessively, Al forms a brittle compound with Ni, decreasing hot workability. In addition, the excessive containing of Al may make it difficult for the internal bead to be formed stably. For this reason, the content of Al is to be 0.40% or less. The content of Al is to be preferably 0.35% or less, more preferably 0.30% or less, and still more preferably 0.28% or less.

O: 0.0004 to 0.0100%

[0025] O is normally contained in the Ni-based alloy as an impurity, but in the alloy tube according to the present invention, O has an effect of increasing capability of forming the internal bead together with S during welding. For this reason, a content of O is to be 0.0004% or more. The content of O is to be preferably 0.0006% or more, and more preferably 0.0008% or more. However, if O is contained excessively, the internal bead is made to have a convex shape, and hot workability is decreased. For this reason, the content of O is set at 0.0100% or less. The content of O is to be preferably 0.0080% or less, and more preferably 0.0060% or less. Note that O is required to satisfy Formula (i) described below together with S and Sn.

One or more elements selected from Nb and Ta: 2.50% or more and 4.60% or less in total

[0026] As with Ti, Nb and Ta both combine with carbon to form their carbides, contributing to strengthening and prevent or reduce formation of Cr carbide to mitigate deterioration in corrosion resistance of grain boundaries. For this reason, one or more elements selected from Nb and Ta need to be contained, and a total content of these elements need to satisfy the following Formula (ii).

$$2.50 \leq \text{Nb} + \text{Ta} \leq 4.60 \quad (\text{ii})$$

where each symbol of an element in the formula indicates a content of the element (mass%) contained in Ni-based alloy, and a content being zero means that the element is not contained.

[0027] If the middle value of Formula (ii), which is the total content of Nb and Ta, is less than 2.50%, it is not possible to obtain the effects of increasing strength and mitigating the deterioration in corrosion resistance of grain boundaries. Therefore, the middle value of Formula (ii) is to be 2.50% or more. The middle value of Formula (ii) is to be preferably 2.70% or more, and more preferably 3.00% or more.

[0028] On the other hand, if the middle value of Formula (ii) is more than 4.60%, carbides and carbo-nitrides of Nb and Ta precipitate in a large quantity, decreasing ductility. In addition, weld crack susceptibility is also increased. For this reason, the middle value of Formula (ii) is to be 4.60% or less, preferably 4.40% or less, and more preferably 4.20% or less.

[0029] In the chemical composition, in addition to the elements described above, Sn may be contained within the range described below.

Sn: 0 to 0.010%

[0030] Sn has an effect of increasing a penetration depth during welding, increasing a capability of forming the internal

bead. Therefore, it may be contained when necessary. However, if Sn is contained excessively, hot workability is decreased, and weld crack susceptibility is increased. In addition, the internal bead is liable to have a convex shape. For this reason, a content of Sn is to be 0.010% or less. The content of Sn is to be preferably 0.009% or less, and more preferably 0.008% or less. On the other hand, to obtain the effects described above, the content of Sn is to be preferably 0.001% or more, more preferably 0.002% or more, and still more preferably 0.003% or more. Note that Sn is required to satisfy Formula (i) described below together with S and O.

[0031] As described above, since S, O, and Sn effectively contribute to formation of an internal bead of the tube, the following Formula (i), which is a numerical relation among the content of S, the content of O, and the content of Sn, needs to be satisfied for the Ni-based alloy tube according to the present invention.

$$0.0010 \leq S + 2O + 0.2Sn \leq 0.0180 \quad (i)$$

where each symbol of an element in the formula indicates a content of the element (mass%) contained in Ni-based alloy, and a content being zero means that the element is not contained. When the content of Sn is less than 0.001%, Sn is treated as Sn = 0 in the above formula.

[0032] S and O are surface-active elements and have an action of strengthening inward convection in a molten pool during welding. In addition, Sn contributes to formation of an arc energizing path and has an effect of increasing a degree of concentration of an arc. Welding heat is thereby transmitted in a depth direction at a center of the molten pool. As a result, although these elements have an effect of stable formation of the internal bead, the middle value of Formula (i) being less than 0.0010% fails to provide this effect. Therefore, the middle value of Formula (i) is to be 0.0010% or more. The middle value of Formula (i) is to be preferably 0.0012% or more, and more preferably 0.0015% or more.

[0033] On the other hand, if the middle value of Formula (i) is more than 0.0180%, a surface tension of molten metal is decreased, or melting of the center of the molten pool is accelerated, which causes sagging. As a result, the internal bead is made to have a convex shape, and it is no longer possible to form the internal bead stably inside the tube. Therefore, the middle value of Formula (i) is to be 0.0180% or less. The middle value of Formula (i) is to be preferably 0.0175% or less, and more preferably 0.0170% or less.

[0034] In the chemical composition, in addition to the elements described above, Fe may be contained within the range described below.

Fe: 5.50% or less

[0035] Fe is useful for increasing hot workability. In addition, Fe contributes to reduction of an alloy cost. Therefore, it may be contained when necessary. However, if Fe is contained excessively, phase stability of metal is decreased. For this reason, a content of Fe is to be 5.50% or less. The content of Fe is to be preferably 5.30% or less, and more preferably 5.00% or less. On the other hand, to obtain the effects described above, the content of Fe is to be preferably 0.01% or more, more preferably 0.50% or more, and still more preferably 1.50% or more.

[0036] In the chemical composition, in addition to the elements described above, Cu and Co may be contained within the ranges described below.

One or more elements selected from Cu and Co: 1.50% or less in total

[0037] Cu and Co increase phase stability of metal and have an effect of increasing corrosion resistance under an environment where non-oxidizing acid and chloride are present. Therefore, one or more elements selected from Cu and Co may be contained when necessary. When contained, the chemical composition preferably satisfies the following Formula (iii).

$$0.01 \leq Cu + Co \leq 1.50 \quad (iii)$$

where each symbol of an element in the formula indicates a content of the element (mass%) contained in Ni-based alloy, and a content being zero means that the element is not contained.

[0038] If a middle value of Formula (iii), which is a total content of Cu and Co, is less than 0.01%, it becomes difficult to obtain the effects described above. Therefore, the middle value of Formula (iii) is to be preferably 0.01% or more, more preferably 0.02% or more, and still more preferably 0.03% or more. However, if the middle value of Formula (iii) is more than 1.50%, hot workability is decreased, and production costs are increased. Therefore, the middle value of Formula (iii) is to be preferably 1.50% or less, and more preferably 1.30% or less. Still more preferably, the middle value of Formula (iii) is to be 1.00% or less.

[0039] In the chemical composition, in addition to the elements described above, one or more elements selected from W, V, Ca, Mg, B, and REM may be contained within the ranges described below. Reasons for limiting a content of each element will be described.

W: 1.00% or less

[0040] W increases corrosion resistance under an environment where non-oxidizing acid and chloride are present. Therefore, it may be contained when necessary. However, if W is contained excessively, phase stability of metal is decreased. Moreover, the containing of W excessively increases production costs because W is an expensive element. For this reason, a content of W is to be 1.00% or less. The content of W is preferably 0.90% or less, and more preferably 0.80% or less. On the other hand, to obtain the effect described above, the content of W is to be preferably 0.01% or more, and more preferably 0.02% or more.

V: 0.40% or less

[0041] V combines with carbon to form its carbide, preventing or reducing formation of Cr carbide, so as to mitigate deterioration in corrosion resistance of grain boundaries. Therefore, it may be contained when necessary. However, if V is contained excessively, carbide and carbo-nitride of V precipitate in a large quantity, decreasing ductility. For that reason, the content of V is to be 0.40% or less. The content of V is to be preferably 0.35% or less, and more preferably 0.30% or less. On the other hand, to obtain the effect described above, the content of V is to be preferably 0.01% or more, and more preferably 0.02% or more.

Ca: 0.0030% or less

[0042] Ca has an effect of improving hot workability. Therefore, it may be contained when necessary. However, if Ca is contained excessively, Ca combines with oxygen, significantly decreasing cleanliness. As a result, hot workability is rather decreased. For this reason, a content of Ca is to be 0.0030% or less. The content of Ca is to be preferably 0.0020% or less, and more preferably 0.0010% or less. On the other hand, to obtain the effect described above, the content of Ca is to be preferably 0.0001% or more, and more preferably 0.0003% or more.

Mg: 0.0030% or less

[0043] As with Ca, Mg has an effect of improving hot workability. Therefore, it may be contained when necessary. However, if Mg is contained excessively, Mg combines with oxygen, significantly decreasing cleanliness. As a result, hot workability is rather decreased. For this reason, a content of Mg is to be 0.0030% or less. The content of Mg is to be preferably 0.0020% or less, and more preferably 0.0010% or less. On the other hand, to obtain the effect described above, the content of Mg is to be preferably 0.0001% or more, and more preferably 0.0003% or more.

B: 0.0100% or less

[0044] B segregates in grain boundaries at high temperature and has effects of strengthening the grain boundaries and increasing hot workability. Therefore, it may be contained when necessary. However, if B is contained excessively, weld crack susceptibility is increased. For this reason, a content of B is set at 0.0100% or less. The content of B is to be preferably 0.0080% or less, and more preferably 0.0060% or less. On the other hand, to obtain the effects described above, the content of B is to be preferably 0.0002% or more, and more preferably 0.0005% or more.

REM: 0.0100% or less

[0045] As with Ca and Mg, REM has an effect of improving hot workability in production. Therefore, it may be contained when necessary. However, if REM is contained excessively, REM combines with oxygen, significantly decreasing cleanliness. As a result, hot workability is rather decreased. For this reason, a content of REM is set at 0.0100% or less. The content of REM is to be preferably 0.0050% or less, and more preferably 0.0030% or less. On the other hand, to obtain the effect described above, the content of REM is to be preferably 0.0001% or more, and more preferably 0.0003% or more. Here, REM refers to Sc, Y, and lanthanoids, and the content of REM refers to the amount of these elements.

[0046] In the chemical composition of the Ni-based alloy according to the present invention, the balance is Ni and impurities. The term "impurities" as used herein means elements that are not added intentionally but are mixed in the Ni-based alloy in producing the Ni-based alloy industrially due to various factors such as raw materials and a production process, and that are allowed to be within ranges in which the impurities have no adverse effect on the present invention.

2. Internal Surface Roughness of Alloy Tube

[0047] An internal bead is formed when end portions of alloy tubes are welded together. To form a favorable internal bead, it is preferable to control, an arithmetic average roughness Ra on an internal surface of the alloy tube in a longitudinal direction. An internal surface roughness of the alloy tube herein refers to a surface roughness after a final process in a production process. In other words, although the internal surface roughness of the alloy tube fluctuates in a course of the production, a surface roughness in a middle of the production does not matter in obtaining an advantageous effect of the present invention, and it will suffice that the internal surface roughness of the tube in the longitudinal direction after the final process satisfies a range specified in the present invention.

[0048] On the internal surface of the Ni-based alloy tube, if the arithmetic average roughness Ra of the tube in the longitudinal direction is more than 7.0 μm , weld metal is hindered from wetting on the internal surface of the tube, and thus the weld metal resists spreading along a width direction, that is, a circumference of the tube. As a result, the internal bead is liable to have a convex shape, and a height of reinforcement is liable to increase. For this reason, on the internal surface of the Ni-based alloy tube, the arithmetic average roughness Ra of the tube in the longitudinal direction is to be preferably 7.0 μm or less. The arithmetic average roughness Ra is to be preferably 5.0 μm or less, and more preferably 3.0 μm or less. A lower limit value of the arithmetic average roughness Ra is not limited to a specific value; however, in many cases, the arithmetic average roughness Ra is normally 0.1 to 1.0 μm or more in a case where a production method described below is used.

[0049] Here, the arithmetic average roughness Ra is specified in JIS B 0601:2001 and can be measured by using a contact-type surface roughness instrument.

3. Welded Joint

[0050] A welded joint of Ni-based alloy tubes described above can be obtained by performing butt welding on tube ends of the Ni-based alloy tubes under predetermined conditions. The welded joint of the Ni-based alloy tubes includes weld metal which is to be a weldment by solidification, and base material portion. The base material portions each include a weld heat affected zone that is influenced by heat input of welding. The base material portion excluding the weld heat affected zone inherits the chemical composition, the surface roughness, and other properties of the Ni-based alloy tube described in Sections 1 and 2 described above. The weldment refers to the weld metal and the weld heat affected zone.

4. Production Method

[0051] A preferable production method for the Ni-based alloy tube according to the present invention will be described. The Ni-based alloy tube according to the present invention provides its advantageous effects irrespective of its production method as long as the Ni-based alloy tube has the requirement described above; nonetheless, the Ni-based alloy tube can be produced stably by a production method described below, for example.

4-1. Ni-Based Alloy Tube

[0052] First, a Ni-based alloy ingot being a starting material of the Ni-based alloy tube is produced. The Ni-based alloy ingot is preferably produced by melting an alloy having the chemical composition described above using an electric furnace, refining the alloy to remove impurities, and casting the alloy. Subsequently, the obtained ingot is preferably subjected to hot forging to be formed into a billet having a columnar shape. Thereafter, the obtained billet is worked to be shaped into a tube.

[0053] Specifically, the billet is preferably subjected to hot extrusion and then to cold rolling or cold drawing. Softening heat treatment and intermediate pickling may be performed in the middle of the working when necessary. Thereafter, the alloy tube is preferably subjected to solution treatment as heat treatment. After the solution treatment, pickling or working may be performed when necessary.

[0054] Here, in order to bring the arithmetic average roughness Ra of the internal surface of tube in the longitudinal direction to 7.0 μm or less, it is preferable to perform the following process. Specifically, the solution treatment is preferably performed under such conditions of heating in a temperature region of 950°C to 1230°C for 1 to 15 minutes and performing water cooling. Additionally, it is preferable to perform one of machining such as grinder processing and grinding, and shotblast or shotpeening treatment, on the internal surface of the tube.

[0055] Although the arithmetic average roughness Ra fluctuates in a course of the production, an advantageous effect of the present invention does not pertain to the surface roughness in the middle of the course and is influenced only by the surface roughness of the tube in the longitudinal direction after the final process.

4-2. Welded Joint of Ni-Based Alloy Tubes

[0056] A welded joint can be obtained by welding together end portions of Ni-based alloy tubes according to the present invention as starting materials. A method for the welding is not limited to a specific method; however, the welding can be performed by arc welding, for example. As a condition for performing arc welding, for example, a heat input is preferably set to be within the range from 4 to 20 kJ/cm. In addition, it is preferable to use Ar gas as shielding gas and back shielding gas during welding. A flow rate of the gas flowed to a welding location is preferably adjusted as appropriate.

[0057] A chemical composition of a welding material (filler material) to be used is not limited to a specific material, either; however, the chemical composition is preferably a composition described below. In other words, it is preferable for the composition to contain, in mass%, C: 0.150% or less, Si: 1.00% or less, Mn: 3.50% or less, P: 0.030% or less, S: 0.0001 to 0.0100%, Fe: 38.0% or less, Cu: 3.00% or less, Co: 15.0% or less, Cr: 14.0 to 26.0%, Mo: 17.0% or less, W: 4.5% or less, at least one of Nb and Ta: 4.20% or less in total, Ti: 1.50% or less, V: 0.35% or less, N: 0.0500% or less, Al: 1.50% or less, and O: 0.0004 to 0.0100%, with the balance being Ni and impurities, and to make a relation between contents of S and O satisfy Formula (a) shown below.

$$0.0010 \leq S + 2O \leq 0.0180 \quad (a)$$

where each symbol of an element in the formulas indicates a content of the element (mass%) contained in the welding material, and a content being zero means that the element is not contained.

[0058] The present invention will be described below more specifically with reference to examples, but the present invention is not limited to these examples.

EXAMPLE

[0059] Alloys having chemical compositions shown in Table 1 were melted and produced into ingots. Thereafter, the ingots were subjected to hot forging and hot rolling to have a thickness of 10 mm. Subsequently, scales formed on their surfaces were removed by pickling. At this point, arithmetic average roughnesses Ra of all steel types were about 10 μm. Thereafter, with a production process of an alloy tube assumed, cold rolling was performed while softening heat treatment and intermediate pickling were performed, by which 3-mm alloy plates were obtained.

[0060] Subsequently, the alloy plates were performed solution treatment that the alloy plates were retained in a hydrogen furnace at 1150°C for 10 minutes and cooled by water cooling. Thereafter, test plates each having a width of 50 mm and a length of 100 mm were cut from the alloy plates. For some of the test plates, shotpeening was conducted on only one side, assuming the internal surface of the alloy tube, as shown in Table 2. For the rest of test plates which were not subjected to the shotpeening, one side of test plates were machine-ground or polished 1 to 5 times using a whetstone with granularity of #40 or #60. In Table 2, for example, polishing (#40 × 1 time) indicates that a test plate was polished once using a whetstone with a granularity of #40.

[Table 1]

[0061]

Alloy type	Chemical Composition (mass%, Balance: Ni and impurities)																							Middle value of Formula (i)	Middle value of Formula (ii)	Middle value of Formula (iii)
	C	Si	Mn	P	S	Cr	Mo	Ti	N	Al	O	Nb	Ta	Sn	Fe	Cu	Co	W	V	Ca	Mg	B	REM			
A	0.018	0.15	0.20	0.010	0.0004	21.3	8.9	0.20	0.0095	0.12	0.0028	3.28	-	-	-	-	-	-	-	-	-	-	-	0.0060	3.28	-
B	0.017	0.19	0.18	0.011	0.0002	21.8	8.6	0.18	0.0070	0.09	0.0031	3.10	0.15	-	3.28	-	0.42	-	-	-	-	-	-	0.0064	3.25	0.42
C	0.029	0.02	0.05	0.012	0.0001	23.0	6.2	0.34	0.0031	0.30	0.0007	2.97	0.03	-	-	-	-	-	-	-	-	-	-	0.0015	3.00	-
D	0.010	0.44	0.47	0.013	0.0017	20.6	10.0	0.11	0.0288	0.03	0.0080	2.71	-	-	-	-	0.03	-	-	-	-	-	-	0.0137	2.71	0.03
E	0.048	0.08	0.45	0.009	0.0002	21.1	10.2	0.38	0.0145	0.02	0.0005	4.05	0.10	0.003	4.97	-	-	-	0.02	-	0.0003	-	-	0.0018	4.15	-
F	0.008	0.48	0.03	0.010	0.0019	23.4	8.5	0.05	0.0020	0.34	0.0070	3.38	-	-	1.52	0.14	0.86	0.12	-	0.0004	-	-	-	0.0159	3.38	1.00
G	0.033	0.32	0.25	0.015	0.0020	22.2	9.0	0.09	0.0340	0.22	0.0079	4.20	0.17	-	-	0.96	0.29	-	-	-	-	0.0002	-	0.0178	4.37	1.25
H	0.005	0.10	0.05	0.008	0.0003	21.6	9.2	0.25	0.0083	0.08	0.0004	-	2.72	-	0.50	-	-	-	-	-	-	0.0008	-	0.0011	2.72	-
I	0.020	0.02	0.30	0.010	0.0025	20.8	10.5	0.16	0.0189	0.02	0.0078	3.40	-	-	5.30	-	0.02	0.05	-	-	-	0.0045	-	0.0182	3.40	0.02
J	0.018	0.49	0.20	0.013	0.0001	23.3	8.8	0.10	0.0289	0.40	0.0004	3.10	0.05	-	-	-	-	-	-	-	-	-	-	0.0009	3.15	-
K	0.006	0.08	0.15	0.010	0.0015	20.2	9.1	0.32	0.0106	0.03	0.0086	3.38	-	-	2.70	0.40	1.05	-	-	-	-	-	-	0.0187	3.38	1.45
L	0.020	0.16	0.18	0.012	0.0006	20.8	9.2	0.22	0.0070	0.15	0.0030	2.85	-	0.006	-	-	-	-	-	-	-	-	-	0.0078	2.85	-
M	0.019	0.42	0.12	0.012	0.0015	21.0	9.0	0.25	0.0064	0.29	0.0069	2.90	0.07	0.010	-	0.12	0.38	-	-	0.0008	-	0.0010	-	0.0173	2.97	0.48
N	0.022	0.03	0.42	0.010	0.0001	21.2	8.8	0.21	0.0092	0.04	0.0004	3.12	0.04	0.004	0.85	0.45	-	0.10	-	-	0.0004	-	0.0004	0.0017	3.15	0.45
O	0.028	0.05	0.38	0.013	0.0003	22.1	9.5	0.19	0.0072	0.09	0.0072	3.21	-	0.013	-	-	0.04	-	-	-	-	-	-	0.0173	3.21	0.04
P	0.015	0.07	0.44	0.010	0.0010	21.9	9.2	0.20	0.0104	0.08	0.0060	2.98	0.32	0.007	-	0.12	-	-	-	-	-	-	-	0.0184	3.30	0.12
Q	0.020	0.45	0.04	0.010	0.0001	22.3	9.1	0.25	0.0065	0.31	0.0003	3.05	-	0.001	0.90	-	-	-	0.05	-	-	-	-	0.0009	3.05	-

0.0010 ≤ S + 2O ≤ 0.0180 (i)

2.50 ≤ Nb + Ta ≤ 4.60 (ii)

0.01 ≤ Cu + Co ≤ 1.50 (iii)

The underlined indicates that the value fell out of the range defined in the present invention.

[Table 2]

[0062]

Test piece	Alloy type	Condition of production	Property
		Treatment of back-side of plate	Arithmetic average roughness Ra (μm)
A1	A	Shotpeening	1.9
A2		Machine grinding	6.2
A3		Polishing (#40 $\times$ 1 time)	9.0 **
A4		Polishing (#40 $\times$ 2 times)	7.2 **
A5		Polishing (#60 $\times$ 1 time)	6.6
A6		Polishing (#60 $\times$ 2 times)	5.4
A7		Polishing (#60 $\times$ 3 times)	2.7
A8		Polishing (#60 $\times$ 4 times)	1.7
A9		Polishing (#60 $\times$ 5 times)	1.0
B1	B	Shotpeening	2.1
B2		Machine grinding	6.5
B3		Polishing (#40 $\times$ 1 time)	9.1 **
B4		Polishing (#40 $\times$ 2 times)	7.4 **
B5		Polishing (#60 $\times$ 1 time)	6.8
B6		Polishing (#60 $\times$ 2 times)	5.2
B7		Polishing (#60 $\times$ 3 times)	2.7
B8		Polishing (#60 $\times$ 4 times)	1.4
B9		Polishing (#60 $\times$ 5 times)	1.2
C1	C	Shotpeening	2.2
D1	D	Shotpeening	1.9
E1	E	Shotpeening	2.1
F1	F	Shotpeening	1.8
G1	G	Shotpeening	19
H1	H	Shotpeening	1.9
I1	I *	Shotpeening	2.1
J1	J *	Shotpeening	2.2
K1	K *	Shotpeening	2.0

(continued)

Test piece	Alloy type	Condition of production	Property
		Treatment of back-side of plate	Arithmetic average roughness Ra (μm)
L1	L	Shotpeening	2.0
L2		Machine grinding	6.3
L3		Polishing (#40 $\times$ 1 time)	8.9 **..
L4		Polishing (#40 $\times$ 2 times)	7.4 **
L5		Polishing (#60 $\times$ 1 time)	6.5
L6		Polishing (#60 $\times$ 2 times)	5.7
L7		Polishing (#60 $\times$ 3 times)	2.6
L8		Polishing (#60 $\times$ 4 times)	1.5
L9		Polishing (#60 $\times$ 5 times)	1.0
M1	M	Shotpeening	2.1
N1	N	Shotpeening	2.1
O1	O *	Shotpeening	1.9
P1	P *	Shotpeening	1.8
Q1	Q *	Shotpeening	2.0
* indicates that the condition fell out of the range defined in the present invention. ** indicates that the condition fell out of the preferable range defined in the present invention.			

[0063] An arithmetic average roughness of each test plate was measured using a contact type roughness gauge. In addition, two test plates of each of the alloy types were prepared, and an end face of each test plates in a rolling direction was beveled as illustrated in Figure 1. Beveled end faces of these test plates were butted against each other and subjected to root pass welding using a filler material having a chemical composition shown in Table 3 and an outer diameter of 1.0 mm, by which a welded joint was obtained. In the welding, a heat input was set at about 5 kJ/cm, and Ar gas was used as shielding gas and back shielding gas and was flowed to a welding location at a flow rate of 10 L/min.

[Table 3]

[0064]

Table 3

Chemical Composition (mass%, Balance: Ni and impurities)												
C	Si	Mn	P	S	Cr	Mo	Ti	N	Al	O	Nb	Ta
0.010	0.04	0.03	0.004	0.0011	22.0	8.4	0.28	0.0015	0.20	0.0025	3.37	0.021
											Others	S+2S
											Fe:0.30, Cu:0.04	0.0061

[0065] Of the obtained welded joints, welded joints each of which a back bead was formed across an overall length of its weld line were determined to have no problem in capability of forming an internal bead of the alloy tube and were rated as "Good". Of such welded joints, welded joints each of which a width of a back bead was 2 mm or more across an overall length of its weld line were rated as "Excellent", and welded joints each of which a width of a back bead formed was less than 2 mm but 1 mm or more were rated as "Acceptable". A back bead in this example corresponds to an internal bead that is formed when the weld is made from the outside of the alloy tube.

[0066] Thereafter, three transverse sections were made to appear from each welded joint, and welded joints each of which the sections all had a back bead height of 1.0 mm or less were determined to be good in shape of an internal bead of an alloy tube and were rated as "Good". Of such welded joints, welded joints each of which the sections all had a back bead height of 0.8 mm or less were rated as "Excellent", and the other welded joints were rated as "Acceptable". Results are collectively shown in Table 4 below.

[Table 4]

[0067]

Table 4

Test piece	Alloy type	Welded joint		
		Capability of forming back bead	Shape of back bead	
A1	A	Good (Excellent)	Good (Excellent)	Inventive example
A2		Good (Excellent)	Good (Excellent)	
A3		Good (Excellent)	Good (Acceptable)	
A4		Good (Excellent)	Good (Acceptable)	
A5		Good (Excellent)	Good (Excellent)	
A6		Good (Excellent)	Good (Excellent)	
A7		Good (Excellent)	Good (Excellent)	
A8		Good (Excellent)	Good (Excellent)	
A9		Good (Excellent)	Good (Excellent)	
B1	B	Good (Excellent)	Good (Excellent)	
B2		Good (Excellent)	Good (Excellent)	
B3		Good (Excellent)	Good (Acceptable)	
B4		Good (Excellent)	Good (Acceptable)	
B5		Good (Excellent)	Good (Excellent)	
B6		Good (Excellent)	Good (Excellent)	
B7		Good (Excellent)	Good (Excellent)	
B8		Good (Excellent)	Good (Excellent)	
B9		Good (Excellent)	Good (Excellent)	
C1	C	Good (Excellent)	Good (Excellent)	
D1	D	Good (Excellent)	Good (Excellent)	
E1	E	Good (Excellent)	Good (Excellent)	
F1	F	Good (Excellent)	Good (Excellent)	
G1	G	Good (Excellent)	Good (Acceptable)	
H1	H	Good (Acceptable)	Good (Excellent)	

(continued)

Test piece	Alloy type	Welded joint		
		Capability of forming back bead	Shape of back bead	
I1	I *	Good (Excellent)	<u>Bad</u>	Comparative example
J1	J *	<u>Bad</u>	Good (Excellent)	
K1	K *	Good (Excellent)	<u>Bad</u>	
L1	L	Good (Excellent)	Good (Excellent)	Inventive example
L2		Good (Excellent)	Good (Excellent)	
L3		Good (Excellent)	Good (Acceptable)	
L4		Good (Excellent)	Good (Acceptable)	
L5		Good (Excellent)	Good (Excellent)	
L6		Good (Excellent)	Good (Excellent)	
L7		Good (Excellent)	Good (Excellent)	
L8		Good (Excellent)	Good (Excellent)	
L9		Good (Excellent)	Good (Excellent)	
M1	M	Good (Excellent)	Good (Excellent)	
N1	N	Good (Excellent)	Good (Excellent)	
O1	O *	Good (Excellent)	<u>Bad</u>	Comparative example
P1	P *	Good (Excellent)	<u>Bad</u>	
Q1	Q *	Bad	Good (Excellent)	
* indicates that the condition fell out of the range defined in the present invention. The underlined indicates that the property fell out of the target property in the present invention.				

[0068] Test pieces made of alloy types A to H and L to N all satisfied the specifications according to the present invention, and their capabilities of forming a back bead and shapes of their back beads were good. Of these, the test piece N1 made of the alloy type N satisfied the range specified by Formula (i), and therefore, its capability of forming a back bead and a height of its back bead were both satisfactory.

[0069] In contrast, for both of test pieces I1 and K1 made of the alloy types I and K, their contents of S, O, and Sn did not satisfy Formula (i) and were higher than the respective specified ranges. Therefore, sagging of its molten metal was significant, and a height of its back bead did not satisfy a target of the height. For a test piece J1 made of the alloy type J, a relation between its contents of S and O did not satisfy Formula (i), and the contents were lower than the respective specified ranges. Therefore, melting in a plate thickness direction was not sufficient, and a capability of forming the back bead as targeted was not obtained.

[0070] For test pieces O1 and P1 made of the alloy types O and P, their contents of Sn exceeded the specified range, or their contents of S, O and Sn were higher than the respective ranges specified by Formula (i). Therefore, sagging of its molten metal was large, and a back bead height as targeted was not satisfied. A test piece Q1 made of the alloy type Q, its contents of S, O, and Sn did not satisfy Formula (i). Therefore, melting in a plate thickness direction was not sufficient, and a capability of forming the back bead did not satisfy a target of the capability.

INDUSTRIAL APPLICABILITY

[0071] The present invention makes it possible to obtain a Ni-based alloy tube that allows an internal bead to be formed stably during butt welding and prevents a reinforcement with excessive height.

Claims

1. A Ni-based alloy tube having a chemical composition consisting of, in mass%:

C: 0.005 to 0.080%,
 Si: 0.01 to 0.50%,
 Mn: 0.01 to 0.50%,
 P: 0.015% or less,
 S: 0.0001 to 0.0030%,
 Cr: 20.0 to 23.5%,
 Mo: 8.0 to 10.5%,
 Ti: 0.01 to 0.40%,
 N: 0.0010 to 0.0400%,
 Al: 0.01 to 0.40%,
 O: 0.0004 to 0.0100%,
 one or more elements selected from Nb and Ta, and
 Sn: 0 to 0.010%, and

optionally,

Fe: 5.50% or less,
 Cu: 1.50% or less,
 Co: 1.50% or less,
 W: 1.00% or less,
 V: 0.40% or less,
 Ca: 0.0030% or less,
 Mg: 0.0030% or less,
 B: 0.0100% or less, and
 REM: 0.0100% or less,
 with the balance: Ni and impurities, and

satisfying Formulas (i) and (ii) below:

$$0.0010 \leq S + 2O + 0.2Sn \leq 0.0180 \quad (i)$$

$$2.50 \leq Nb + Ta \leq 4.60 \quad (ii)$$

where each symbol of an element in the formulas indicates a content of the element (mass%) contained in Ni-based alloy, and a content being zero means that the element is not contained.

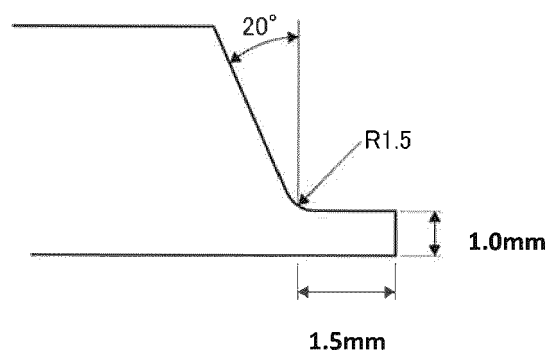
2. The Ni-based alloy tube according to claim 1, wherein on an internal surface of the Ni-based alloy tube, an arithmetic average roughness Ra of the tube in a longitudinal direction is 7.0 μm or less.
3. The Ni-based alloy tube according to claim 1 or 2, wherein the chemical composition contains one or more elements selected from Cu and Co and satisfies Formula (iii) below:

$$0.01 \leq Cu + Co \leq 1.50 \quad (iii)$$

where each symbol of an element in the formulas indicates a content of the element (mass%) contained in Ni-based alloy, and a content being zero means that the element is not contained.

4. A welded joint including the Ni-based alloy tube according to any one of claims 1 to 3.

Figure 1





EUROPEAN SEARCH REPORT

Application Number
EP 21 17 5393

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	WO 2019/107456 A1 (NIPPON STEEL CORP) 6 June 2019 (2019-06-06)	1-4	INV. C22C19/05 C22F1/10
Y	* the whole document * -& EP 3 719 165 A1 (NIPPON STEEL CORP [JP]) 7 October 2020 (2020-10-07) * paragraph [0001] * * paragraph [0002] * * paragraph [0055] - paragraph [0069] * * paragraph [0091] * * page 23, paragraph 0141; example 1; table 1 * * page 28, paragraph 0155; example 1; table 3 * * page 34, paragraph 0167; example 3; table 5 * * page 38, paragraph 0174; example 4; table 7 * * claim 1 * * claim 6 *	1	
Y	----- US 3 160 500 A (LOUIS EISELSTEIN HERBERT ET AL) 8 December 1964 (1964-12-08) * column 4, lines 67-74 * * examples 1,3; table I *	1,2,4	TECHNICAL FIELDS SEARCHED (IPC) C22C C22F
Y	----- DE 10 2013 214464 A1 (EYL JOHANNES [DE]) 29 January 2015 (2015-01-29) * pages 13,15; example INCONEL 625; table 2 *	1,2,4	
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 28 September 2021	Examiner Ugarte, Eva
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 21 17 5393

5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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28-09-2021

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2019107456 A1	06-06-2019	CA 3082754 A1	06-06-2019
		CN 111417739 A	14-07-2020
		EP 3719165 A1	07-10-2020
		JP W02019107456 A1	26-11-2020
		KR 20200087256 A	20-07-2020
		US 2020392612 A1	17-12-2020
		WO 2019107456 A1	06-06-2019

EP 3719165 A1	07-10-2020	CA 3082754 A1	06-06-2019
		CN 111417739 A	14-07-2020
		EP 3719165 A1	07-10-2020
		JP W02019107456 A1	26-11-2020
		KR 20200087256 A	20-07-2020
		US 2020392612 A1	17-12-2020
		WO 2019107456 A1	06-06-2019

US 3160500 A	08-12-1964	GB 955459 A	15-04-1964
		US 3160500 A	08-12-1964

DE 102013214464 A1	29-01-2015	NONE	

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 54110918 A [0003]
- JP 63089637 A [0003]
- JP 2156034 A [0003]
- JP 3173732 A [0003]
- JP 5271832 A [0003]
- JP 9087786 A [0003]
- JP 10030140 A [0003]
- JP 2012072446 A [0003]