(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 3 216 888 A1

(12) EUROPEAN PATENT APPLICATION

published in accordance with Art. 153(4) EPC

(43) Date of publication:
13.09.2017 Bulletin 2017/37

(21) Application number: **15857850.0**

(22) Date of filing: **16.10.2015**

(51) Int Cl.:
C22C 38/00 $^{(2006.01)}$ ***C22C 38/58*** $^{(2006.01)}$

(86) International application number:
PCT/JP2015/079342

(87) International publication number:
WO 2016/072244 (12.05.2016 Gazette 2016/19)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
MA

(30) Priority: **05.11.2014 JP 2014225576**

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(54) STAINLESS STEEL MATERIAL FOR DIFFUSION BONDING

(57) Provided is a stainless steel material suitable for diffusion bonded moldings in which diffusion bondability has been further improved without being affected by the extent of surface roughness. The present invention is a stainless steel material for diffusion bonding in which the metal structure before diffusion bonding has a multi-phase structure obtained from two or more of a ferrite phase, a martensite phase and an austenite phase, wherein: the mean crystal grain diameter in the multi-phase structure is not more than 20 μm; γmax represented by formula (a) is 10-90; and creep elongation when a 1.0 MPa load is applied at 1000°C for 0.5 h is at least 0.2%.

$$\gamma\mathrm{max}=420\mathrm{C}-11.5\mathrm{Si}+7\mathrm{Mn}+23\mathrm{Ni}-11.5\mathrm{Cr}-12\mathrm{Mo}+9\mathrm{Cu}-49\mathrm{Ti}-47\mathrm{Nb}-52\mathrm{Al}+470\mathrm{N}+189 \quad \cdots \text{ Formula (a)}$$

The element notations in formula (a) represent the contents (mass%) of the respective elements.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a dual-phase stainless steel material used in a molding, which is allowed to undergo diffusion bonding.

BACKGROUND ART

[0002] One method of bonding stainless steel materials to each other includes a diffusion bonding method. A stainless steel diffusion bonded product assembled by diffusion bonding has been applied in various applications such as heat exchangers, machine components, fuel cell components, home appliance components, plant components, ornament constituent members, and building materials. The diffusion bonding method includes an "insert material inserting method" of inserting an insert material into a bonding interface, and performing bonding by solid phase diffusion or liquid phase diffusion; and a "direct method" of directly bringing surfaces of both stainless steel materials into contact with each other, and performing diffusion bonding.

[0003] The insert material inserting method is advantageous in that it is capable of realizing certain diffusion bonding in a relatively simple manner. However, this method becomes disadvantageous as compared with a direct method for the following reasons. That is, an insert material is used, thus leading to an increase in costs, and also a bonding portion is formed of metal which is different from that forms a base material, thus leading to deterioration of corrosion resistance. On the other hand, it is commonly said to be difficult for the direct method to obtain sufficient bonding strength as compared with the insert material inserting method. However, this direct method includes the possibility to become advantageous in that it can reduce production costs, so that various methods have been studied. For example, Patent Document 1 discloses technology in which the amount of S in a stainless steel is set at 0.01% by weight or less and also diffusion bonding is performed in a non-oxidizing atmosphere at a predetermined temperature, thereby avoiding deformation of the material, thus leading to an improvement in diffusion bondability of a stainless steel material. Patent Document 2 discloses a method using a stainless steel foil material whose surface is imparted with unevenness by a pickling treatment. Patent Document 3 discloses a method using, as a material to be bonded, a stainless steel whose Al content is suppressed so that an alumina film, which causes inhibition of diffusion bonding, is less easily to be formed during diffusion bonding. Patent Document 4 discloses a method in which diffusion is promoted using a stainless steel foil imparted with deformation by cold working. Patent Documents 5 and 6 describe a ferritic stainless steel for direct diffusion bonding, the component composition of which is optimized.

[0004]

Patent Document 1: Japanese Unexamined Patent Application, Publication No. S62-199277
Patent Document 2: Japanese Unexamined Patent Application, Publication No. H02-261548
Patent Document 3: Japanese Unexamined Patent Application, Publication No. H07-213918
Patent Document 4: Japanese Unexamined Patent Application, Publication No. H09-279310
Patent Document 5: Japanese Unexamined Patent Application, Publication No. H09-99218
Patent Document 6: Japanese Unexamined Patent Application, Publication No. 2000-303150
Patent Document 7: Japanese Unexamined Patent Application, Publication No. 2013-103271
Patent Document 8: Japanese Unexamined Patent Application, Publication No. 2013-173181
Patent Document 9: Japanese Unexamined Patent Application, Publication No. 2013-204149
Patent Document 10: Japanese Unexamined Patent Application, Publication No. 2013-204150

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

[0005] The above-mentioned bonding technology enabled implementation of diffusion bonding of a stainless steel material even when using a direct method. However, from the industrial point of view, the direct method is yet to be taken root as the mainstream of a diffusion bonding method of the stainless steel material. The main reason is the fact that it is difficult to achieve both two issues, for example, security of reliability in the bonding portion, such as bonding strength or adhesiveness, and suppression of a load in the production, such as bonding device or bonding time. According to conventional technical knowledge, in order that the bonding portion to be produced by the direct method, there is a need to employ a step requiring a large production load, such as a step in which a bonding temperature is set at high temperature of higher than 1,100°C, or a step in which high surface pressure is imparted by hot press, HIP, or the like, so that it was impossible to avoid an increase in costs due to the step. When an attempt is made to carry out diffusion bonding of a stainless steel material by the direct method under the same workload as in a conventional insert material inserting method, it is difficult to sufficiently secure reliability of the bonding portion in the current situation.

[0006] Thus, there has been proposed a method for producing a diffusion bonded product by a direct method, which can be carried out under the same workload as in a conventional insert material inserting method without applying special high-temperature heating or high surface pressure by making use of a driving force when a ferrite phase is transformed into an austenite phase during diffusion bonding (Patent Document 7) or a driving force of crystal grain growth (Patent Document 8). There has also been proposed a method in which an amount of a surface oxide of a stainless steel material to be allowed to undergo diffusion bonding is reduced as much as possible, thereby enhancing diffusion bondability (Patent Documents 9 and 10). To secure good bondability, there is a need for these methods to regulate surface roughness before bonding of a stainless steel material to be used. Therefore, there is a need to further improve bondability in a stainless steel material to be used in a diffusion bonded product.

[0007] An object of the present invention is to provide a stainless steel material suitable for diffusion bonded molding, diffusion bondability of which is further improved without being influenced by the extent of surface roughness. Means for Solving the Problems

[0008] The present inventors have found that, by controlling an average crystal grain size before diffusion bonding, an amount of γmax, and creep elongation of a dual-phase stainless steel material having a dual-phase structure composed of at least two phases of a ferrite phase, a martensite phase, and an austenite phase, good diffusion bondability can be obtained without being influenced by surface roughness of the steel material. Thus, the present invention has been completed as a stainless steel material for diffusion bonding. Specifically, the present invention provides the followings.

[0009]

(1) The present invention is directed to a dual-phase stainless steel material for diffusion bonding, a metal structure before diffusion bonding having a dual-phase structure composed of at least two phases of a ferrite phase, a martensite phase, or an austenite phase, wherein the dual-phase structure has an average crystal grain size of 20 μm or less, γmax represented by the formula (a) mentioned below is 10 to 90, and creep elongation is 0.2% or more when a load of 1.0 MPa is applied at 1,000°C for 0.5 hour:

$$\gamma\mathrm{max} = 420\mathrm{C} - 11.5\mathrm{Si} + 7\mathrm{Mn} + 23\mathrm{Ni} - 11.5\mathrm{Cr} - 12\mathrm{Mo} + 9\mathrm{Cu} - 49\mathrm{Ti} - 47\mathrm{Nb} - 52\mathrm{Al} + 470\mathrm{N} + 189 \ldots \text{Formula (a)}$$

where an element symbol in the formula (a) mentioned above denotes the content (% by mass) of each element.

(2) The present invention is directed to the stainless steel material for diffusion bonding according to (1), including, in % by mass: C: 0.2% or less, Si: 1.0% or less, Mn: 3.0% or less, P: 0.05% or less, S: 0.03% or less, Ni: 10.0% or less, Cr: 10.0 to 30.0%, N: 0.3% or less, Ti: 0.15% or less, and Al: 0.15% or less, with the remainder being Fe and inevitable impurities, wherein the total amount of Ti and Al is 0.15% or less.

(3) The present invention is directed to the stainless steel material for diffusion bonding according to (1) or (2), further including, in % by mass: one or two or more elements of Nb: 4.0% or less, Mo: 0.01 to 4.0%, Cu: 0.01 to 3.0%, and V: 0.03 to 0.15%.

(4) The present invention is directed to the stainless steel material for diffusion bonding according to any one of (1) to (3), further including, in % by mass: B: 0.0003 to 0.01%.

Effects of the Invention

[0010] According to the present invention, a dual-phase stainless steel having a dual-phase structure composed of at least two phases of a ferrite phase, a martensite phase, and an austenite phase is provided with an average crystal grain size and γmax before diffusion bonding, and creep elongation at a bonding temperature in an optimum range, whereby, a stainless steel material having excellent diffusion bondability is provided, thus providing a diffusion bonded molding which exhibits a good bonding interface. The total content of Ti and Al is suppressed, thereby obtaining a diffusion bonded molding having improved diffusion bondability.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] Fig. 1 is a drawing showing a measurement test piece used in a bondability test.

PREFERRED MODE FOR CARRYING OUT THE INVENTION

[0012] Embodiments of the present invention will be described below. The present invention is not limited to the description thereof.

[0013] It is considered that diffusion bonding by a direct method of a stainless steel material is completed by simultaneous proceeding of three types of processes, for example, a process (i) in which unevenness of a bonding surface undergoes deformation leading to adhesion, thus increasing a bonding area of the bonded position, a process (ii) in which a surface oxide film of the steel material before bonding disappears at the adhered position, and a process (iii) in which a residual gas in voids as the unbonded portion reacts with a base material, according to a conventional technique.

[0014] Heretofore, the present inventors have studied so as to avoid deterioration of productivity, which creates an industrial obstacle, by regulating a base material component, components included in a passive film, and surface roughness of a bonding surface, focusing attention on the process (ii) mentioned above. However, it is sometimes difficult to secure industrially stable bondability even when the step (ii) mentioned above is controlled. Therefore, numerous studies have been performed on a steel material for obtaining stable bondability considering the step (i) mentioned above. As a result, it has been found that, when a stainless steel to be allowed to undergo diffusion bonding is a dual-phase stainless steel having a dual-phase structure, it is extremely effective to reduce a crystal grain size before diffusion bonding.

[Dual-Phase Structure]

[0015] Stainless steels are commonly classified into an austenitic stainless steel, a ferritic stainless steel, a martensitic stainless steel, and the like based on a metal structure at normal temperature. A "dual-phase structure" of the present invention has a metal structure composed of at least two phases of a ferrite phase, a martensite phase, and an austenite phase. The "dual-phase stainless steel material" of the present invention means a steel which has such a dual-phase structure, and exhibits an austenitic-ferritic two-phase structure within a bonding temperature range. Stainless steels classified into a ferritic stainless steel and a martensitic stainless steel are sometimes included in such a two-phase stainless steel.

[0016] In the present invention, in order to realize diffusion bonding by a direct method at low temperature under low surface pressure, a dual-phase stainless steel having a dual-phase structure composed of at least two phases of a ferrite phase, a martensite phase, and an austenite phase is used as a stainless steel material to be allowed to undergo diffusion bonding. Regarding this stainless steel, within a temperature range where diffusion bonding proceeds, a ferrite phase and a martensite phase are partially transformed into an austenite phase to form a two-phase structure composed of an austenite phase and a ferrite phase. There will easily take place creep deformation which is considered to cause grain boundary sliding as a result of maintenance of a fine structure due to suppression of crystal grain growth of each phase in the two-phase structure at high temperature. As a result, easy deformation is promoted at the unevenness portion of a bonding surface, leading to an increase in a bonding area of the bonded portion, thus enabling diffusion bonding by a direct method at low temperature under low surface pressure.

[0017] The dual-phase stainless steel material of the present invention can be used as both or one of stainless steel materials which are directly brought into contact with each other and integrated by diffusion bonding. It is possible to apply, as a mating material to be integrated, in addition to the stainless steel material of the present invention, other types of two-phase steels, types of austenitic steels in which an austenite single-phase is formed within a heating range of diffusion bonding, types of ferritic steels in which a ferrite single-phase is formed within the heating range, and the like.

[Component Composition]

[0018] In the dual-phase stainless steel which is an application object in the present invention, there is no need to be particular about component elements other than Ti and Al from the viewpoint of diffusion bondability, and it is possible to employ various component compositions according to the uses. The present invention is directed to an austenitic-ferritic two-phase structure within a temperature range where diffusion bonding proceeds, so that there is a need to employ a steel having a component composition in which γmax represented by the formula (a) mentioned below satisfies a range of 10 to 90. It is possible to exemplify, as a specific component composition range, the followings.

[0019] Component composition including, in % by mass: C: 0.2% or less, Si: 1.0% or less, Mn: 3.0% or less, P: 0.05% or less, S: 0.03% or less, Ni: 10.0% or less, Cr: 10.0 to 30.0%, N: 0.3% or less, Ti: 0.15% or less, and Al : 0.15% or less, with the remainder being Fe and inevitable impurities, wherein the total amount of Ti and Al is 0.15% or less.

[0020] Component composition further comprising, in % by mass: one or two or more elements of Nb: 4.0% or less, Mo: 0.01 to 4.0%, Cu: 0.01 to 3.0%, and V: 0.03 to 0.15%. Component composition further including, in % by mass: B: 0.0003 to 0.01%.

[0021] Components included in the stainless steel material will be described below.

[0022] C improves strength and hardness of a steel by solid solution strengthening. Meanwhile, an increase in C content causes deterioration of workability and toughness of the steel, so that the C content is preferably 0.2% by mass or less, and more preferably 0.08% by mass or less.

[0023] Si is an element used for deoxidation of the steel. Meanwhile, excessive Si content causes deterioration of toughness and workability of the steel. Thus, a firm surface oxide film is formed to inhibit diffusion bondability. Therefore, the Si content is preferably 1.0% by mass or less, and more preferably 0.6% by mass or less.

[0024] Mn is an element which improves high-temperature oxidation properties. Meanwhile, excessive Mn content allows the steel to undergo work hardening, leading to deterioration of cold workability of the steel. Therefore, the Mn content is preferably 3.0% by mass or less.

[0025] P is an inevitable impurity element and enhances intergranular corrosion properties and also causes deterioration of toughness of the steel. Therefore, the P content is preferably 0.05% by mass or less, and more preferably 0.03% by mass or less.

[0026] S is an inevitable impurity element and causes deterioration of hot workability of the steel. Therefore, the S content is preferably 0.03% by mass or less.

[0027] Ni is an austenite formation element and has a function of improving corrosion resistance of the steel in a reducing acid environment. Meanwhile, excessive Ni content makes an austenite phase stable, thus failing to suppress the growth of a ferrite crystal, so that a stable austenite single-phase is formed to suppress the growth of the ferrite crystal. Therefore, the Ni content is preferably 10.0% or less.

[0028] Cr is an element which forms a passive film to impart corrosion resistance. The Cr content of less than 30.0% by mass does not exert a sufficient effect of imparting corrosion resistance. The Cr content exceeding 10.0% by mass causes deterioration of workability. Therefore, the Cr content is preferably 10.0 to 30.0% by mass.

[0029] N is an inevitable impurity element and causes deterioration of cold workability, so that the content thereof is preferably 0.3% by mass or less.

[0030] Ti has a function of fixing C and N and is therefore an element effective in improving corrosion resistance and workability. Al is often added as a deoxidizing agent. Meanwhile, Ti and Al are easily oxidizable elements, so that Ti oxide and Al oxide included in an oxide film on a surface of the steel material are less likely to be reduced in a heat treatment of vacuum diffusion bonding. Therefore, numerous Ti oxide or Al oxide may cause prevention of proceeding of the process (ii) mentioned above during diffusion bonding, so that the Ti content is preferably 0.15% by mass or less, while the Al content is preferably 0.15% by mass or less, and more preferably 0.05% by mass. The total content of Ti and Al is preferably set at 0.15% by mass or less, and more preferably 0.05% by mass or less.

[0031] Nb is an element which forms carbide or carbonitride to refine crystal grains of the steel, thus exerting the effect of enhancing the toughness. Meanwhile, excessive Nb content causes deterioration of workability of the steel, so that the Nb content is preferably 4.0% by mass or less.

[0032] Mo is an element which has a function of improving corrosion resistance without reducing the strength. Excessive Mo content causes deterioration of workability of the steel, so that the Mo content is preferably 0.01 to 4.0% by mass.

[0033] Cu is an element which is effective in improving corrosion resistance, and also has a function of forming a ferrite phase. Meanwhile, excessive Cu content causes deterioration of workability of the steel, so that the Cu content is preferably 0.01 to 3.0% by mass.

[0034] V is an element which contributes to an improvement in workability and toughness of the steel by fixing solid-soluted C as carbide. Meanwhile, excessive content of a V element causes deterioration of productivity, so that the V content is preferably 0.03 to 0.15%.

[0035] B is an element which contributes to an improvement in corrosion resistance and workability by fixing N. Meanwhile, excessive content of a B element causes deterioration of hot workability of the steel, so that the B content is preferably 0.0003 to 0.01%.

[0036] It is possible to apply, as a dual-phase stainless steel having the chemical composition mentioned above, a steel in which γmax represented by the formula (a) mentioned below is 10 to 90:

$$\gamma\mathrm{max} = 420\mathrm{C} - 11.5\mathrm{Si} + 7\mathrm{Mn} + 23\mathrm{Ni} - 11.5\mathrm{Cr} - 12\mathrm{Mo} + 9\mathrm{Cu} - 49\mathrm{Ti} - 47\mathrm{Nb} - 52\mathrm{Al} + 470\mathrm{N} + 189 \ldots \text{Formula (a)}$$

where an element symbol of C, Si, and the like in the above formula (a) means the content (% by mass) of each element.

[0037] γmax is an indicator which represents an amount (% by volume) of an austenite phase formed when heated and retained at about 1,100°C. When γmax is 100 or more, it is possible to regard as types of austenitic steels in which an austenite single-phase is formed. When γmax is 0 or less, it is possible to regard as types of ferrite steels in which a ferrite single-phase is formed. Regarding the dual-phase stainless steel of the present invention, when γmax is 10 to 90, an austenitic-ferritic two-phase is formed within a temperature range where diffusion bonding proceeds, and two phases mutually suppress crystal grain growth at high temperature, so that it is effective for obtaining a fine crystal structure. γmax is more preferably 50 to 80.

[Average Crystal Grain Size before Bonding]

[0038] The more the grain structure of the dual-phase stainless steel of the present invention becomes fine, more quickly the process (i) mentioned above can be allowed to proceed. Therefore, the average crystal grain size before bonding is preferably 20 μm or less, and more preferably 10 μm or less.

[Surface Roughness]

[0039] Regarding the dual-phase stainless steel including fine crystal grains of the present invention, the process (i) mentioned above quickly proceeds, so that the process (ii) mentioned above exerts a small influence and there is low possibility that bondability is restricted by the extent of surface roughness Ra. If surface roughness of the stainless steel material to be allowed to undergo diffusion bonding increases, disappearance of an oxide film in the process (ii) mentioned above tends to become late. Therefore, a surface of the stainless steel material is preferably smooth, and surface roughness Ra is preferably 0.3 μm or less.

[Method for Producing Diffusion bonded product]

[0040] Regarding the stainless steel material of the present invention, a diffusion bonded product having good bondability is obtained by performing vacuum diffusion bonding using a direct method. Specific diffusion bonding treatment is as follows, for example, diffusion bonding can be allowed to proceed by heating and retaining in a furnace under the conditions of a pressure of 1.0×10^{-2} Pa or less (preferably 1.0×10^{-3} Pa or less) and a dew point of -40°C or lower at 900 to 1,100°C in a state of being directly contacted under a contact surface pressure of 0.1 to 1.0 MPa. The retention time can be adjusted within a range of 0.5 to 3 hours.

EXAMPLES

[0041] Examples of the present invention will be described below. The present invention is not limited to the following Examples, and can be carried out within the scope of the present invention by making appropriate modifications.

[0042] A stainless steel with the chemical composition shown in Table 1 was melted by vacuum melting (30 kg). The steel ingot thus obtained was forged into a 30 mm thick plate and then hot-rolled at 1,230°C for 2 hours to obtain a 3.0 mm thick hot rolled sheet. Then, annealing, pickling, and cold rolling was performed to obtain a 1.0 mm thick cold rolled sheet. Thereafter, the cold rolled sheet was subjected to an annealing treatment mentioned below to produce a cold rolled annealed sheet, which was used as a test material.

[Table 1]

Phase	Steel material	C	Si	Mn	P	S	Ni	Cr	Cu	Mo	Al	Ti	Nb	V	B	N
α + M	FM-1	0.064	0.54	0.31	0.01	0.002	1.90	16.37	0.04	0.04	0.004	0.004	-	-	-	0.011
	FM-2	0.095	0.06	0.50	0.02	0.003	0.10	16.28	-	-	0.007	-	-	-	-	0.010
	FM-3	0.080	0.20	0.44	0.03	0.005	0.11	17.02	0.02	0.01	0.090	0.033	-	-	0.0015	0.015
	FM-4	0.018	0.38	0.49	0.02	0.004	0.09	16.82	0.01	0.01	0.002	0.001	-	-	-	0.009
α + γ	FA-1	0.010	0-44	0.57	0.02	0.004	6.55	23.55	0.46	3.21	0.055	-	0.18	0.08	-	0,109
	FA-2	0.013	0.48	0.62	0.01	0.009	6.44	24.54	0.46	2.88	0.080	-	-	0.06	0.0020	0.150
α	F-1	0.009	0.33	0.99	0.02	0.010	0.13	18.32	0.17	2.00	0.017	0.010	0.61	0.05	-	0.009
γ	A-1	0.060	0.44	1.04	0.02	0.003	8.06	18.05	-	0.11	-	0.010	-	-	-	0.015
M	M-1	0.133	0.45	0.60	0.03	0.011	0.09	12.34	0.06	0.02	0.001	-	-	-	0.0009	0.014

(α : Ferrite phase M: Martensits phase γ : Austenite phase)

[0043] Plural steel materials are shown in Table 1. The metal structure before diffusion bonding of each of FM-1 steel to FM-4 steel is composed of a ferritic-martensitic two-phase (α + M phase). The metal structure before diffusion bonding of each of FA-1 steel and FA-2 steel is composed of a ferritic-austenitic two-phase ($\alpha + \gamma$ phase). The metal structure before diffusion bonding of F-1 steel is composed of a ferrite single-phase (α phase). The metal structure before diffusion bonding of A-1 steel is composed of an austenite single-phase (γ phase). The metal structure before diffusion bonding of M-1 steel is composed of a martensite single-phase (M phase). By changing an annealing temperature of each steel sheet after cold rolling within a range of 900°C to 1,200°C, test materials each having a different average crystal grain size were obtained. To examine an influence of surface roughness, test materials each having different surface roughness Ra were obtained by changing a finishing treatment of a cold rolled annealed sheet using a part of a steel sheet.

(Average Crystal Grain Size)

[0044] An average crystal grain size before diffusion bonding (μm) of a steel sheet was measured by a quadrature procedure as mentioned below. A metal structure of a sheet thickness cross-section parallel to a cold rolling direction was observed with respect to a continuous area of 1 mm^2 or more, and then the number of crystal grains included in a unit area was calculated using a quadrature procedure. Thereafter, an average area per one crystal grain was determined and a value obtained by raising variable the average area to the power of 1/2 was used as an average crystal grain size.

(Surface Roughness)

[0045] Regarding surface roughness Ra (μm), surface roughness Ra in a direction perpendicular to a rolling direction was measured using a surface roughness measuring instrument (SURFCOM2900DX; manufactured by TOKYO SEIMITSU CO., LTD.).

(Creep Elongation)

[0046] Creep elongation was measured by the method mentioned below. A JIS13B test piece was cut out from each steel sheet and a φ5 mm hole was made at the center of one grip. A making-off line (50 mm in length, between gauge marks) was formed on the test piece, and then the test piece was attached to a high temperature tensile testing machine so that the grip with a hole faces downward. After temperature rise until the temperature between the gauge marks becomes 1,000°C and soaking at the same temperature for 15 minutes, a wire made of SUS310S provided with a weight calculated so as to apply stress of 1.0 MPa was attached to the hole of the grip, followed by retaining for 0.5 hour. The wire made of SUS310S was removed from the test piece and cooled to normal temperature by air cooling. Then, the length L between gauge marks was measured and $(L-50)/50 \times 100$ was calculated as creep elongation (%).

(Bondability Test)

[0047] Plane test pieces measuring 20 mm × 20 mm were cut out from each steel sheet and diffusion bonding was performed by the following method. Two test pieces made of the same steel material were laminated in a state where surfaces of the test pieces come into contact with each other. Using a jig with a weight, surface pressure to be applied to a contact surface of these two test pieces was adjusted to 0.1 MPa. Hereinafter, the plane test piece thus laminated is referred to as a "steel material". Those in which the steel materials are laminated are referred to as a "laminate". Then, the jig and the laminate were placed in a vacuum furnace. Vacuuming was performed until the pressure reaches initial vacuum degree of $1.0\,0 \times 10^{-3}$ to 1.0×10^{-4} Pa and the temperature was raised to 1,000°C over about 1 hour, followed by retaining at the same temperature for 2 hours. After transferring to a cooling chamber, cooling was performed. During cooling, the vacuum degree was maintained up to 900°C and then an Ar gas was introduced, followed by cooling to about 100°C or lower in an Ar gas atmosphere under 90 kPa. Regarding the laminate after completion of the heat treatment, using a ultrasonic thickness gage (manufactured by OLYMPUS CORPORATION; Model 35DL), the thickness was measured at 49 measurement points formed at 3 mm pitch on a laminate surface measuring 20 mm × 20 mm as shown in Fig. 1. A probe diameter was set at 1.5 mm. When a measured value of the sheet thickness at certain measurement point exhibits the total sheet thickness of two steel materials, it is possible to consider that both steel materials are integrated with each other by diffusion of atoms at the position of an interface between both steel materials corresponding to the measurement point. Meanwhile, when a measured value of the sheet thickness is different from the total sheet thickness of two steel materials, it is possible to consider that the unbonded portion (defect) exists at the position of an interface between both steel materials corresponding to the measurement point. A correspondence relation between a cross-sectional structure of the laminate after a heating treatment and the measurement results obtained by this measurement technique was examined. As a result, it has been confirmed that it is possible to accurately evaluate an area ratio of the bonded portion in a contact area by the value obtained by dividing the number of measurement points where the measurement results exhibited the total sheet thickness of both steel materials by the total number of measurement 49 (hereinafter this is referred to as a "bonding ratio"). Diffusion bondability was evaluated by the following evaluation criteria.

A: Bonding ratio of 100% (excellent)
B: Bonding ratio of 90 to 99% (good)
C: Bonding ratio of 60 to 89% (fairly good)
D: Bonding ratio of 0 to 59% (bad)

As a result of various studies, sufficient strength of the diffusion bonded portion was secured and also sealability (property not causing leakage of a gas through communicating defects) between both members is good in ratings A and B, so that ratings A and B were considered as passing.

[0048] An average crystal grain size and γmax after cold rolling annealing of each steel, surface roughness, creep elongation, and bondability are shown in Table 2.

[Table 2]

Category	Steel material	γ max	Average crystal grain size (μm)	Creep elongation (%)	Surface roughness R a (μm)	Bondability	Remarks (phase)
Inventive Example 1	FM-1	71.9	9	1.42	0.40	A	α+M
Inventive Example2	FM-1	71.9	15	0.80	0.56	B	
Inventive Example3	FM-2	50.0	18	0.42	0.22	B	
Inventive Example4	FM-3	31.0	11	0.95	0.12	B	
Inventive Example5	FA-1	77.5	12	1.11	0.33	A	α + γ
Inventive Example6	FA-1	77.5	16	0.65	0.49	B	
Comparative Example 1	FM-1	71.9	35	0.11	0.28	C	α + M
Comparative Example2	FM-4	8.3	16	0.12	0.43	C	
Comparative Example3	FA-1	77.5	26	0.14	0.27	C	α + γ
Comparative Examples4	FA-2	95.1	18	0.09	0.15	C	
Comparative Example5	F-1	-60.0	15	0.08	0.41	D	α
Comparative Example6	F-1	-60.0	41	0.05	0.32	D	
Comparative Example7	F-1	-60.0	41	0.05	0.05	B	
Comparative Example8	A-1	199.5	12	0.17	0.31	D	r
Comparative Example9	A-1	199.5	25	0.13	0.04	B	

(continued)

Category	Steel material	γ max	Average crystal grain size (μm)	Creep elongation (%)	Surface roughness R a (μm)	Bondability	Remarks (phase)
Comparative Example 10	M-1	110.9	35	0.12	0.54	D	M
(Underlined numerical value shows a value deviating from the scope or the present invention)							

[0049] As shown in Table 2, in Inventive Examples 1 to 6, a bonding ratio was 90% or more and good diffusion bondability was exhibited even at comparatively low temperature, for example, 1,000°C under low surface pressure, for example, 0.1 MPa. In Inventive Examples 1 to 6, good diffusion bondability was exhibited regardless of the extent of surface roughness Ra, and there was no influence of surface roughness. Since dual-phase stainless steel material having a structure of the present invention does not cause deterioration of diffusion bondability even when surface roughness increases, it is apparent that diffusion bondability thereof is not restricted to surface property of the steel material.

[0050] To the contrary, in Comparative Examples 1 to 10, an average crystal grain size, γmax, and creep elongation deviated from the scope of the present invention, leading to small deformation of the unevenness portion of the bonding surface within a two-phase high temperature range, thus failing to increase the bonding area at the bonded position. Therefore, numerous bonding ratios are less than 80% and rated fairly bad or bad. Regarding ferrite single-phase steels of Comparative Examples 5 to 7 and austenite single-phase steels of Comparative Examples 8 to 9, according to a change in bonding ratio depending on the surface roughness Ra, Comparative Example 7 and Comparative Example 9 with very small surface roughness exhibited a bonding ratio of 90% or more. Meanwhile, other Comparative Examples exhibited large surface roughness, and a bonding ratio decreased. As is apparent from the above results, in a single-phase steel, large surface roughness leads to bad bonding ratio, so that diffusion bondability is restricted by surface roughness.

Claims

1. A dual-phase stainless steel material for diffusion bonding, a metal structure before diffusion bonding having a dual-phase structure composed of at least two phases of a ferrite phase, a martensite phase, or an austenite phase, wherein
   the dual-phase structure has an average crystal grain size of 20 μm or less,
   γmax represented by the formula (a) mentioned below is 10 to 90, and
   creep elongation is 0.2% or more when a load of 1.0 MPa is applied at 1,000°C for 0.5 hour:

$$\gamma\text{max} = 420C - 11.5Si + 7Mn + 23Ni - 11.5Cr - 12Mo + 9Cu - 49Ti - 47Nb - 52Al + 470N + 189 \quad \ldots \text{ Formula (a)}$$

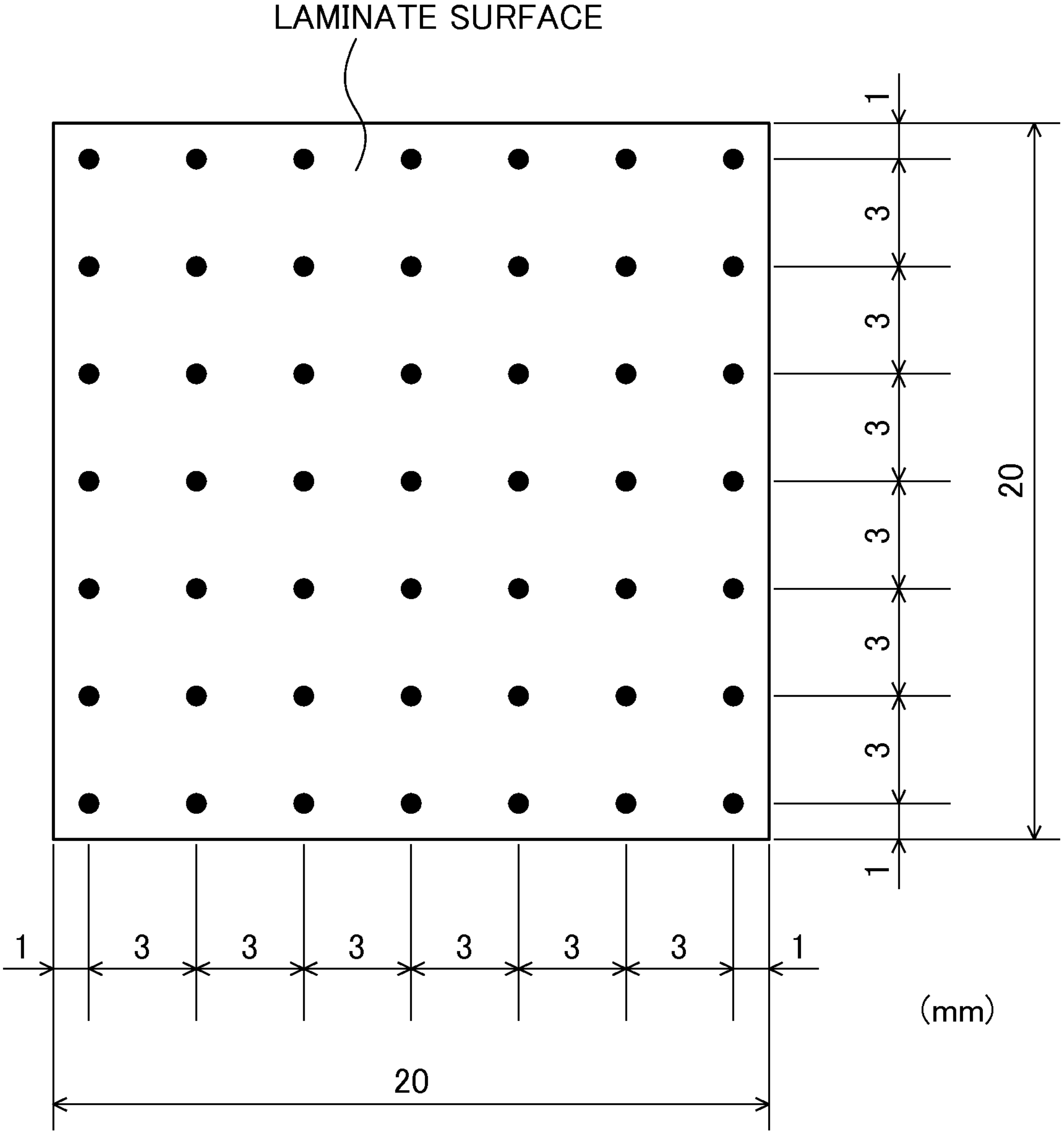
   where an element symbol in the formula (a) mentioned above denotes the content (% by mass) of each element.

2. The stainless steel material for diffusion bonding according to claim 1, comprising, in % by mass: C: 0.2% or less, Si: 1.0% or less, Mn: 3.0% or less, P: 0.05% or less, S: 0.03% or less, Ni: 10.0% or less, Cr: 10.0 to 30.0%, N: 0.3% or less, Ti: 0.15% or less, and Al : 0.15% or less, with the remainder being Fe and inevitable impurities, wherein the total amount of Ti and Al is 0.15% or less.

3. The stainless steel material for diffusion bonding according to claim 1 or 2, further comprising, in % by mass: one or two or more elements of Nb: 4.0% or less, Mo: 0.01 to 4.0%, Cu: 0.01 to 3.0%, and V: 0.03 to 0.15%.

4. The stainless steel material for diffusion bonding according to any one of claims 1 to 3, further comprising, in % by mass: B: 0.0003 to 0.01%.

FIG. 1



SYMBOL ●: MEASUREMENT POINT

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/079342

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C22C38/58*(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C38/00-C22C38/60

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2016
Kokai Jitsuyo Shinan Koho	1971-2016	Toroku Jitsuyo Shinan Koho	1994-2016

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	JP 7-256468 A (Suzuki Motor Corp.), 09 October 1995 (09.10.1995), 0002 (Family: none)	1-4

☒ 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
"E"	earlier application or patent but published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"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 January 2016 (04.01.16)	Date of mailing of the international search report 12 January 2016 (12.01.16)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Authorized officer Telephone No.

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

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/079342

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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