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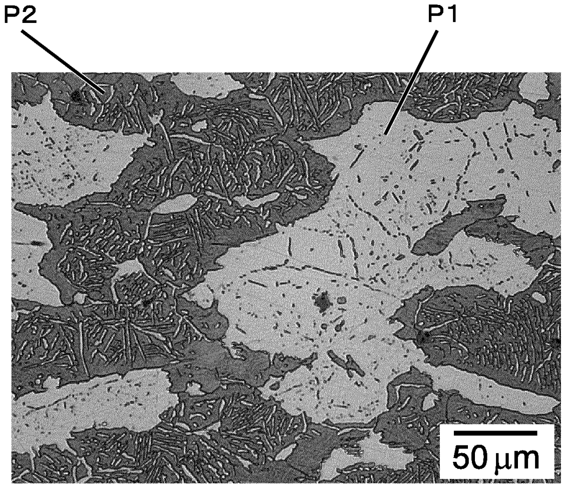
(54) Cr-BASED TWO-PHASE ALLOY AND PRODUCT THEREOF

(57) An object of the invention is to provide a two-phase alloy which contains inexpensive Cr as a main component, and which is superior in strength properties including corrosion resistance and toughness, and in abrasion resistance to conventional ones under a high corrosion circumstance such as in an oil well. The invention is a Cr based two-phase alloy including two phases of a ferrite phase and an austenite phase in a mixed state, in which a chemical composition of the Cr based two-phase alloy consists of a major component, an accessory component, impurities, a first optional accessory component, and a second optional accessory component, and the major component consists of 33% by mass or more and 65% by mass or less of Cr, 18% by mass or more and 40% by mass or less of Ni, and 10% by mass or more and 33% by mass or less of Fe.

FIG. 4



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Description

TECHNICAL FIELD

[0001] The present invention relates to a two-phase alloy containing a Cr (chromium).

BACKGROUND ART

[0002] Materials for apparatus for oil wells or natural gas wells are often exposed to an extremely severe acidified corrosion atmosphere containing a chloride ion, or containing a corrosive gas of carbon dioxide (CO_2) or hydrogen sulfide (H_2S). Materials exposed to such a severe corrosion atmosphere are also found in those of apparatus constituting, for example, a waste product plant, a chemical plant, an atomic power plant, and a nuclear fuel reprocessing facility. Properties required for these materials for apparatus generally include good corrosion resistance and strength. In addition, in slide member materials for a product, abrasion resistance is additionally required.

[0003] As materials for apparatus having such properties, for example, low-alloy steels, stainless steels, and Ni based alloys have been used in accordance with severity of a corrosion atmosphere. In choosing materials, when better strength properties (maintaining high proof stress and toughness) and cost advantage are required in addition to a higher corrosion resistance, stainless steels are more advantageous. Ni based alloys are inferior in cost advantage because it is mainly composed of costly Ni. When abrasion resistance is required, alloys, in which a hard phase is precipitated in its corrosion resistance matrix phase, such as Stellite(R) of Co based alloys are widely used as, for example, cladding materials.

[0004] In the stainless steels, a two-phase stainless steel is advantageous in balance between corrosion resistance and strength properties. The two-phase stainless steel generally contains Cr, Ni, Mo, and N to maintain corrosion resistance. In addition, two-phase stainless steels containing Cu to improve the corrosion resistance are disclosed (see, e.g., PTL 1 and PTL 2). However, from the viewpoints of further extending lifetime and maintaining reliability of structural materials in application under a more severe corrosion atmosphere, further enhancement and improvement of the corrosion resistance and strength of the two-phase stainless steel are required. Further, sufficient abrasion resistance of the two-phase stainless steel cannot be expected as a slide member used under a corrosion atmosphere.

[0005] On the other hand, Cr based alloys which contains more than 60% by mass of Cr and includes a ferrite single phase having a crystalline structure of the body-centered cubic structure to improve corrosion resistance and heat resistance are disclosed (see PTL 3, PTL 4, and PTL 5). In these Cr based alloys, corrosion resistance and abrasion resistance can be expected. However, with respect to strength, they lack ductility and are very brittle.

CITATION LIST

PATENT LITERATURE

[0006]

PTL 1: JP Hei 4 (1992)-72013 A;
PTL 2: WO 2013/058274 A1;
PTL 3: JP Hei 4 (1992)-301048 A;
PTL 4: JP Hei 4 (1992)-301049 A; and
PTL 5: JP Hei 8 (1996)-291355 A.

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0007] In a conventional Fe based two-phase stainless steel (see, e.g., PTL 1 and PTL 2) and Cr based alloys including a ferrite single phase (see, e.g., PTL 3 to PTL 5), improvements in corrosion resistance, strength, and abrasion resistance of the materials to deal with influence of a severe corrosion atmosphere are required, and are problematic. In addition, an alloy having these properties and containing as a main component Cr which is inexpensive in price compared to Ni based alloys is not found.

[0008] Accordingly, an object of the present invention is to provide a two-phase alloy including a ferrite phase and an austenite phase, which is superior in strength properties such as corrosion resistance, proof stress, and toughness, and in abrasion resistance to conventional materials of a two-phase stainless steel and a Cr based single phase alloy even under a severe corrosion atmosphere, and which contains inexpensive Cr as a main component, by adding an element such as Cu which is effective for further improving the high corrosion resistance achieved by enrichment of the Cr.

SOLUTION TO PROBLEMS

[0009] The present inventors produced a Cr based two-phase alloy which has a main composition of Cr-Ni-Fe containing 33% by mass or more of Cr, and which contains Cu and others using different production processes. That is, an alloy having a two-phase structure including ferrite and austenite which contains Cu is produced by using an ingot produced in a melting-casting step as a master ingot followed by steps of 1) a step of heat treatment including a hot forging-solution treatment of the master ingot, 2) a step of re-melting-casting the master ingot, and 3) a step of re-melting-gas atomization of the master ingot. Then, the present inventors evaluated corrosion resistance, mechanical properties, and abrasion resistance of the alloy to accomplish the present invention.

[0010] The present invention is a Cr based two-phase alloy including two phases of a ferrite phase and an austenite phase in a mixed state, in which a chemical composition of the Cr based two-phase alloy consists of a major component, an accessory component, impurities, a first optional accessory component, and a second optional accessory component; the major component consists of 33% by mass or more and 65% by mass or less of Cr (chromium), 18% by mass or more and 40% by mass or less of Ni (nickel), and 10% by mass or more and 33% by mass or less of Fe (iron); the accessory component consists of 0.1% by mass or more and 2% by mass or less of Mn (manganese), 0.1% by mass or more and 1.0% by mass or less of Si (silicon), 0.005% by mass or more and 0.05% by mass or less of Al (aluminum), and 0.1% by mass or more and 5.0% by mass or less of Cu (copper); and the impurities contain more than 0% by mass and 0.04% by mass or less of P (phosphorus), more than 0% by mass and 0.01% by mass or less of S (sulfur), more than 0% by mass and 0.03% by mass or less of C (carbon), more than 0% by mass and 0.02% by mass or less of N (nitrogen), and more than 0% by mass and 0.03% by mass or less of O (oxygen).

ADVANTAGEOUS EFFECTS OF THE INVENTION

[0011] According to the present invention, a two-phase alloy which contains inexpensive Cr as a main component, and which is superior in strength properties such as corrosion resistance and toughness, and in abrasion resistance to conventional ones under a high corrosion circumstance can be provided.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012]

Fig. 1 is an operation flowchart for illustrating hot working in a method for producing a two-phase alloy according to an embodiment of the present invention;
Fig. 2 is an operation flowchart for illustrating casting in a method for producing a two-phase alloy according to an embodiment of the present invention;
Fig. 3 is an operation flowchart for illustrating powderization in a method for producing a two-phase alloy according to an embodiment of the present invention;
Fig. 4 is an optical microscope photograph of a two-phase alloy produced by hot working;
Fig. 5 is an optical microscope photograph of a two-phase alloy produced by casting; and
Fig. 6 is an optical microscope photograph of a powder cladding welded two-phase alloy.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0013] A two-phase alloy of an embodiment of the present invention is described in detail below.

<Two-phase alloy>

[0014] A two-phase alloy of an embodiment of the present invention is a two-phase alloy which has a composition of Cr-Ni-Fe containing Cr as a main component, and which contains Cu and other elements to further improve corrosion resistance. This two-phase alloy is formed of two phases including a ferrite phase and an austenite phase as a main phase structure, and contains Ni, Fe, Mn, Si, Al, Cu, Mo, and others in predetermined amounts, and the remnants consisting of Cr and unavoidable impurities. In addition, in order to control C, N, and O which have an influence on strength and corrosion resistance, at least one of V, Nb, Ta, and Ti is added. Each of the constituents of the two-phase alloy is described below.

<Material structure>

[0015] A material structure in s two-phase alloy of the present embodiments is a two-phase structure including a ferrite phase and an austenite phase. The two-phase structure is formed by different production methods described below, that is, via the steps of thermal processing, casting, or gas atomizing a master ingot. Then, a material structure of hot working materials differs from a material structure of cast materials or cladding materials using a gas atomized powder. The former basically facilitates sufficient elimination of segregation of components, and micronization of the structure. However, the latter basically has a solidified structure which allows segregation of components.

[0016] Generally, Cr based alloys including a ferrite single phase having a crystalline structure of the body-centered cubic structure has higher mechanical strength and superior in abrasion resistance, but is inferior in toughness. In particular, it is characterized in that when contents of C, N, and O increase, plastic deformation properties decrease sensitively. Ni based alloys including an austenite single phase having a face-centered cubic structure is ductile and superior in toughness, but is costly.

[0017] On the other hand, a two-phase alloy of the present embodiments contains Cr as a main component, and consists of a ferrite phase and an austenite phase. The two-phase alloy has a high corrosion resistance due to high Cr concentration and addition of Cu, and is superior in strength including toughness and in abrasion resistance, and also is economical.

[0018] An occupation ratio of the ferrite phase in a two-phase alloy of the present embodiments (hereinafter simply referred to as a "ferrite ratio") can be set to in a range of 10% or more and 95% or less, and the occupation ratio of the austenite phase can be set to in a range of 5% or more and 90% or less in accordance with the ferrite ratio. The reason why the ferrite ratio is set to 95% or less so that the austenite phase is contained is to maintain toughness. A structure having a higher ferrite ratio contains a higher concentration of Cr in the composition, and is observed in a quench-solidified structure, for example, in cladding welding.

[0019] In order to realize this set range of phase fraction, a range of chemical compositions of a two-phase alloy of the present embodiments is defined. The range of the chemical compositions is especially controlled between contents of Cr and Ni, which are the main components. Then, in the above-described two-phase alloy produced in the thermal processing step, when a solution treatment temperature is 1100°C or more and ferrite ratio is more than 95%, heat treatment for phase ratio control can be performed at in a range of 800 to 1000°C to maintain a ferrite ratio of 95% or less.

[0020] On the other hand, since structure of the above-described two-phase alloy produced in casting or gas atomizing step becomes a solidified structure affected by structures formed at a higher temperature of 1100°C or more, the ferrite ratio further increases in a high Cr content two-phase alloy. Accordingly, in order to maintain the above-described predetermined ferrite ratio of 95% or less, decreasing the Cr content ratio to increase the Ni content is generally required as shown in the following <chemical composition>. However, in a cast material in which heat treatment can be performed, by controlling the ratio between a ferrite and an austenite phases (phase ratio control) in a range of 800 to 1000°C, the ferrite ratio of 95% or less can certainly be maintained.

[0021] The "ferrite ratio" in the present embodiments refers to an occupation ratio of ferrite [%] obtained by EBSP (Electron BackScattering Pattern) analysis.

[0022] In terms of ensuring both corrosion resistance and strength properties including favorable toughness, a ferrite ratio in a two-phase alloy of the present embodiments is more preferably 20% or more and 70% or less.

[0023] In addition, the two-phase alloy in the present embodiments, for example in a two-phase stainless steel, is preferably a two-phase alloy containing no hard different phase such as a sigma (σ) phase which is precipitated by phase-transition from a ferrite phase. However, the hard phase is tolerated when it is contained to such an extent that diverse properties such as mechanical properties are not considerably impaired.

<Chemical composition>

[0024] Next, reasons for restricting a numerical range of a chemical composition in a two-phase alloy of the present embodiments are described. A content of each of the components is shown in % by mass.

[0025] Cr is a component of remnants, and its concentration is the highest in those of constituent components of the two-phase alloy. In a Cr-Ni-Fe based two-phase alloy of the present embodiments, Cr is a Cr based ferrite phase-forming element with a high mechanical strength as a material, and it improves corrosion resistance as a solid solution element.

[0026] The Cr content is set so that a two-phase structure including a ferrite phase and an austenite phase may be formed as a thermal equilibrium state structure of the major ternary system at a solution treatment temperature of 1050 to 1250°C as described below.

[0027] The content of Cr is preferably 33% or more in consideration of an amounts of the major components including Ni and Fe, an amounts of minor components such as active elements including Mn, Si, Al, Cu, Mo, P, S, C, N, O, and V, and amounts of unavoidable impurities. When the amount of Cr is set to 33% or more, a high concentration of Cr is achieved to result in further improvement in corrosion resistance of the two-phase alloy.

[0028] In a two-phase alloy produced in a hot working step, the content of Cr is preferably 65% or less. When the content of Cr is set to 65% or less, superior toughness can be imparted to the two-phase alloy while high proof stress and high hardness are maintained. On the other hand, since a two-phase alloy produced in a casting or gas atomization step, specifically in a composition with a high Cr concentration, forms a structure with a high ferrite ratio, the content of Cr is reduced to maintain a ferrite ratio of 95% or less, and is preferably 60% or less.

[0029] In the present examples, a chemical composition of the Cr based two-phase alloy consists of a major component, an accessory component, impurities, a first optional accessory component, and a second optional accessory component. The major component is composed of Cr, Ni, and Fe; the accessory component is composed of Mn, Si, Al, and Cu; the impurities is composed of P, S, C, N, and O; the first optional accessory component is composed of Mo (molybdenum); and the second optional accessory component is composed of V (vanadium), Nb (niobium), Ta (tantalum), and Ti (titanium).

[0030] Ni stabilizes an austenite phase and maintains a two-phase state with a ferrite phase in a solution treatment. In addition, Ni ensures and imparts corrosion resistance, and also ductility and toughness to the two-phase alloy.

[0031] In a two-phase alloy produced in a hot working, the content of Ni is set to 18% or more. This results in the occupation ratio of the austenite phase of 10% or more at solution treatment temperature described below, and contributes to further improving toughness of the structure. On the other hand, in a two-phase alloy produced in a casting or gas atomization, a structure with a high ferrite ratio is formed as described above, the content of Ni is increased to maintain a ferrite ratio of 95% or less, and is preferably 23% or more. In addition, the content of Ni is set to 40% or less. This results in a ferrite ratio of 10% or more at solution treatment temperature described below.

[0032] The content of Fe is set to 10% or more. This reduces the contents of Ni and Cr, which are more expensive than Fe, and suppresses production of an intermetallic compound which may exert a harmful effect on strength properties in a melt extraction process of a two-phase alloy.

[0033] The content of Fe is set to 33% or less. In general, in a ternary alloy of Cr-Ni-Fe, when the concentration of Fe is increased, a σ phase is produced at temperature range around 800°C as the center. However, in a two-phase alloy of the present embodiments, since the content of Fe is set to 33% or less, production of the σ phase is suppressed.

[0034] The total content ratio of Ni component and Fe component is preferably 37% by mass or more and 65% by mass or less. When the total content ratio becomes less than 37% by mass, ductility/toughness of the two-phase alloy becomes insufficient. On the other hand, when the total content ratio becomes more than 65% by mass, mechanical strength is significantly reduced.

[0035] The content of Mn is set to 0.1% or more. This allows desulfurization and deoxidation of the two-phase alloy to improve strength and toughness of the two-phase alloy. Preferred lower limit is 0.3%.

[0036] The content of Mn is set to 2.0% or less. This prevents deterioration of corrosion resistance and strength caused by formation of bulky MnS, and maintains preferred resistance properties of the two-phase alloy against corrosion by carbon dioxide gas.

[0037] The content of Si is set to 0.1% or more. This allows deoxidation of the two-phase alloy, and improves strength and toughness of the two-phase alloy. Preferred lower limit is 0.3%.

[0038] The content of Si is set to 1.0% or less. This brings about sufficient effects of a hot forging step described below, and maintains a preferred toughness of the two-phase alloy.

[0039] The content of Al is set to 0.005% or more. This improves a deoxidation effect in conjunction with Mn and Si. More preferred lower limit is 0.008%.

[0040] In addition, the content of Al is set to 0.05% or less. Reduction of the amount of oxygen in a Cr based two-phase alloy of the present invention is indispensable for maintaining hot forging properties and toughness of an alloy of the present invention. The content of oxygen is reduced as low as possible during production. On the other hand, Al_2O_3 and AlN, which are produced when a lot of Al is contained, impair toughness of the alloy, and thus the production should be suppressed as low as possible. The content of Al is preferably 0.05% or less.

[0041] Cu is an element which increases corrosion resistance of a Cr based two-phase alloy of the present invention similarly to Mo, and can be included together as required to enhance the effect cooperatively. When it is included, in order to improve corrosion resistance, the content is set to 0.1% or more. When Cu is included, an austenite phase is stabilized. However, when the amount included is excessive, Cu precipitates are produced during hot working specifically in a ferrite phase, leading to decreased processability. Accordingly, it is desirably 5.0% or less, and preferably 3.0% or less.

[0042] Mo is an element which increases corrosion resistance of the Cr based two-phase alloy, is effective specifically in stabilization of passivation film, and raises an increased expectation of pitting resistance properties. Thus, Mo can be included together as required to enhance the effect cooperatively. When it is included, in order to improve corrosion resistance, the content is set to 0.1% or more. On the other hand, when Mo is included, a ferrite phase is stabilized. However, when the content is too high in concentration, formation of σ phase and formation of an intermetallic compound in thermal processing may occur, leading to further decreased processability and corrosion resistance. Accordingly, it is desirably 3% or less, and preferably 2% or less.

[0043] The content of P is set to 0.04% or less. P is an element which deteriorates corrosion resistance, weldability, and processability, and thus it should be limited as low as possible in production. When the content of P is set to 0.04% or less, segregation of P at the crystal grain boundary is prevented, and preferred toughness of the two-phase alloy and corrosion resistance at the grain boundary are maintained. Furthermore, when cleaner refine and production processes are used, the content of P can be further reduced. Accordingly, the lower limit of P is the detection limit of an analysis or less, and it must not be included in the two-phase alloy, that is, may be 0%.

[0044] The content of S is set to 0.01% or less. S is an element which produces a sulfide such as MnS to deteriorate corrosion resistance and processability, and thus it should be limited as low as possible in production. When the content of S is set to 0.01% or less, the amount of a sulfide is reduced, and preferred pitting resistance properties and toughness are maintained.

[0045] Furthermore, when cleaner refine and production processes are used, the content of S can be further reduced. Accordingly, the lower limit of S is the detection limit of an analysis or less, and it must not be included in the two-phase alloy, that is, may be 0%.

[0046] C provides, when its concentration is increased, solid solution hardening of C at a low concentration, and significantly prevents plastic deformation specifically in a ferrite phase. At a high concentration, specifically, it causes formation of a Cr carbide and reduces local Cr concentration around it, leading to decrease in corrosion resistance. Large amount of the carbide causes decrease in toughness. In addition, when active elements of V, Nb, Ta, and Ti are added, in order to reduce formation of their carbides, the content of C is desirably reduced, and is preferably 0.03% or less.

[0047] Furthermore, when cleaner refine and production processes are used, the content of C can be further reduced. Accordingly, the lower limit of C is the detection limit of an analysis or less, and it must not be included in the two-phase alloy, that is, may be 0%.

[0048] N improves, when its concentration is increased, solid solution hardening and corrosion resistance of N. However, at a higher concentration, there is a concern that toughness may be decreased by formation of a nitride such as Cr. In a two-phase alloy of the present invention produced in a hot working production process described below, in order to maintaining processability, the content of N is desirably 0.02% or less. Furthermore, when cleaner refine and production processes are used, the content of N can be further reduced. Accordingly, the lower limit of N is the detection limit of an analysis or less, and it must not be contained in the two-phase alloy, that is, may be 0%.

[0049] On the other hand, in a cast material or power of a two-phase alloy of the present invention produced in a casting step or a gas atomization step described below, even if the above-described atmosphere for production is an inert gas atmosphere, unavoidable intrusion of N should be taken into consideration, and thus the content becomes higher. The upper limit of N is set to 0.04%, and the lower limit is set to 0.005%.

[0050] O readily forms an oxide with metallic elements in the two-phase alloy, and thus there is a concern that toughness may be decreased by increase in the content of O accompanied by increase in the oxide. In a two-phase alloy of the present invention produced in a hot working production step described below, in order to maintain processability, the content of O is desirably 0.03% or less. Furthermore, when cleaner refine and production processes are used, the content of O can be further reduced. Accordingly, the lower limit of O is the detection limit of an analysis or less, and it must not be contained in the two-phase alloy, that is, may be 0%.

[0051] On the other hand, in a cast material or power of a two-phase alloy of the present invention produced in a casting step or a gas atomization step described below, even if the above-described atmosphere for production is an inert gas atmosphere, unavoidable intrusion of O should be adequately taken into consideration, and thus the content becomes higher. The upper limit is set to 0.05%, and the lower limit is set to 0.005%.

[0052] V binds to gaseous impurities of C, N, and O to form respective compounds, and then gaseous impurities are gathered and immobilized. This effect of cleaning substrate materials is effective for improving toughness. However, when V is added excessively, V readily reacts with other component elements to form respective intermetallic compounds, leading to concern about decrease in toughness. A preferred amount of V added in production in which an amount of V in excess of that used for immobilization is reduced as low as possible is, in atomic % (at%), preferably in a range between 0.8 times or more and 2 times or less of the total at% of C, N, and O. When at least one of Nb, Ta, and Ti is added together with V, the total amount including V is also preferably in a range between 0.8 times or more and 2 times or less.

[0053] Nb binds to gaseous impurities of C, N, and O to form respective compounds, and then gaseous impurities are gathered and immobilized. This effect of cleaning substrate materials is effective for improving toughness. However, when Nb is added excessively, Nb readily reacts with other component elements to form respective intermetallic compounds, leading to concern about decrease in toughness. A preferred amount of Nb added in production in which an amount of Nb in excess of that used for immobilization is reduced as low as possible is, in atomic % (at%), preferably in a range between 0.8 times or more and 2 times or less of the total at% of C, N, and O. When at least one of V, Ta, and Ti is added together with Nb, the total amount including Nb is also preferably in a range between 0.8 times or more and 2 times or less.

[0054] Ta binds to gaseous impurities of C, N, and O to form respective compounds, and then gaseous impurities are gathered and stabilized. This effect of cleaning substrate materials is effective for improving toughness. However, when Ta is added excessively, Ta readily reacts with other component elements to form respective intermetallic compounds, leading to concern about decrease in toughness. A preferred amount of Ta added in production in which an amount of Ta in excess of that used for immobilization is reduced as low as possible is, in atomic % (at%), preferably in a range between 0.8 times or more and 2 times or less of the total at% of C, N, and O. When at least one of V, Nb, and Ti is added together with Ta, the total amount including Ta is also preferably in a range between 0.8 times or more and 2 times or less.

[0055] Ti binds to gaseous impurities of C, N, and O to form respective compounds, and then gaseous impurities are gathered and stabilized. This effect of cleaning substrate materials is effective for improving toughness. However, when Ti is added excessively, Ti readily reacts with other component elements to form respective intermetallic compounds, leading to concern about decrease in toughness. A preferred amount of Ti added in production in which an amount of Ti in excess of that used for immobilization is reduced as low as possible is, in atomic % (at%), preferably in a range between 0.8 times or more and 2 times or less of the total at% of C, N, and O. When at least one of V, Nb, and Ta is added together with Ti, the total amount including Ti is also preferably in a range between 0.8 times or more and 2 times or less.

<Method for producing a two-phase alloy>

[0056] Next, a method for producing a two-phase alloy of the present embodiments is described. A two-phase alloy of the present invention is provided, as the final product form, as hot working materials produced in a series of production steps of, for example, melting-ingot forming-hot forging-solution treatment steps, a cast material from re-melting of the master ingot, and a powder from an atomizing process.

<Hot working>

[0057] Fig. 1 is an operation flowchart for illustrating a method for producing a two-phase alloy according to the present embodiments.

[0058] As shown in Fig. 1, in the production method, the above-described Cr, Ni, Fe, Mn, Si, Al, Cu, and Mo as the materials, and as required, at least one or more of V, Nb, Ta, and Ti in predetermined amounts are melted in a high frequency vacuum melting furnace to form an alloy (step F1). The melting furnace used in this step is not limited to the high frequency vacuum melting furnace, but other melting furnaces can be used in the present invention.

[0059] Next, an ingot is formed by casting using a predetermined die (step F2). The resulting ingot can be also used as a cast material of the two-phase alloy and a master ingot for powder production as described below. Then, the ingot is subjected to hot forging treatment (step F3) . In this step, hot forging can be performed on the ingot using a press forging machine or a hammer forging machine to provide a required product shape. The temperature for hot forging is set to about 1050 to 1250°C. The hot forging can prevent component segregation and facilitate structure micronization in the ingot. Furthermore, as the following thermal processing, for example, hot rolling can be performed at a temperature in a range of 1050°C or more if a plate-shaped two-phase alloy is desired, and hot extrusion can be performed at the above-described temperature range if a tube-shaped two-phase alloy is desired.

[0060] Next, the above-described hot forged material is subjected to a solution heat treatment step (step F4). By this solution heat treatment, structure of the two-phase alloy is basically defined. The temperature of the solution heat treatment is, in order to sufficiently produce solid solution of constituent atoms and eliminate lattice defects such as dislocation which remains after hot working, desirably in a range of 1050 to 1250°C, and preferably 1100 to 1200°C. By setting this solution treatment temperature range, the ferrite ratio of the two-phase alloy of 10 to 95% can be adequately achieved.

[0061] In addition, as an additional heat treatment to improve strength after the solution heat treatment, a so-called an aging heat treatment is performed (step F5) to facilitate phase-transition from a ferrite phase to an austenite phase, and from an austenite phase to a ferrite phase in high Ni conditions. By this treatment, the phase ratio can be controlled to be a desired value in a range of 10 to 95%. Conditions of the aging heat treatment desirably include, in accordance with an extent of the phase ratio control, a solution treatment temperature of 1050 to 1250°C, an aging treatment temperature of 800 to 1000°C, and an aging time of 0.5 to 6 hours In a two-phase alloy with higher Cr concentration, although it is expected that at a solution treatment temperature of 1150°C or more the ferrite ratio may be more than 90%, a phase ratio can be controlled within the above-defined phase ratio by an aging heat treatment.

[0062] Accordingly, in a solution treated alloy, when the two-phase alloy has a ferrite ratio of about 30% or more, the ferrite phase can be decreased and an austenite phase can be increased in amounts to improve elongation and toughness of the two-phase alloy. In an alloy having a ferrite ratio of about 30% or less in which an austenite phase is fairly dominant, when an austenite phase is decreased and a ferrite phase is increased by aging, proof stress and tensile strength can be improved.

[0063] On the other hand, an active element-added two-phase alloy is subjected to a solution heat treatment, and then subjected to an aging heat treatment step similar to that described above is performed (step F5) to complete a series of the method for producing the two-phase alloy. The aging heat treatment can cause an appropriate aging reaction between the active element and C, N, and O, that is, it can produce precipitates of these compounds. At the same time, the above-described phase ratio control can be achieved. Conditions of the aging heat treatment desirably include a solution treatment temperature of 1050 to 1250°C, an aging treatment temperature of 800 to 1000°C, and an aging time of 0.5 to 6 hours.

[0064] The final heat treatment step in such a method for producing the two-phase alloy may, in accordance with desired corrosion resistance and strength properties, be a solution heat treatment step, or the method may be carried out including an aging heat treatment step subsequent to the solution heat treatment.

[0065] In addition, in accordance with such a method for producing the two-phase alloy, a hot forging step of an ingot and a subsequent heat treatment step are performed, which leads to elimination of casting defects and destruction of a bulky two-phase cast solidified structure containing segregates of alloy elements and having a high ferrite phase occupation ratio. Accordingly, a two-phase alloy of the present embodiments having a two-phase structure which is homogeneous in chemical composition and structure, and thermodynamically more stable can be obtained.

[0066] In the two-phase alloy containing at least one or more of the above-mentioned V, Nb, Ta, and Ti, when the above-described heat treatment step is carried out, more efficient stabilization of the above-described C, N, and O can be achieved.

[0067] A two-phase alloy according to the present embodiments, which is obtained by hot forging and heat treating an ingot consisting of the above-specified chemical composition under the above-specified conditions, includes two phases of a ferrite phase containing Cr as a main component and an austenite phase. Such a two-phase alloy of the present embodiments contains inexpensive Cr as a main component, and is superior in strength properties such as corrosion resistance and toughness to conventional ones even under a high corrosion circumstance such as in an oil well.

<Casting>

[0068] Fig. 2 is an operation flowchart for illustrating a method for producing a two-phase alloy cast material according to the present embodiments.

[0069] A master ingot casted in step F2 of the steps in Fig. 1 is used as a raw material. The master ingot is re-melted in a melting furnace such as a high frequency or induction furnace (step C1), and then casted in a mold (step C2) to produce a cast material. An atmosphere for melting and casting may be the air, an inert gas, or a vacuum depending on purposes. In order to prevent pollution such as oxidation as low as possible, a clean casting in an inert gas or vacuum is preferred.

[0070] The cast material has a solidified structure. An additional heat treatment can be further performed after the casting to improve segregation of component elements. Accordingly, desired corrosion resistance and strength properties can be achieved. Specifically, the cast material can be subjected to a solution treatment for, for example, homogenization of constituent components, and subsequently subjected to a heat treatment including aging (step C3) . The temperature of the solution heat treatment is desirably about 1050 to 1250°C, and preferably 1100 to 1200°C. When phase ratio control is carried out and an active element-added two-phase alloy is subjected to an aging heat treatment to facilitate an appropriate aging reaction between the active element and C, N, and O, solution treatment temperature of 1050 to 1250°C, an aging treatment temperature of 800 to 1000°C, and an aging time of 0.5 to 6 hours are preferred.

[0071] Fig. 5 is an optical microscope photograph of a two-phase alloy produced by casting.

<Powderization>

[0072] Fig. 3 is an operation flowchart for illustrating a method for producing a two-phase alloy powder according to the present embodiments.

[0073] A master ingot casted in step F2 of the steps in Fig. 1 is used as a raw material. The master ingot is re-melted in a melting furnace such as a high frequency or induction furnace (step A1), and then subjected to a gas atomization method using an inert gas of Ar or He to obtain a two-phase alloy powder containing lower amount of oxygen (step A2). Then, the powders were classified into a range of about 50 to 200 (step A3), and used as a two-phase alloy powder of the present invention. The range of size of the two-phase alloy powder can be changed in accordance with purposes by controlling the classification. A structure of the two-phase alloy powder is a solidified structure by quenching from about liquid phase temperature. Accordingly, in particular in a part of the alloy powder having a high Cr (55% or more) and low Ni (25% or less) composition, a ferrite phase is likely to be enriched, and thus the above-defined range of the ferrite ratio of 95% or less can not necessarily be satisfied. However, when these alloy powders are thermally processed subsequently in accordance with purposes to provide a two-phase alloy product having a structure satisfying the above-defined range, the alloy powder having a ferrite ratio of 95% or more is acceptable. The alloy powder can be provided as a two-phase alloy powder for purposes including, for example, cladding, 3D printing, or sintering.

[0074] Fig. 6 is an optical microscope photograph of a powder cladding welded two-phase alloy.

[0075] Such a two-phase alloy can preferably be used as a component material of apparatuses such as compressors and pumps used under a high corrosion circumstance in an oil well, for example, as a slide part. Furthermore, the two-phase alloy can be used not only as such materials for apparatus, but also as structural materials used in a sea water environment such as umbilical, a sea water purification plant, and a LNG vaporizer, and structural materials of, for example, various chemical plants.

EXAMPLES

[0076] Next, examples of studying effects of a two-phase alloy of the present invention are described.

<Hot working alloy>

(Examples 1 to 22)

[0077] In the Examples, hot working two-phase alloys containing no active element such as V in the present invention were studied. Chemical compositions of alloys of alloy numbers A1 to A16 used in Examples 1 to 22 are shown in Table 1. Production of these alloys are described in detail below. Master ingots of these alloys are produced by melting them using a high frequency vacuum melting furnace (Ar atmosphere under reduced pressure; melting temperature: 1500°C or more).

[Table 1]

	Chemical composition [% by mass]													
	Alloy number	Si	Mn	Al	P	S	Cr	Ni	Fe	Cu	Mo	C	N	O
Example	A1	0.55	1.33	0.011	0.018	0.0015	60.23	25.89	11.79	0.13		0.012	0.017	0.011
	A2	0.51	1.24	0.014	0.016	0.0017	52.48	33.2	12.32	0.17		0.013	0.016	0.012
	A3	0.49	1.28	0.013	0.020	0.0013	47.8	38.96	11.28	0.11		0.011	0.014	0.013
	A4	0.53	1.29	0.017	0.013	0.0011	57.11	21.15	19.71	0.13		0.014	0.014	0.014
	A5	0.51	1.31	0.023	0.017	0.0017	45.23	30.51	21.27	1.08		0.013	0.017	0.015
	A6	0.52	1.43	0.016	0.016	0.0016	46.71	30.11	20.04	0.11		0.012	0.016	0.013
	A7	0.54	1.34	0.019	0.014	0.0019	43.33	29.88	20.18	4.65		0.011	0.015	0.014
	A8	0.48	1.49	0.013	0.015	0.0014	39.82	37.38	20.62	0.14		0.014	0.014	0.012
	A9	0.52	1.26	0.022	0.013	0.0016	50.26	20.22	27.52	0.13		0.015	0.016	0.017
	A10	0.51	1.46	0.018	0.021	0.0012	41.69	26.07	30.07	0.11		0.012	0.017	0.016
	A11	0.56	1.35	0.024	0.017	0.0017	41.64	26.11	30.12	0.13		0.011	0.016	0.017
	A12	0.54	1.46	0.016	0.016	0.0018	37.95	26.24	30.22	3.51		0.013	0.015	0.015
	A13	0.51	1.35	0.017	0.015	0.0013	34.59	32.48	30.85	0.14		0.017	0.014	0.014
	A14	0.47	1.46	0.015	0.017	0.0016	43.27	25.13	29.04	0.16	0.38	0.016	0.017	0.016
	A15	0.59	1.26	0.019	0.016	0.0019	40.45	25.91	30.08	0.14	1.48	0.014	0.016	0.014
	A16	0.55	1.33	0.020	0.020	0.0017	37.49	26.57	31.18	0.13	2.66	0.014	0.013	0.014
Comparative Example	A17	0.54	1.27	0.022	0.014	0.0020	46.35	30.58	21.18			0.013	0.012	0.013
	A18	0.55	1.39	0.021	0.021	0.0016	40.26	26.2	31.54			0.012	0.014	0.017
	A19	0.52	1.42	0.019	0.013	0.0019	62.5	13.07	22.41			0.014	0.015	0.016
	A20	0.57	1.45	0.017	0.015	0.0017	25.71	46.68	25.51			0.015	0.017	0.014
	A21	0.58	1.39	0.016	0.018	0.0016	25.30	7.23	bal.	0.51	3.08	0.011	0.016	0.011

(Note) Remnants of the chemical compositions of alloy numbers A1 to A20 are Cr and impurities; and remnants of the chemical compositions of alloy number A21 are Fe and impurities.

[0078] The resulting ingots were subjected to hot forging. The hot forging was carried out at a temperature in a range of 1250 to 1050°C at which reduction in area in a tensile test becomes 60% or more. No forging crack was formed. These forging conditions also applied to all alloys of Examples and Comparative Examples concerning the following hot forging. Next, a solution treatment was carried out, in most two-phase alloys, under the following conditions: holding at 1100°C for 60 minutes, followed by water cooling. However, in alloys of A6 (Examples 7 to 9), A11 (Examples 15 to 17), and A15 (Examples 21), the solution treatment was carried out at 1100, 1200, or 1250°C, and subsequently additional aging heat treatments were carried out for phase ratio control under the following conditions: holding at 900 to 1000°C for 60 minutes, followed by water cooling. The alloys of alloy numbers A1 to A16 having chemical compositions shown in Table 1 were produced by the steps described above.

[Table 2]

		Alloy number	Solution heat treatment	Aging heat treatment (°C)	Ferrite ratio (%)	Vickers hardness (1 kg)	Proof stress (MPa)	Tensile strength/ breaking stress *(Mpa)	Evaluation of plastic elongation	Evaluation of sulfuric acid resistance	Evaluation of abrasion resistance
Example	1	A1	1100	-	77	566	1088	1116*	C	A	52
	2	A2	1100	-	46	418	944	1235*	B	A	63
	3	A3	1100	-	22	268	580	957	A	A	83
	4	A4	1100	-	76	541	1066	1176*	C	A	49
	5	A5	1100	-	43	416	965	1183*	B	A	67
	6	A6	1100	-	46	425	651	1192*	B	A	67
	7	A6	1100	900	41	374	879	1123*	A	A	70
	8	A6	1200	1000	42	379	912	1257*	B	A	71
	9	A6	1250	1000	40	349	864	1204*	A	A	68
	10	A7	1100	-	45	412	932	1258*	B	A	70
	11	A8	1100	-	23	271	586	976	A	A	75
	12	A9	1100	-	75	550	1124	1179*	C	A	53
	13	A10	1100	-	46	438	931	1221*	B	A	66
	14	A11	1100	-	47	441	954	1103*	C	A	61
	15	A11	1100	900	41	369	601	1206*	A	A	74
	16	A11	1200	1000	43	408	934	1239*	B	A	69
	17	A11	1250	1000	42	380	913	1268*	B	A	66
	18	A12	1100	-	46	421	966	1227*	B	A	65
	19	A13	1100	-	19	253	541	907	B	A	76
	20	A14	1100	-	44	421	942	1161*	C	A	71
	21	A15	1200	1000	48	423	964	1263*	B	A	69
	22	A16	1100	-	48	428	983	1241*	B	A	68

(continued)

		Alloy number	Solution heat treatment	Aging heat treatment (°C)	Ferrite ratio (%)	Vickers hardness (1 kg)	Proof stress (MPa)	Tensile strength/ breaking stress *(Mpa)	Evaluation of plastic elongation	Evaluation of sulfuric acid resistance	Evaluation of abrasion resistance
Comparative Example	1	A17	1100	-	46	421	931	1264*	B	B	67
	2	A18	1100	-	47	426	975	1217*	B	B	71
	3	A19	1100	-	100	711	-	1356*	D	D	40
	4	A20	1100	-	0	173	247	547	A	B	177
	5	A21	1100	-	43	-	-	-		B	-
(Note) "-" represents no treatment, and no measurement and evaluation.											

[0079] The alloys of alloy numbers A1 to A16 were Cr based alloys containing Cr as a main component and Cu in an amount of 0.11 to 4.65% by mass, and were two-phase alloys consisting of a ferrite phase and an austenite phase. The alloys of alloy numbers A14 to A16 further contained Mo. Ferrite ratios of the alloys of Examples 1 to 22 (alloy numbers A1 to A16) are shown in Table 2. The ferrite ratios in the present embodiments are shown in ferrite ratios [%] obtained by EBSP analysis. The ferrite ratios had a tendency to increase with increase in Cr concentration. In the above-described Examples 7 to 9, 15 to 17, and 21 subjected to the aging treatment, ferrite ratios were decreased by aging, which leads to structures in which secondary austenite phases were minutely precipitated in ferrite phases by phase-transition.

[0080] Fig. 4 is an optical microscope photograph of the two-phase alloy of alloy number A10 produced in Examples 13. This optical microscope photograph was taken after the surface of the two-phase alloy of Examples 13 was subjected to mirror polishing and electric field etching in an aqueous oxalic acid solution.

[0081] As shown in Fig. 4, the structure of the alloy of Examples 13 which was subjected to a solution treatment at 1100°C after hot forging consisted of an austenite phase P1 having a light color and a ferrite phase P2 having a dark color, and the phases contain minute ferrite and austenite phase, respectively. Similar structures were observed in other two-phase alloys of the present invention which was subjected to thermal processing. Alloys of alloy numbers A9 and A11 which have higher Fe contents and in which a σ phase might be generated were subjected to a heat treatment at 800°C for 60 minutes to study whether σ phase generation occurred or not. These alloys after the heat treatment were analyzed by X-ray diffraction to verify that no σ phase was generated. This indicates that also in other alloys of other Examples including addition of activation elements of, for example, Cu and V, excluding in the following Mo-containing case, a σ phase is hardly produced at an intermediate temperature range around 800°C. In the alloy of alloy numbers 16 having higher content of Fe and containing a higher amount of Mo, a σ phase was not observed in a solution treatment, but production of the σ phase was observed in the subsequent 800°C aging.

[0082] In addition, as shown in Table 2, a strength test, a corrosion test, and an abrasion test were performed on alloys of the present Examples 1 to 22 (alloy numbers A1 to A16) .

(Strength test)

[0083] Vickers hardness and tensile tests were performed to measure 0.2% proof stress, tensile strength, and plastic elongation. Vickers hardness was obtained by performing 5 measurements using a Vickers hardness meter under conditions of load of 1 kg and load application time of 15 seconds and averaging the values.

[0084] A tensile test was performed using a test piece having a size of 4.0 mm in diameter and 20 mm in length of the parallel portion at room temperature of 23°C. Strain rate was 3×10^{-4}/s. In the tensile test, 3 specimens of each alloy were tested to obtain the average value of the measurements. In a stress-strain curve, when brittle fracture of a test piece occurred before a yield point of stress-strain curve or in a midpoint of a flow stress having positive work hardening, a breaking stress was defined instead of a proof stress or tensile strength. The results of these measurements are shown in Table 2. In Table 2, the symbol "*" represents that the value refers to a breaking stress obtained instead of a proof stress or tensile strength. Plastic elongation was evaluated as follows and the results are shown in Table 2: A: 15% or more, B: 5 to less than 15%, C: 0.2 to less than 5.0%, and D: less than 0.2%.

(Corrosion test)

[0085] A corrosion test was performed with respect to pitting resistance properties and oxidation resistance properties. First, pitting resistant properties were evaluated according to JIS G0577 (2005). Specifically, 2 polarized test pieces having an area of 10 mm × 10 mm were obtained from each of the alloys of Examples 1 to 22, and subjected to the following test to evaluate pitting resistance properties. A polarized test piece was installed on a gap corrosion-preventing electrode. An anode polarization curve was obtained using a gap corrosion-preventing electrode to give an average electric potential corresponding to a corrosion current density of 100 μA/cm^2. A saturated calomel electrode was used as a reference electrode. After the measurement, observation using an optical microscope was carried out to study whether pitting was generated or not.

[0086] Next, oxidation resistance properties were evaluated by corrosion rate in sulfuric acid according to JIS G0591 (2000). From each of the alloys of Examples 1 to 22, 2 test pieces having dimensions of 3 mm (thickness) × 1.30 mm (width) × 40 mm (length) were obtained, and subjected to an immersion test in 5% boiling sulfuric acid for 6 hours to evaluate sulfuric acid resistance. Each test piece was weighted before and after the measurement to evaluate an average rate of weight loss by corrosion $m[g/(m^2 \cdot h)]$. The rate of weight loss in sulfuric acid with respect to each of the alloys of Examples 1 to 22 was classified into the following grades of A to D to evaluate sulfuric acid resistance: A: $m < 0.1$, B: $0.1 \leq m < 0.3$, C: $0.3 \leq m < 0.5$, and D: $0.5 \leq m$. The results of these evaluations are shown in Table 2.

(Abrasion test)

[0087] Abrasion resistance was evaluated by an abrasive wear test. From each of the alloys of Examples 1 to 22, 2 test pieces having a cylindrical pin shape of 10 mm (diameter) × 20 mm (length) were obtained, and subjected to an abrasion test. The abrasion test was carried out using a Pin-on-Disk abrasion tester. The test method is described below. The abrasion test was performed as follows: fixing waterproof abrasive paper having grit size of 240 (fixed piece) on a disk, rotating the disk at a rotation rate of 200 rpm, pressing a pin of a test piece (movable piece) against the waterproof abrasive paper under a load of 4 kgf, and moving the waterproof abrasive paper from the outermost circumference to the center. Similar tests were performed sequentially using 3 pieces of waterproof abrasive paper. The outmost grinding diameter was 156 mm, and the total moving distance of the pin was 6 m. Accordingly, an average length of decrease in pin length by abrasion in two specimens was measured as an amount of abrasion under conditions of at room temperature of 22 ± 2°C in an atmospheric environment.

[0088] As shown in Table 6 below, decrease in size with respect to a cladding material (Comparative Examples 11) of a powder of Stellite(R) No. 6 (alloy numbers C19) was 0.088 mm. As compared to this value as 100, a relative value of decrease in size of each of the two-phase alloys of Examples 1 to 22 was calculated, and the value is shown Table 2 as an evaluation of abrasive resistance.

[0089] Similar strength test, corrosion test, and abrasion test were performed on other alloys of the following Examples and Comparative Examples.

(Comparative Examples 1 to 5)

[0090] Chemical compositions of alloys of alloy numbers A17 to A21 used in Comparative Examples 1 to 5 corresponding to Examples 1 to 22 are shown in Table 1. Similar steps to those in alloys of the alloy numbers A1 to A16 were performed to produce alloys of alloy numbers A17 to A21.

[0091] The alloys of alloy numbers A17 and A18 are Cr based two-phase alloys containing no Cu. The alloys of alloy numbers A19 and 20 contain no Cu and are a ferrite single phase Cr based alloy containing Cr as a main component and an austenite single phase Ni based alloy containing Ni as a main component, respectively. The alloy of alloy number A21 is a two-phase stainless steel containing Cu. Ferrite ratios of these alloys were measured similarly to the two-phase alloys of alloy numbers 1 to 16 of Examples. The results of the measurements are shown in Table 2.

[0092] As shown in Table 2, it was found that a ferrite ratio of the alloy of Comparative Examples 3 (alloy numbers A19) was 100% and had a ferrite single phase, and a ferrite ratio of the alloy of Comparative Examples 4 (alloy numbers A20) was 0% and had a austenite single phase. In addition, Comparative Examples 5 (alloy numbers A21) was a two-phase steel having a ferrite ratio of 43%.

[0093] The strength test was performed on alloys of Comparative Examples 1 to 4, and the corrosion test was performed on alloys of Comparative Examples 1 to 5, and the abrasion test was performed on alloys of Comparative Examples 1 to 4. The results of the tests are shown in Table 2.

(Examples 23 to 38)

[0094]

[Table 3]

	Chemical composition [% by mass]																	
	Alloy number	Si	Mn	Al	P	S	Cr	Ni	Fe	Cu	Mo	V	Nb	Ta	Ti	C	N	O
Example	B1	0.51	1.42	0.014	0.011	0.0016	59.69	26.02	11.99	0.14		0.16 (1.15				0.012	0.012	0.014
	B2	0.54	1.38	0.020	0.016	0.0014	52.61	32.9	12.07	0.11			0.31 (1.09)			0.016	0.011	0.015
	B3	0.52	1.39	0.021	0.015	0.0012	45.89	38.96	12.21	0.16				0.79 (1.58)		0.013	0.013	0.012
	B4	0.53	1.40	0.024	0.013	0.0013	57.46	21.24	18.92	0.20					0.17 (1.30)	0.012	0.012	0.014
	B5	0.51	1.37	0.023	0.017	0.0017	46.92	30.1	20.53	0.12			0.37 (1.46)			0.011	0.014	0.013
	B6	5.54	1.34	0.018	0.020	0.0019	40.38	30.94	20.24	1.34					0.14 (1.02)	0.013	0.016	0.010
	B7	0.52	1.29	0.020	0.019	0.0011	42.75	29.88	20.7	4.53					0.24 (1.43)	0.017	0.015	0.016
	B8	0.57	1.38	0.017	0.016	0.0018	39.68	37.54	20.38	0.16			0.14 (0.51)		0.07 (0.49)	0.016	0.015	0.009
	B9	0.53	1.37	0.016	0.015	0.0016	49.51	20.11	28.01	0.13					0.13 (1.09)	0.012	0.012	0.010
	B10	0.53	1.43	0.014	0.017	0.0014	41.72	25.97	29.87	0.21		0.19 (1.27)				0.015	0.013	0.012
	B11	0.54	1.46	0.022	0.013	0.0015	38.09	26.24	30.89	2.31		0.16 (1.03)				0.014	0.014	0.014
	B12	0.51	1.34	0.026	0.013	0.0017	37.56	26.34	30.33	3.52			0.32 (1.32)			0.012	0.013	0.011
	B13	0.52	1.31	0.021	0.014	0.0018	33.95	32.55	31.12	0.18		0.1 (0.75)	0.19 (0.79)			0.012	0.011	0.013
	B14	0.53	1.27	0.020	0.016	0.0025	39.96	25.43	31.14	0.13	1.07		0.38 (1.33)			0.016	0.012	0.014

(Note) Remnants of the chemical compositions of alloy numbers B1 to B14 are Cr and impurities.

(Note) Numbers in parentheses of V, Nb, Ta, and Ti represent rates relative to the total atomic % of C, N, and O.

[0095] In the Examples, hot working alloys of the present invention containing active elements such as V were studied. Chemical compositions of alloys of alloy numbers B1 to B14 used in Examples 23 to 38 are shown in Table 3. Each of the master ingots of alloys of alloy numbers B1 to B14 was produced by melting using a high frequency vacuum melting furnace. The number in parentheses in Table 3 represents a rate of each of the V, Nb, Ta, and Ti as compared to the total atomic % of C, N, and O. In alloy of B8, Nb and Ti were added together, and the rates of the amounts added were 0.51 and 0.49 respectively, and the total rate was 1.00.

[0096] The resulting ingots were subjected to a hot forging treatment and a solution heat treatment under conditions similar to those in the alloys of alloy numbers A1 to A21. Then, all of the alloys were subjected to an aging heat treatment.

[Table 4]

		Alloy number	Solution heat treatment	Aging heat treatment (°C)	Ferrite ratio (%)	Vickers hardness (1 kg)	Proof stress (MPa)	Tensile strength/ breaking stress *(Mpa)	Evaluation of plastic elongation	Evaluation of sulfuric acid resistance	Evaluation of abrasion resistance
Example	23	B1	1100	900	51	443	977	1257*	B	A	65
	24	B2	1100	900	41	366	873	1158*	A	A	70
	25	B3	1100	900	32	318	701	1002*	A	A	74
	26	B4	1100	900	67	502	1058	1186*	C	A	58
	27	B5	1100	900	37	384	879	1151*	A	A	72
	28	B6	1100	800	39	382	883	1121	A	A	66
	29	B6	1100	900	40	361	881	1127*	B	A	71
	30	B6	1200	1000	42	367	914	1184*	B	A	67
	31	B7	1250	900	39	366	904	1129	A	A	73
	32	B8	1100	900	26	279	627	904	A	A	65
	33	B9	1100	900	57	451	1004	1195*	C	A	61
	34	B10	1100	900	37	377	866	1164*	A	A	70
	35	B11	1100	900	42	361	908	1187*	B	A	66
	36	B12	1100	900	40	381	897	1131*	B	A	69
	37	B13	1100	900	26	274	635	901	A	A	74
	38	B14	1100	900	42	386	904	1174*	B	A	70

[0097] The aging heat treatment was carried out, as shown in Table 4, under the following conditions: holding at temperatures of 800, 900, and 1000°C in the alloy number B6 or at 900°C in all the other alloys for 60 minutes, followed by water cooling. Consequently, C, N, and O were stabilized by reactions with active elements of V, Nb, Ta, and Ti, and at the same time, phase ratio control occurred to result in Examples 23 to 38 of alloys of alloy numbers B1 to B14.

[0098] Accordingly, the alloys of alloy numbers B1 to B14 stabilized by active elements were Cr based alloys containing Cr as a main component and containing 0.11 to 4.53% by mass of Cu, and were two-phase alloys consisting of a ferrite phase and an austenite phase. The alloy of alloy numbers B14 further contained Mo. Ferrite ratios of the alloys of alloy numbers B1 to B14 are shown in Table 4. The ferrite ratios of the present embodiments were obtained by EBSP analysis similarly to Examples 1 to 22. Furthermore, the alloys of alloy numbers B12 and B13 which had a higher Fe content and in which σ phase could be generated were subjected to a heat treatment at 800°C for 60 minutes to study whether σ phase generation occurred or not. These heat treated alloys were analyzed by X-ray diffraction to verify that no σ phase was generated similarly to alloys of the A series. This indicates that a σ phase is hardly produced at an intermediate temperature range around 800°C in B series alloys of Examples.

[0099] In addition, a strength test, a corrosion resistance test, and an abrasion test were performed on alloys of Examples 23 to 38 (alloy numbers B1 to B14). The results are shown in Table 4.

<Casting alloy and powder alloy>

(Examples 39 to 51)

[0100] Two-phase alloy cast materials and powder alloys of the present invention were studied. Chemical compositions of alloys of alloy numbers C1 to C8 which are cast materials of two-phase alloys of the present invention used in Examples 39 to 46 are shown in Table 5.

[Table 5]

	Chemical composition [% by mass]																		
	Alloy number	Si	Mn	Al	P	S	Cr	Ni	Fe	Co	Cu	Mo	W	V	Nb	Ta	Ti	C	N	O
Example	C1	0.51	1.30	0.029	0.015	0.0016	56.14	21.65	20.16		0.14							0.013	0.017	0.017
	C2	0.53	1.29	0.028	0.016	0.0014	45.65	31.01	20.21		1.21							0.017	0.015	0.016
	C3	0.51	1.27	0.032	0.012	0.0012	40.78	30.89	19.92		4.52	2.01						0.015	0.015	0.016
	C4	0.52	1.34	0.030	0.014	0.0013	41.21	36.22	20.46		0.15							0.016	0.013	0.019
	C5	0.51	1.31	0.024	0.014	0.0017	56.5	21.38	19.86		0.13			0.21 (1.12)				0.017	0.014	0.020
	C6	0.51	1.30	0.026	0.011	0.0019	46.78	30.87	19.97		0.12				0.36 (1.18)			0.015	0.016	0.014
	C7	0.52	1.26	0.027	0.012	0.0011	39.88	36.86	20.18		0.17					1.04 (1.62)		0.016	0.018	0.015
	C8	0.54	1.38	0.024	0.016	0.0018	42.47	25.29	29.84		0.18						0.21 (1.39)	0.013	0.015	0.016
	C9	0.53	1.42	0.028	0.014	0.0016	57.67	20.99	19.18		0.11							0.0140.015	0.021	0.017
	C10	0.52	1.34	0.029	0.013	0.0014	48.83	30.01	19.04		0.17							0.014	0.017	0.015
	C11	0.52	1.34	0.031	0.014	0.0015	56.73	21.27	19.6		0.15			0.29 (1.48)				0.018	0.016	0.019
	C12	0.53	1.29	0.036	0.016	0.0017	45.14	30.26	20.13		0.14	1.89			0.51 (1.48)			0.017	0.017	0.017
	C13	0.51	1.36	0.030	0.014	0.0018	42.64	25.23	29.75		0.16						0.25 (1.32)	0.019	0.019	0.016
Comparative Example	C14	0.55	1.33	0.041	0.019	0.0021	47.86	30.03	20.11									0.019	0.020	0.013
	C15	0.52	1.34	0.036	0.016	0.0016	63.45	13.06	21.53									0.011	0.014	0.014
	C16	0.53	1.32	0.028	0.024	0.0018	25.84	7.28	bal.		0.12	2.99						0.013	0.013	0.015
	C17	0.51	1.33	0.027	0.015	0.0019	46.86	30.49	20.71									0.015	0.015	0.017
	C18	0.51	1.28	0.034	0.018	0.0025	63.15	13.01	21.94									0.014	0.016	0.016
	C19	0.52	-	-	0.024	0.0023	29.25	1.71	2.97				4.16					0.016	0.017	0.014

(Note) Remnants of the chemical compositions of alloy numbers C1 to C15, 17, and 18 are Cr and impurities, remnants of the chemical compositions of alloy number C16 are Fe and impurities, and remnants of the chemical compositions of alloy number C19 are Co and impurities.

(Note) Numbers in parentheses of V, Nb, Ta, and Ti represent rates relative to the total atomic % of C, N, and O.

[0101] First, a cast material of an alloy of each of the alloy numbers C1 to C4 was produced by adding minute amounts of Cu and Al, and Mo formulated as required to a master ingot of an alloy of each of the alloy numbers A4, 5, and 8 under Ar atmosphere, re-melting them, and casting the liquid material into a water-cooling cupper die equipped with an inlet for liquid materials in the upper portion. The size of the casted ingot was 40 mm in outer diameter and 100 mm in length. Next, alloy cast materials of alloy numbers C5 to C8 were produced by adding at least one or more of V, Nb, Ta, and Ti formulated with minute amounts of Cu and Al together when re-melting the master ingots of the alloys of alloy numbers A4, 5, 8, and 10, melting them, and casting in the same size as that described above. The alloy of alloy numbers C5 was subjected to a solution treatment at 1100°C for 1 hour, and the alloy of alloy numbers C8 is subjected to a solution treatment at 1200°C for 1 hour followed by an aging treatment at 900°C for 1 hour to produce Examples 43 and 46, respectively.

[Table 6]

		Alloy number	Solution heat treatment	Aging heat treatment (°C)	Ferrite ratio (%)	Vickers hardness (1 kg)	Proof stress (MPa)	Tensile strength/ breaking stress *(Mpa)	Evaluation of plastic elongation	Evaluation of sulfuric acid resistance	Evaluation of abrasion resistance
Example	39	C1	-	-	81	599	1121	1196*	C	A	46
	40	C2	-	-	66	508	1057	1183*	C	A	61
	41	C3	-	-	61	516	1052	1165*	C	A	58
	42	C4	-	-	22	294	659	881	A	A	77
	43	C5	1100	-	65	580	1071	1201*	C	A	60
	44	C6	-	-	63	512	1053	1192*	C	A	60
	45	C7	-	-	27	297	699	962	A	A	74
	46	C8	1200	900	40	361	917	1164*	B	A	71
	47	C9	-	-	85	712	-	-	-	A	45
	48	C10	-	-	66	585	-	-	-	A	61
	49	C11	-	-	79	713	-	-	-	A	53
	50	C12	-	-	64	566	-	-	-	A	59
	51	C13	-	-	67	548	-	-	-	A	61
Comparative Example	6	C14	-	-	65	499	1031	1145*	C	B	58
	7	C15	-	-	100	710	-	1346*	D	D	41
	8	C16	-	-	61	-	-	-	-	C	-
	9	C17	-	-	66	583	-	-	-	B	56
	10	C18	-	-	100	801	-	-	-	D	42
	11	C19	-	-	-	473	-	-	-	D	100
(Note) - represents no treatment, and no measurement and evaluation											

[0102] Test pieces were obtained from lower and center portion of the prepared ingot and were subjected to a structure examination, a Vickers hardness measurement, a strength test, a corrosion test, and an abrasion test. The results of ferrite ratios, Vickers hardness, strength properties, strength properties, and results of the corrosion test and the abrasion test of alloys of Examples 39 to 46(alloy numbers C1 to 8) are shown in Table 6.

[0103] Next, chemical compositions of alloys of alloy numbers C9 to C13, which are powder alloys of two-phase alloys of the present invention used in Examples 47 to 51 are shown in Table 5. First, powder alloys of alloy numbers C9 and C10 were obtained by adding minute amounts of Cu and Al to master ingots of alloys of alloy numbers A4 and 5 under Ar atmosphere, re-melting them, and powderizing by a gas atomization method. In addition, powder alloys of alloy numbers C11 to C13 were obtained by adding minute amounts of Cu and Al, and Mo formulated as required and further at least one or more of V, Nb, Ta, and Ti together to master ingots of alloys of alloy numbers A4, 5, and 10, melting them, and powderizing by a gas atomization method. Each of the powder alloys having a particle diameter in a range of 50 to 200 μm was obtained by classification. These powders alloys were built-up on a surface of commercially available SUS 304 steel by a powder plasma cladding welding method up to about a thickness of 5 mm. The cladding welding conditions were arc current of 120 A, voltage of 25 V, and a welding rate of 9 cm/minutes.

[0104] Test pieces for a structure examination, a Vickers hardness measurement, a corrosion test, and an abrasion test were obtained from a surface of the built-up portion of the two-phase alloys of the present invention, and properties of the test pieces were evaluated. The results of the evaluation of the above-described properties of alloys of Examples 47 to 51 (alloy numbers C9 to C13) are shown in Table 6.

(Comparative Examples 6 to 11)

[0105] Chemical compositions of alloys of alloy numbers C14 to C19 used in Comparative Examples 6 to 11 corresponding to Examples 39 to 51 are shown in Table 5. The alloys of alloy numbers C14 to C16 were produced by a casting step similar to that described above using a Cr based two-phase alloy of alloy numbers A17 containing no Cu, a Cr based single-phase ferrite alloy of A19, and a two-phase steel of A21 containing Cu as master ingots. Powder alloys of alloy numbers C17 to C19 were produced by a gas atomization step similar to that described above by re-melting the same master ingots of the alloys of alloy numbers A17 and A19, and the commercially available Stellite(R) No. 6.

[0106] Using test pieces obtained from cladding materials made from the above-described alloys of the cast materials and powder alloys, a measurement and a test similar to those in the cast material two-phase alloy of Examples 39 to 46 and cladding materials of Examples 47 to 51 which were for comparison. The results are shown in Table 6 as Comparative Examples 6 to 11.

[0107] Next, evaluation results of strength, corrosion resistance, and abrasion resistance of a two-phase alloy of the present invention are described.

[Evaluation of strength]

[0108] Vickers hardness was linearly increased in accordance with increase in the ferrite ratio. The Vickers hardness became 400 or more when the ferrite ratio became about 40% or more.

[0109] Proof stress was increased in accordance with the increase in the ferrite ratio. As shown in Table 2 or Table 4, excessively high proof stress can be decreased by reducing the ferrite ratio by an aging treatment. This contributes to improvement of ductility as described below.

[0110] When the ferrite ratio exceeded 60%, plastic elongation becomes 5.0% or less (rated as C) in inverse proportion to the increase in the proof stress, and a single-phase ferrite alloy with the ferrite ratio of 100% was fractured before the yield point (rated as D).

[0111] Two-phase alloys in which an amount of Cr was decreased or an amount of the ferrite phase was decreased by an aging heat treatment at 800 to 1000°C showed elongation exceeding 20%.

[0112] As shown in Table 4, two-phase alloys to which active elements such as V were added had a tendency to clearly increase in plastic elongation as compared to two-phase alloys containing no active element shown in Table 2. In Table 2 and 4, more alloys in Table 4 were rated as A. On the other hand, since two-phase alloys (alloy numbers C1 to C8) produced by casting steps had a solidified structure by quenching from a high temperature, the ferrite ratios became higher to reduce elongation.

[Evaluation of corrosion resistance]

[0113] In two-phase alloys containing Cu and alloys of Comparative Examples 1 to 10, favorable results were produced with respect to pitting resistance properties. That is, electric potential of each of the alloys corresponding to corrosion current density of 100 μA/cm^2 was 1000 mV (vs. SHE) or more, and in the range more than this electric potential, oxygen was generated in the transpassive region. In all alloys tested, generation of pitting was not observed. On the other hand, in Stellite(R) of Comparative Examples 11, corrosion current density exceeded 100 $\mu A/cm^2$ at electric potential of 400 mV (vs. SHE) .

[0114] As shown in Tables 2, 4, and 6, in two-phase alloys containing 0.1 to 4.65% by mass of Cu, an average rate of weight loss by corrosion m was smaller than 0.1 $g/(m^2 \cdot h)$, and sulfuric acid resistance was rated as the best class A. Comparative Examples 1 and 2, which were two-phase alloy without addition of Cu were rated as B, and the effect of addition of Cu on corrosion resistance was confirmed. In alloys containing Cu and Mo together, the m value was smaller than 0.1 $g/(m^2 \cdot h)$ and was rated as the best class A.

[0115] On the other hand, Comparative Examples 5 and 8 of Cu-added two-phase stainless steels were rated as class B and C, respectively. In Stellite(R) No. 6 of Comparative Examples 11, the rate of weight loss was 152 $g/(m^2 \cdot h)$ and was unfavorable in sulfuric acid resistance.

[0116] According to the results of corrosion tests with respect to pitting resistance properties and sulfuric acid resistance, a corrosion resistance of a two-phase alloy containing Cr as a main component was rated as good, and the sulfuric acid resistance of the two-phase alloy was further improved by addition of Cu, and overall high corrosion resistance could be further improved.

[Evaluation of abrasion resistance]

[0117] Abrasion resistance was expressed in a relative value based on the amount of abrasion of Stellite(R) No. 6 as 100, and decreased generally in inverse proportion to increase in hardness, that is, increase in the amount of a ferrite phase. All alloys except for Comparative Examples 4 (alloy numbers A20), which is a single-phase austenite alloy, are superior to Stellite(R) No. 6 in abrasion resistance.

[0118] Thus, each of the two-phase alloys of hot working materials, cast materials, and cladding materials formed with powders of the present invention contains a hard ferrite phase, which can lead to improvement of abrasive resistance effectively.

[0119] By enriching Cr as described above to provide a two-phase alloy including ferrite and austenite phases of Examples rather than a ferrite single phase, strength and elongation as material properties can be maintained. In addition, since the constituent elements include Cu, high corrosion resistance can be achieved. Furthermore, since a hard ferrite phase is contained, abrasion resistance can be improved.

[0120] Such a two-phase alloy having versatile and various favorable properties can be used as a hot working material, a cast material, and a cladding material formed from powders, and is specifically appropriate for a materials for apparatus subjected to severe corrosion atmosphere.

[0121] The above-described two-phase alloys of Examples of the present invention contains inexpensive Cr as a main component, and it is confirmed that the two-phase alloys are superior in overall strength, corrosion resistance, and abrasion resistance to conventional ones even under a high corrosion circumstance such as in an oil well.

LEGEND

[0122]

P1	austenite phase; and
P2	ferrite phase.

Claims

1. A Cr based two-phase alloy comprising two phases of a ferrite phase and an austenite phase in a mixed state, wherein

a chemical composition of the Cr based two-phase alloy consists of a major component, an accessory component, impurities, a first optional accessory component, and a second optional accessory component,
the major component consists of 33% by mass or more and 65% by mass or less of Cr, 18% by mass or more and 40% by mass or less of Ni, and 10% by mass or more and 33% by mass or less of Fe,
the accessory component consists of 0.1% by mass or more and 2% by mass or less of Mn, 0.1% by mass or more and 1.0% by mass or less of Si, 0.005% by mass or more and 0.05% by mass or less of Al, and 0.1% by mass or more and 5.0% by mass or less of Cu, and
the impurities contain more than 0% by mass and 0.04% by mass or less of P, more than 0% by mass and 0.01% by mass or less of S, more than 0% by mass and 0.03% by mass or less of C, more than 0% by mass

and 0.02% by mass or less of N, and more than 0% by mass and 0.03% by mass or less of O.

2. The Cr based two-phase alloy according to claim 1, wherein
the first optional accessory component is 0.1% by mass or more and 3.0% by mass or less of Mo.

3. The Cr based two-phase alloy according to claim 1 or 2, wherein
the second optional accessory component consists of at least one of V, Nb, Ta and Ti, and
a total atomic content ratio of the V, Nb, Ta and Ti is in a range of 0.8 times or more and 2 times or less of a total atomic content ratio of the C, N and O.

4. The Cr based two-phase alloy according to any one of claims 1 to 3, wherein
an occupation ratio of the ferrite phase is 10% or more and 95% or less.

5. The Cr based two-phase alloy according to claim 1, wherein
the component of Ni is in a range of 23% by mass or more and 40% by mass or less.

6. The Cr based two-phase alloy according to claim 5, wherein
the first optional accessory component is 0.1% by mass or more and 3.0% by mass or less of Mo.

7. The Cr based two-phase alloy according to claim 5 or 6, wherein

the second optional accessory component consists of at least one of V, Nb, Ta and Ti, and
the total atomic content ratio of the V, Nb, Ta and Ti is in a range of 0.8 times or more and 2 times or less of the total atomic content ratio of the C, N and O.

8. The Cr based two-phase alloy according to any one of claims 5 to 7, wherein
an occupation ratio of the ferrite phase is 10% or more and 95% or less.

9. A two-phase alloy product which is a product using a two-phase alloy, wherein
the two-phase alloy is the Cr based two-phase alloy according to any one of claims 1 to 4.

10. A two-phase alloy product which is a product using a two-phase alloy, wherein
the two-phase alloy is the Cr based two-phase alloy according to any one of claims 5 to 8.

11. The two-phase alloy product according to claim 9, wherein
the product is a molded body having a forged structure.

12. The two-phase alloy product according to claim 10, wherein
the product is a molded body having a cast structure.

13. The two-phase alloy product according to claim 10, wherein
the product is a powder.

FIG. 1

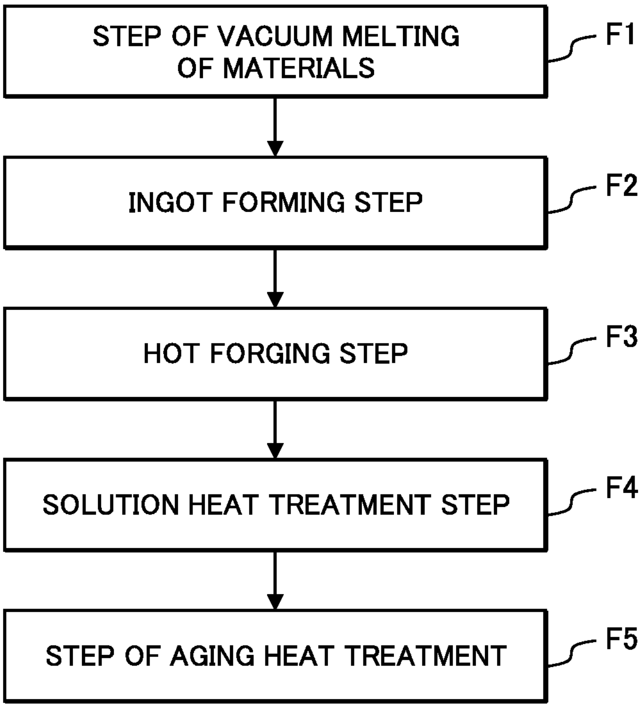
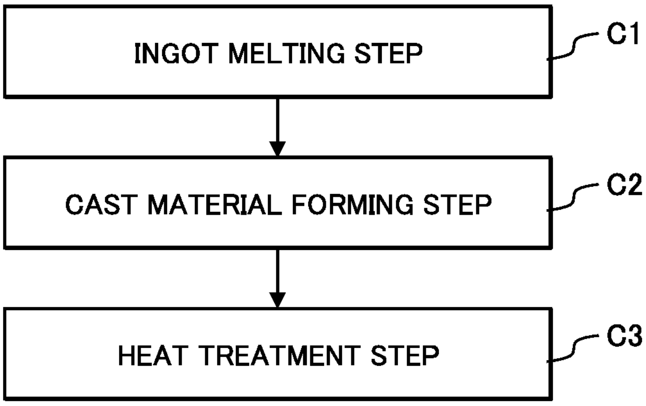

STEP OF VACUUM MELTING OF MATERIALS
F1
INGOT FORMING STEP
F2
HOT FORGING STEP
F3
SOLUTION HEAT TREATMENT STEP
F4
STEP OF AGING HEAT TREATMENT
F5

FIG. 2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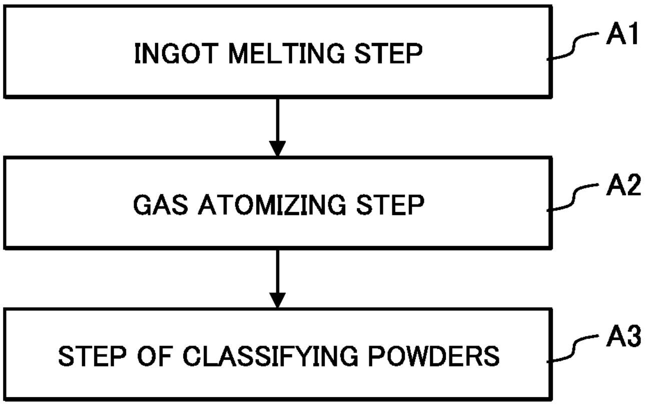
CAST MATERIAL FORMING STEP
C2
HEAT TREATMENT STEP
C3

FIG. 3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GAS ATOMIZING STEP
A2
STEP OF CLASSIFYING POWDERS
A3

FIG. 4

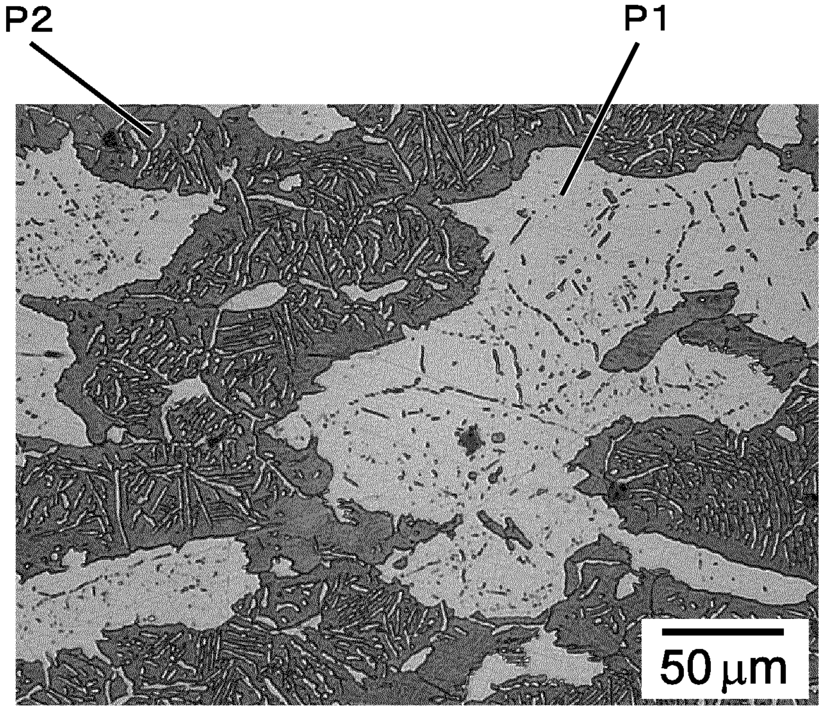


FIG. 5

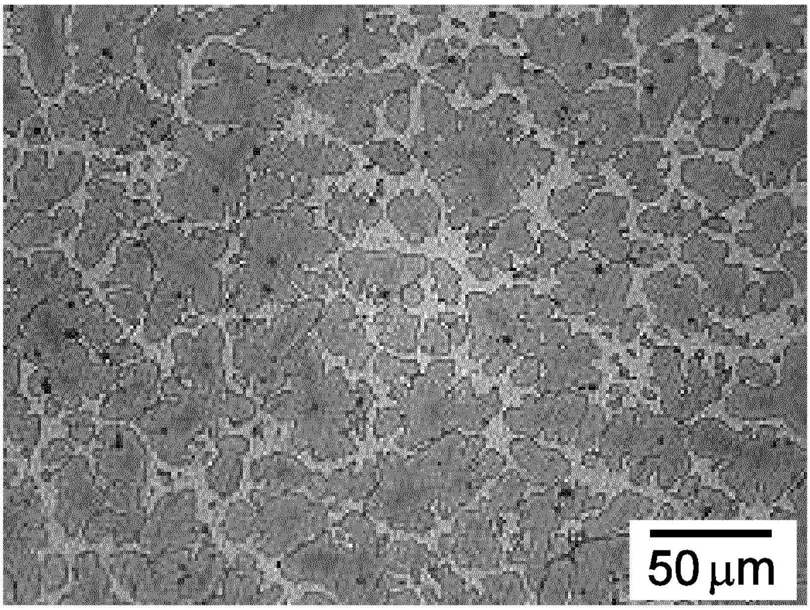
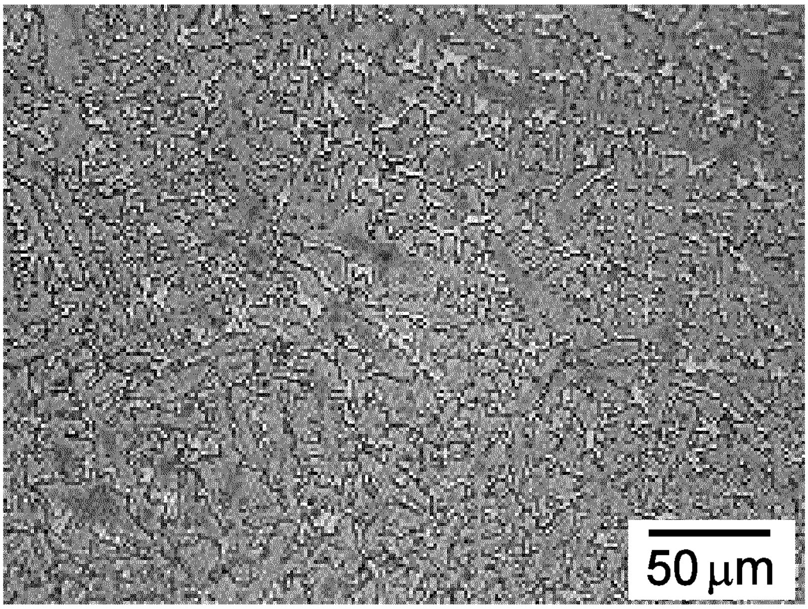


FIG. 6



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/003081

A. CLASSIFICATION OF SUBJECT MATTER
C22C27/06(2006.01)i, *B22D21/02*(2006.01)i, *B22F1/00*(2006.01)i, *C22C30/02*(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)
C22C27/06, B22D21/02, B22F1/00, C22C30/02

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	1996-2017
Kokai Jitsuyo Shinan Koho	1971-2017	Toroku Jitsuyo Shinan Koho	1994-2017

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.
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A	JP 10-140290 A (Sumitomo Metal Industries, Ltd.), 26 May 1998 (26.05.1998), (Family: none)	1-13
A	JP 58-11735 A (Sumitomo Metal Industries, Ltd.), 22 January 1983 (22.01.1983), & US 4421571 A & GB 2104100 A & DE 3224865 A1 & FR 2508930 A1	1-13

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

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"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
"&"	document member of the same patent family

Date of the actual completion of the international search 10 April 2017 (10.04.17)	Date of mailing of the international search report 25 April 2017 (25.04.17)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/003081

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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- JP HEI4199272013 A **[0006]**
- WO 2013058274 A1 **[0006]**
- JP HEI41992301048 A **[0006]**
- JP HEI41992301049 A **[0006]**
- JP HEI81996291355 A **[0006]**