



US 20150368770A1

(19) **United States**

(12) **Patent Application Publication**
Baker et al.

(10) **Pub. No.: US 2015/0368770 A1**

(43) **Pub. Date: Dec. 24, 2015**

(54) **NICKEL-CHROMIUM-IRON-MOLYBDENUM
CORROSION RESISTANT ALLOY AND
ARTICLE OF MANUFACTURE AND
METHOD OF MANUFACTURING THEREOF**

Publication Classification

(71) Applicant: **Huntington Alloys Corporation,**
Huntington, WV (US)

(51) **Int. Cl.**
C22F 1/00 (2006.01)
C22C 30/02 (2006.01)
(52) **U.S. Cl.**
CPC .. **C22F 1/00** (2013.01); **C22C 30/02** (2013.01)

(72) Inventors: **Brian A. Baker,** Kitts Hill, OH (US);
Debajyoti Maitra, Huntington, WV
(US)

(57) **ABSTRACT**

A solid-solution nickel-based alloy for use in sour gas and oil environments, including, in percent by weight: chromium: min. of 21.0 and max. of 24.0%; iron: min. of 17.0 and max. of 21.0%; molybdenum: min. of 6.5 and max. of 8.0%; copper: min. of 1.0 and max. of 2.5%; tungsten: min. of 0.1 and max. of 1.5%; sol. nitrogen: min. of 0.08 and max. of 0.20%; manganese: max. of 4.0%; silicon: max. of 1.0%; carbon: max of 0.015%; aluminum: max of 0.5%; and a total amount of niobium, titanium, vanadium, tantalum, and zirconium: max of 0.45%; the balance being nickel and incidental impurities, along with a method of manufacturing an article from the alloy, and an article of manufacture formed from the alloy.

(21) Appl. No.: **14/744,515**

(22) Filed: **Jun. 19, 2015**

Related U.S. Application Data

(60) Provisional application No. 62/014,803, filed on Jun. 20, 2014.

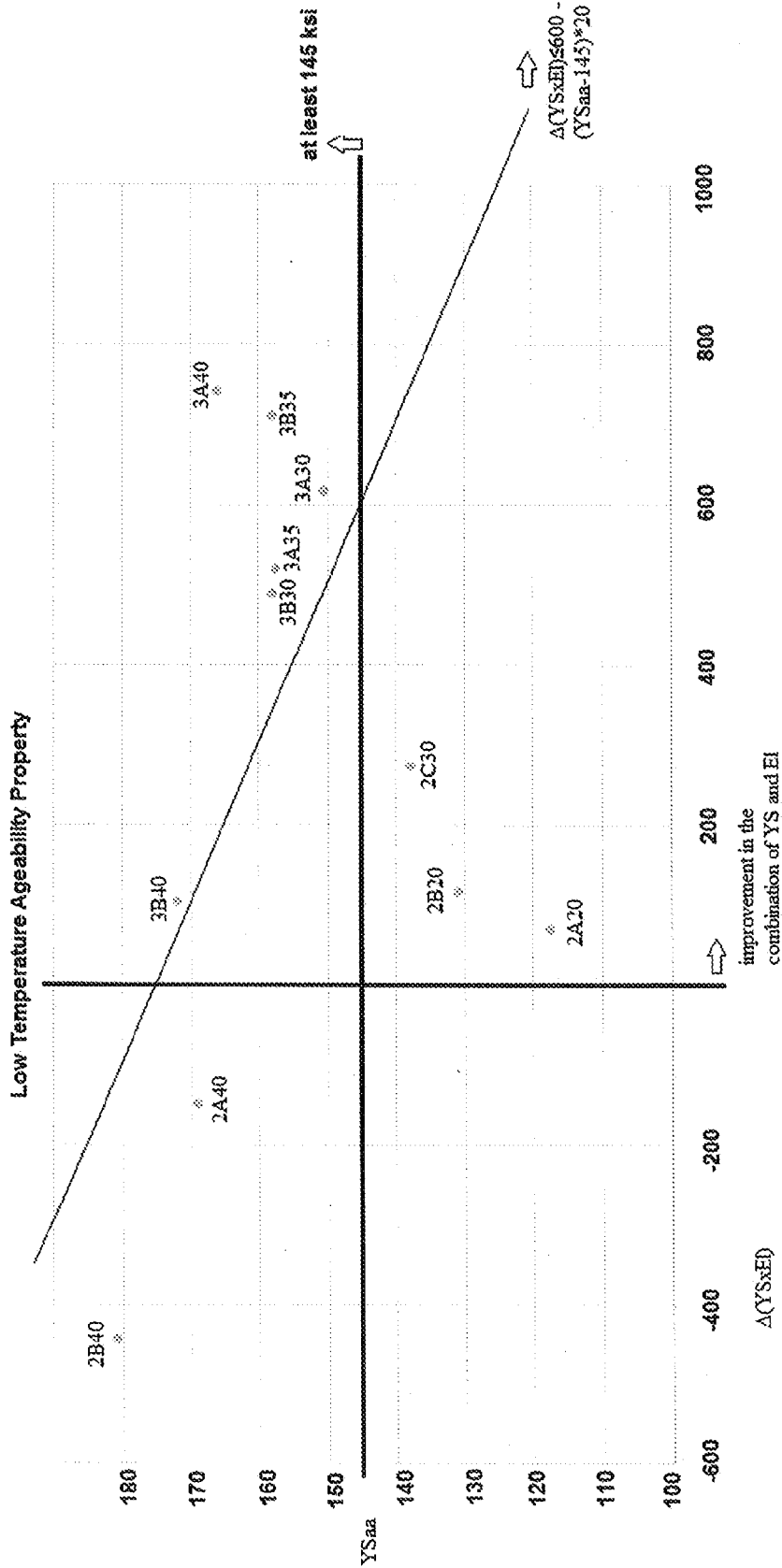


FIG. 1

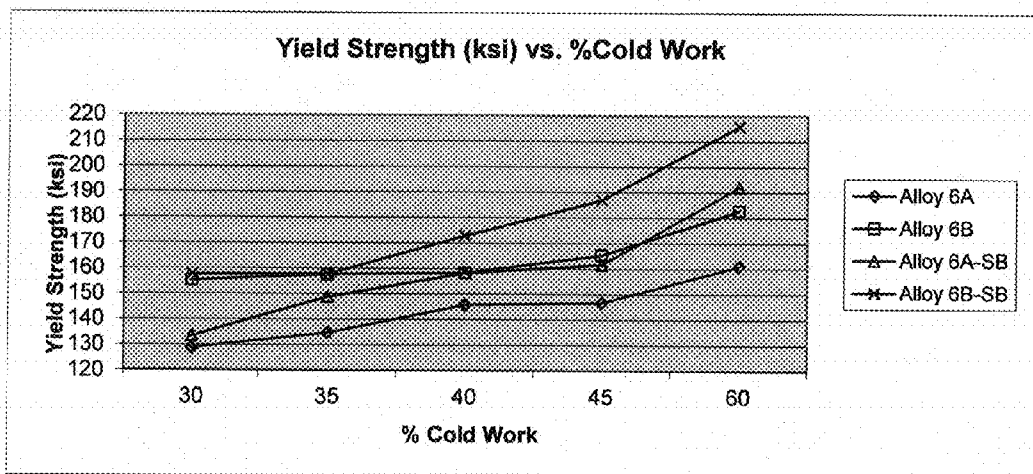


FIG. 2

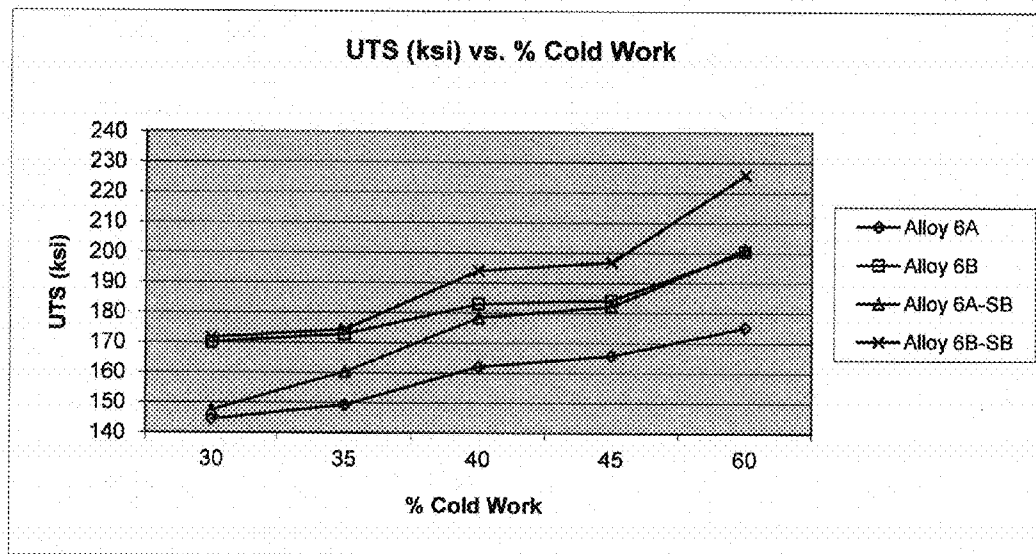


FIG. 3

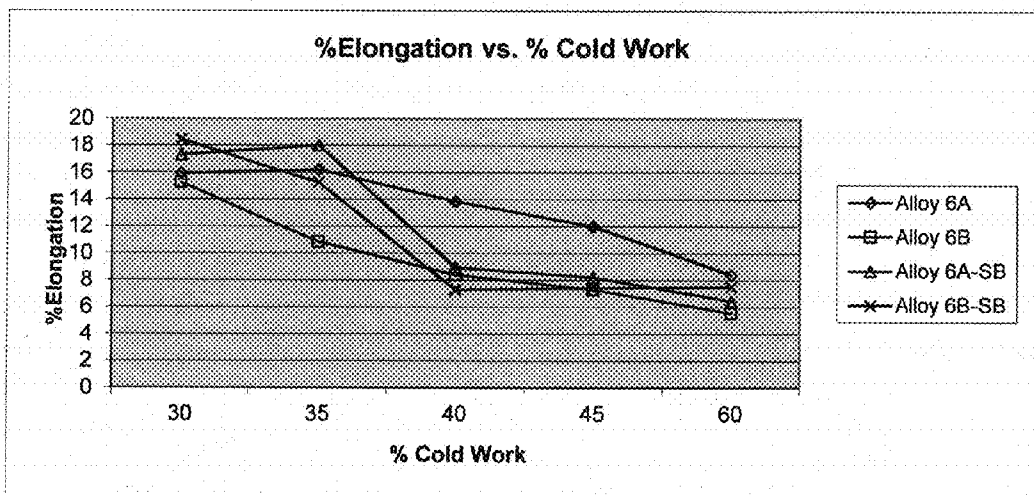


FIG. 4

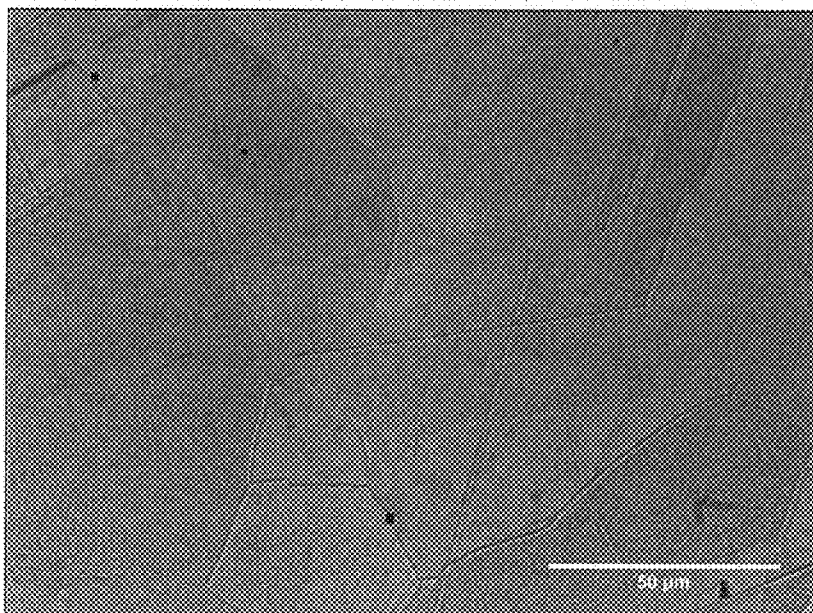


FIG. 5

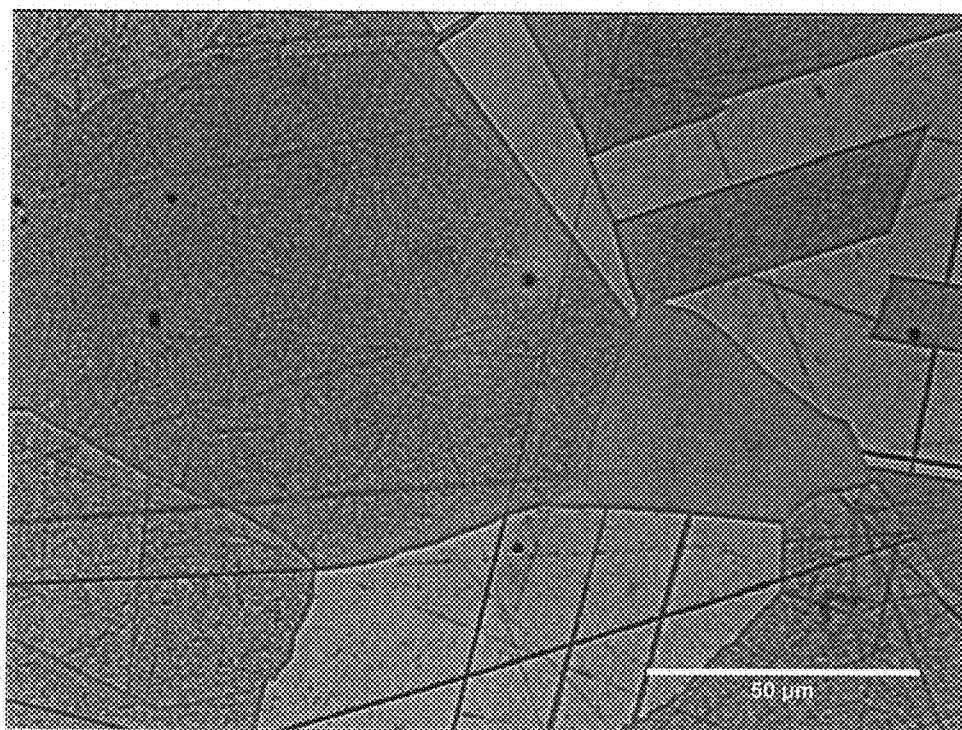


FIG. 6

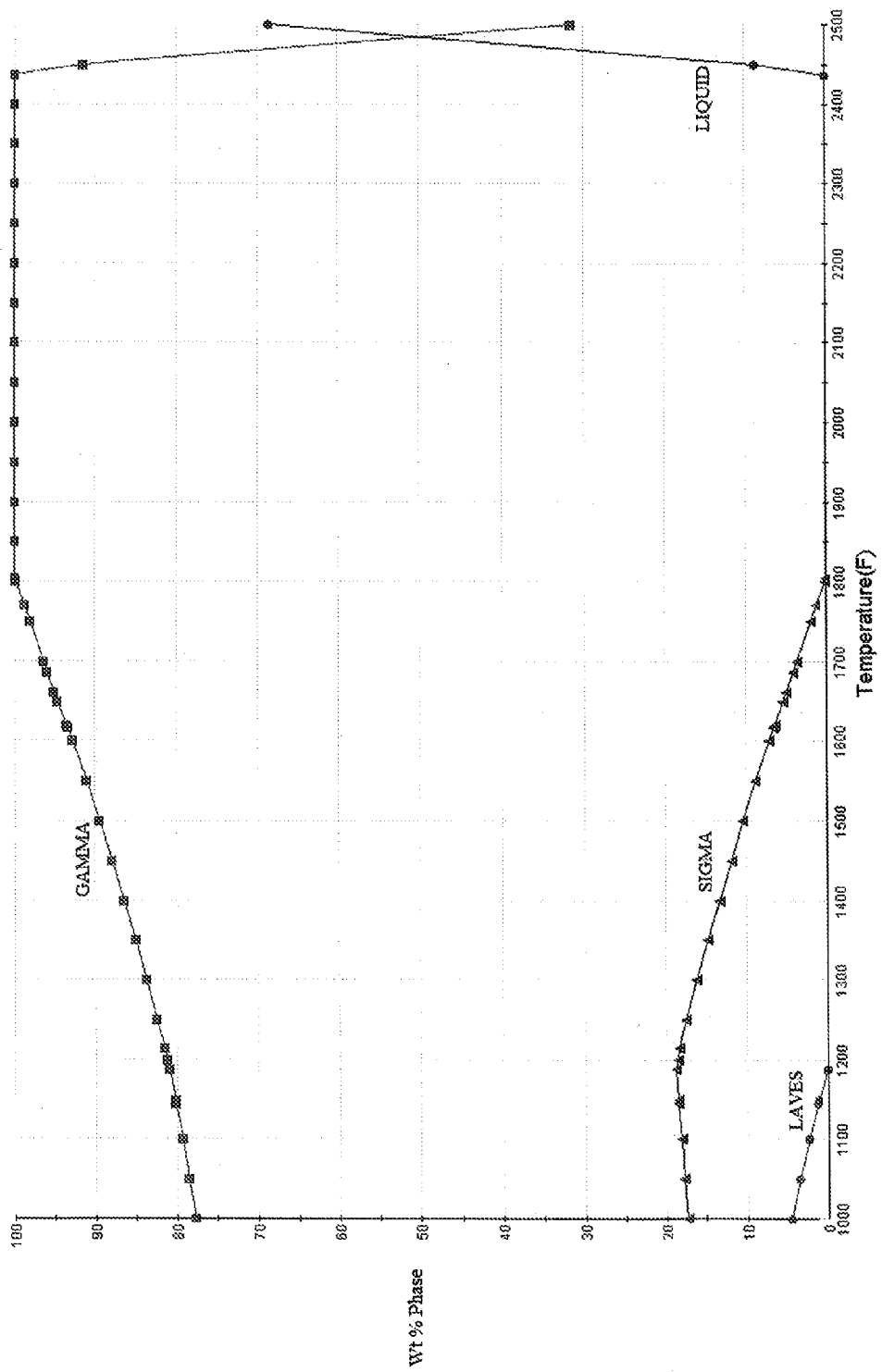


FIG. 7

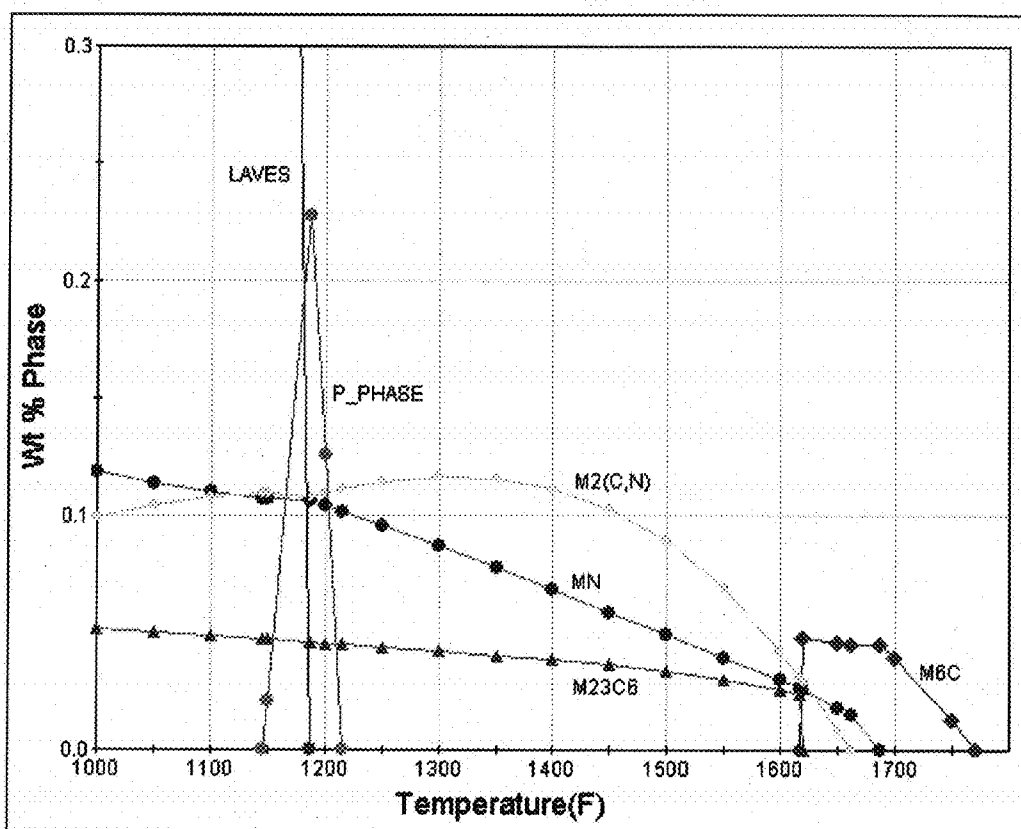


FIG. 8

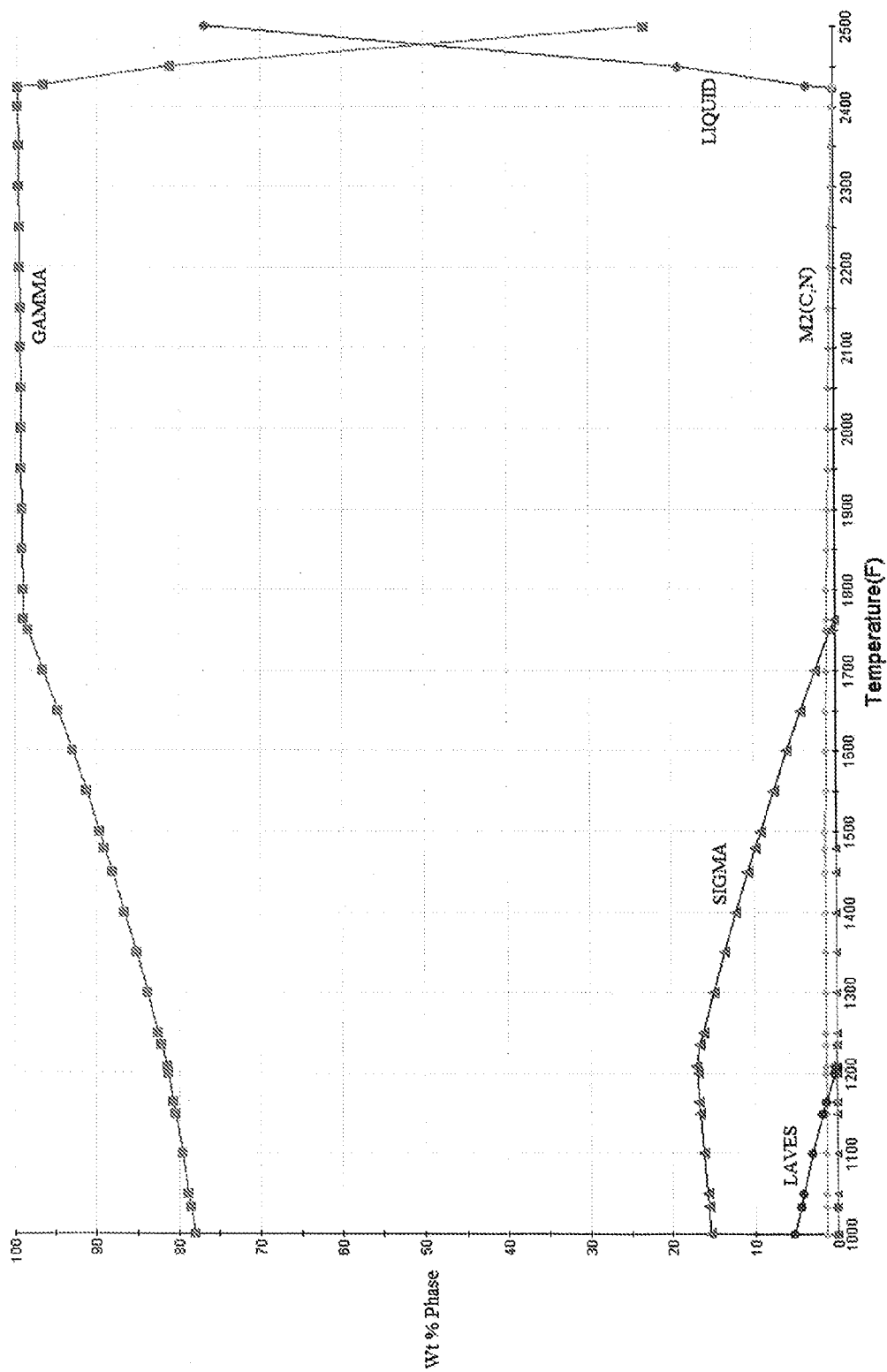


FIG. 9

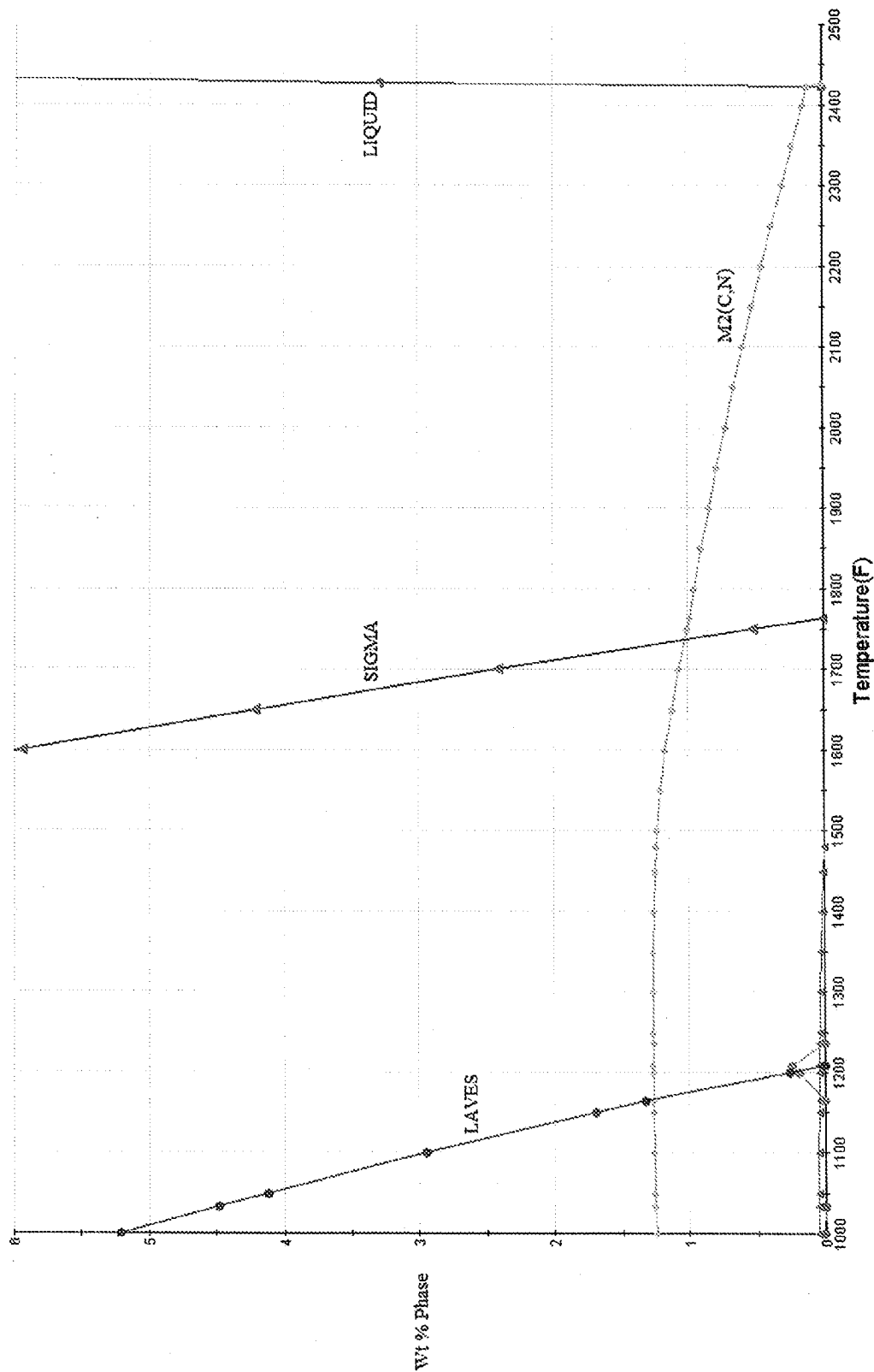


FIG. 10

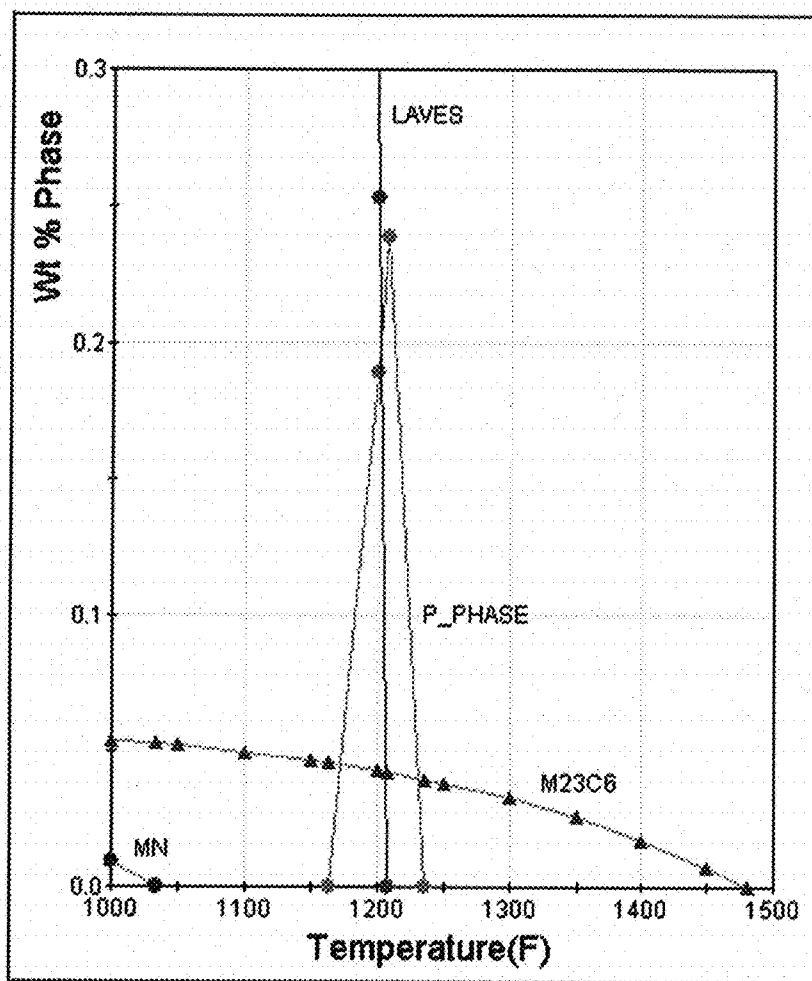


FIG. 11

TTT NiFe Based Superalloy

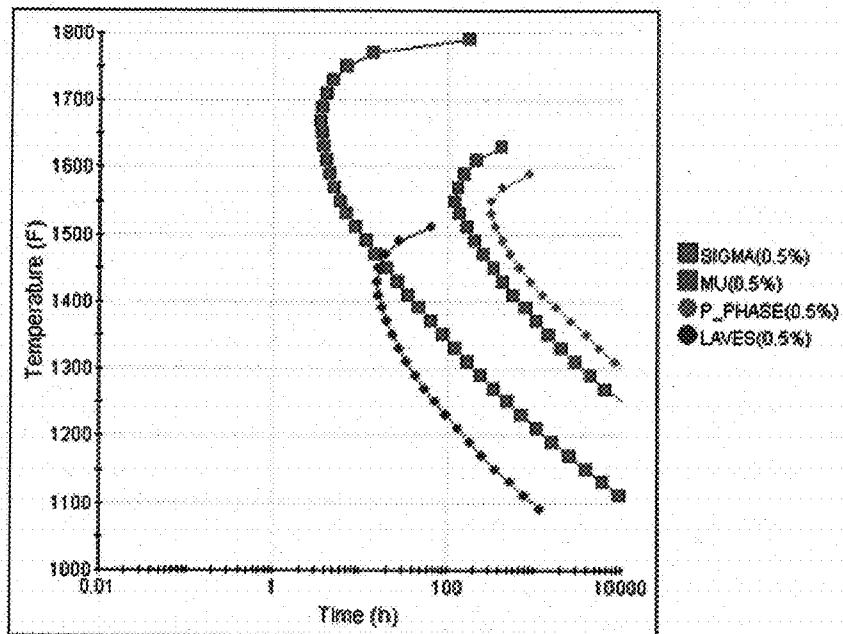


FIG. 12

CCT NiFe Based Superalloy

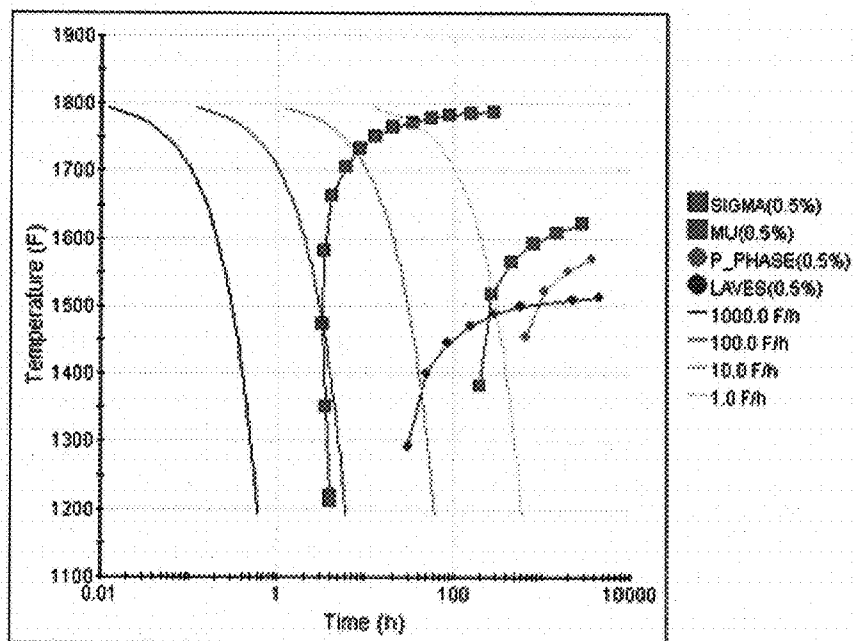


FIG. 13

TTT NiFe Based Superalloy

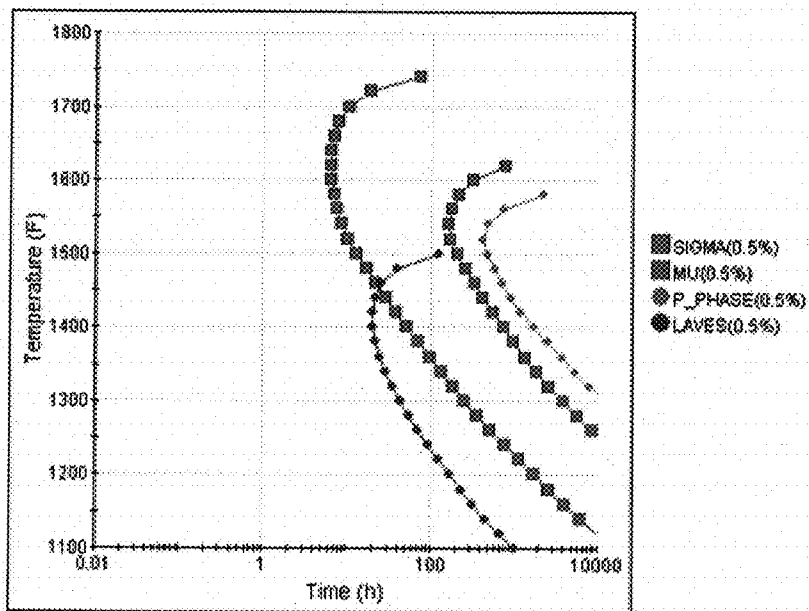


FIG. 14

CCT NiFe Based Superalloy

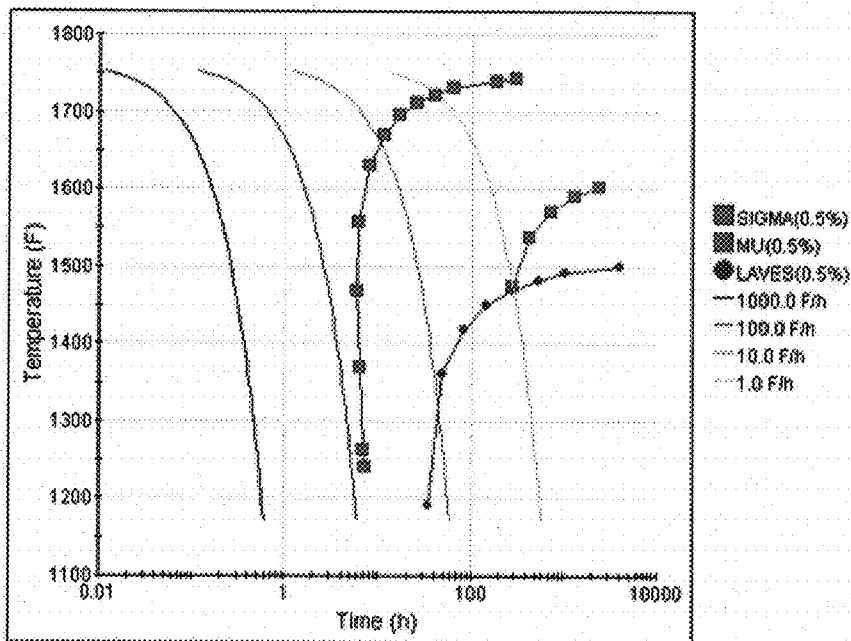


FIG. 15

**NICKEL-CHROMIUM-IRON-MOLYBDENUM
CORROSION RESISTANT ALLOY AND
ARTICLE OF MANUFACTURE AND
METHOD OF MANUFACTURING THEREOF**

**CROSS REFERENCE TO RELATED
APPLICATIONS**

[0001] This application claims priority to U.S. Provisional Patent Application No. 62/014,803 filed Jun. 20, 2014, the disclosure of which is hereby incorporated by reference for all purposes in its entirety.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The field of the present invention relates to solid solution strengthened nickel-chromium-iron-molybdenum corrosion resistant alloys suitable for use in sour gas and oil environments.

[0004] 2. Description of Related Art

[0005] Nickel alloys generally have the ability to withstand a wide variety of severe operating conditions involving corrosive environments, high temperatures, and high stresses. From commercially pure nickel to complex alloys containing as many as twelve or more alloying elements, nickel alloys are used for a wide variety of applications, including, for example: chemical and petrochemical industries; pulp and paper mills; aircraft gas turbines; steam turbine power plants, reciprocating engines; metal processing; medical applications; space vehicles, heat-treating equipment; nuclear power systems; pollution control equipment; metals processing mills; coal gasification and liquefaction systems; automotive industries; and oil and gas industries.

[0006] Deep wells are important for the future of oil and gas exploration. Deep wells are generally categorized as being either sweet or sour, with sweet wells being mildly corrosive and sour wells being highly corrosive, containing combinations of corrosive agents, such as hydrogen sulfide, carbon dioxide, chlorides, and free sulfur. The corrosive conditions of sour wells are compounded by high temperatures and high pressures. Thus, for sour oil and gas environments, materials are selected to meet stringent criteria for corrosion resistance while achieving excellent mechanical properties.

[0007] Nickel-chromium-iron-molybdenum alloys offer advantages over other materials used in oil and gas industries, including high strength, high toughness, and excellent corrosion resistance. Nickel-chromium-iron-molybdenum alloys include solid solution alloys and precipitation hardenable alloys. Solid solution alloys generally obtain their strength through solid solution strengthening and cold working. Precipitation hardenable alloys are generally used for heavier cross sections, which cannot be easily strengthened by cold working, or are used at higher temperatures, at which the effect of cold working is not sustained. The precipitation hardenable alloys primarily obtain their strength as a result of precipitation of secondary phases within the matrix of the alloy. Precipitation hardening is often the result of the precipitation via heat treatment of gamma prime or gamma double prime phases. Formation of carbides and nitrides may also strengthen precipitation hardenable alloys. However, precipitation hardenable alloys have disadvantages compared to solid solution alloys. Therefore, the use of precipitation hardenable alloys is generally limited to applications for which solid solution alloys are not desirable.

[0008] INCOLOY® alloy 028 (UNS N08028/W. Nr. 1.4563), a nickel-iron-chromium alloy with additions of molybdenum and copper, is especially resistant to sulfuric and phosphoric acid and is commonly used for chemical processing, pollution control equipment, oil and gas well piping, nuclear fuel reprocessing, acid production, and pickling equipment. The chemical composition of INCOLOY® alloy 028 is, by weight percent: Ni: 30-32; Fe: 22 min.; Cr: 26-28; Mo: 3-4; Cu: 0.60-1.40; C: 0.02 max; Mn: 2 max; S: 0.03 max; and Si: 0.70 max.

[0009] INCONEL® alloy C-276 (UNS N10276/W.Nr. 2.4819), a nickel-molybdenum-chromium alloy with an addition of tungsten, is designed to have excellent corrosion resistance in a wide range of severe environments. High nickel and high molybdenum contents make the alloy especially resistant to pitting and crevice corrosion in reducing environments while chromium conveys resistance to oxidizing media. The low carbon content minimizes carbide precipitation during welding to maintain corrosion resistance in as-welded structures. This alloy is resistant to the formation of grain boundary precipitates in the weld heat-affected zone, thus making it suitable for most chemical process applications in an as-welded condition. INCONEL® alloy C-276 (UNS N10276/W.Nr. 2.4819) is widely used in the most severe environments, such as chemical processing, pollution control, pulp and paper production, industrial and municipal waste treatment, and recovery of sour natural gas. The chemical composition of INCONEL® alloy C-276 (UNS N10276/W.Nr. 2.4819) is, by weight percent: Mo: 15.0-17.0; Cr: 14.5-16.5; Fe: 4.0-7.0; W: 3.0-4.5; Co: 2.5 max; Mn: 1.0 max; C: 0.01 max; V: 0.35 max; P: 0.04 max; S: 0.03 max; Si: 0.08 max; and remainder nickel.

[0010] INCONEL® alloy G-3 (UNS N06985/W. Nr. 2.4619), a solid solution strengthened nickel-chromium-iron-molybdenum alloy, provides an excellent combination of mechanical properties and corrosion resistance, and has been used extensively in tubular goods used in hot, sour environments of the gas and oil industries. The compositional limits for INCONEL® alloy G-3 (UNS N06985/W. Nr. 2.4619) are generally indicated as 21.0-23.5 wt % chromium, 18.0-21.0 wt % iron, 6.0-8.0 wt % molybdenum, 1.5-2.5 wt % copper, a maximum of 0.50 wt % niobium plus tantalum, a maximum of 0.015 wt % carbon, a maximum of 1.5 wt % tungsten, a maximum of 1.0 wt % silicon, a maximum of 1.0 wt % manganese, a maximum of 0.04 wt % phosphorus, a maximum of 0.03 wt % sulfur, a maximum of 5.0 wt % cobalt, and balance nickel. INCONEL® alloy G-3 (UNS N06985/W. Nr. 2.4619) has excellent corrosion resistance to oxidizing chemicals and atmospheres and is resistant to reducing chemicals because of its nickel and copper contents. It also has exceptional stress-corrosion-cracking resistance in chloride-containing environments, very good resistance to pitting and crevice corrosion, and good weldability and resistance to intergranular corrosion in the as-welded condition.

[0011] However, the current worldwide demand for ever increasing quantities of gas and oil has caused the gas and oil industries to begin extracting these commodities from deeper and sourer wells. Deeper wells mean higher temperatures, higher pressures, and more corrosive environments, especially with regard to sour gas environments. INCOLOY® alloy 028 (UNS N08028/W. Nr. 1.4563), INCONEL® alloy C-276 (UNS N10276/W.Nr. 2.4819), and INCONEL® alloy G-3 (UNS N06985/W. Nr. 2.4619) do not achieve a level of strength and ductility desired for high strength applications

for the oil and gas industries. Thus, there is a need for improvement in the combination of mechanical properties and corrosion resistance compared to what is currently offered by existing alloys. More specifically, there is a need to dramatically increase the strength of solid solution nickel alloys without loss of ductility, toughness, fabricability, and corrosion resistance. Furthermore, an alloy certified for oil and gas field applications possesses a clean microstructure in addition to the usual required properties needed for any given application.

[0012] U.S. Pat. No. 4,400,210 to Kudo et al. (hereinafter “Kudo ’210”) discloses an alloy described to be useful for manufacturing high strength deep well casing, tubing, and drill pipes for use in oil well operations. Kudo ’210 states that the alloy exhibits improved resistance to stress-corrosion-cracking in an $H_2S-CO_2Cl^-$ environment. The alloy comprises: C: not more than 0.10%, Si: not more than 1.0%, Mn: not more than 2.0%, P: not more than 0.030%, S: not more than 0.005%, N: 0-0.30%, Ni: 25-60%, Cr: 22.5-35%, Mo: less than 7.5% and W: less than 15%, and balance iron with incidental impurities with the following equations being satisfied: $Cr(\%)+10Mo(\%)+5W(\%) \geq 70\%$, and $3.5\% \leq Mo(\%)+1/2W(\%) < 7.5\%$. Kudo ’210 further states that the alloy may further comprise any combination of the following: (i) one of Cu: not more than 2.0%, and/or Co: not more than 2.0%; (ii) one or more of rare earths: not more than 0.10%; Y: not more than 0.20%, Mg: not more than 0.10%; and Ca: not more than 0.10%; (iii) one or more of Nb, Ti, Ta, Zr, and V in the total amount of from 0.5-4.0%; and (iv) nitrogen in an amount of 0.05-0.30%, preferably 0.10-0.25% may be intentionally added to the alloy. Kudo ’210 also states that nitrogen may be added in an amount of 0.05-0.25% in combination with Nb and/or V added in the total amount of 0.5-4.0%. However, Kudo ’210 does not provide an alloy having a high strength without loss of ductility, toughness, fabrication, and corrosion resistance while possessing a clean microstructure as required by the oil and gas industries.

[0013] U.S. Pat. No. 4,400,211 to Kudo et al. (hereinafter “Kudo ’211”) discloses another alloy described to be useful for manufacturing high strength deep well casing, tubing, and drill pipes for use in oil well operations. Kudo ’211 states that the alloy exhibits improved resistance to stress-corrosion-cracking in an $H_2S-CO_2-Cl^-$ environment. The alloy comprises: C: not more than 0.10%, Si: not more than 1.0%, Mn: not more than 2.0%, P: not more than 0.030%, preferably not more than 0.003%, S: not more than 0.005%, Ni: 30-60%, Cr: 15-35%, at least one of Mo: not more than 12%, and W: not more than 24%, and the balance iron with incidental impurities with the following equations being satisfied: $Cr(\%)+10Mo(\%)+5W(\%) \geq 110\%$, and $7.5\% \leq Mo(\%)+1/2W(\%) \leq 12\%$. Kudo ’211 further states that the alloy may further comprise any combination of the following: (i) one of Cu: not more than 2.0%, and/or Co: not more than 2.0%; (ii) one or more of rare earths: not more than 0.10%; Y, not more than 0.20%; Mg: not more than 0.10%; and Ca: not more than 0.10%; (iii) one or more of Nb, Ti, Ta, Zr, and V in the total amount of from 0.5-4.0%; and (iv) nitrogen in an amount of 0.05-0.30%, preferably 0.10-0.25% may be intentionally added to the alloy. However, Kudo ’211 does not provide an alloy having a high strength without loss of ductility, toughness, fabrication, and corrosion resistance while possessing a clean microstructure as required by the oil and gas industries.

SUMMARY OF THE INVENTION

[0014] According to one or more embodiments, it is an object to overcome one or more problems of the related art.

[0015] It is another object to provide an alloy with increased strength relative to existing solid solution alloys, especially INCONEL® alloy G-3 (UNS N06985/W. Nr. 2.4619), while avoiding substantial losses of ductility, toughness, fabricability, and corrosion resistance and possessing a clean microstructure as described by International Standard ANSI/NACE MR0175/ISO15156-3 [Petroleum and Natural Gas Industries—Materials for use in H_2S -containing environments in oil and gas production].

[0016] These and other features and characteristics will become more apparent upon consideration of the following description and the appended claims with reference to the accompanying figures, all of which form a part of this specification. As used in the specification and the claims, the singular form of “a”, “an”, and “the” include plural referents unless the context clearly dictates otherwise.

[0017] Every effort has been made to correctly convert the units of measurement to SI units. To the extent that any discrepancy exists in the conversion, the non-SI units should be understood to be correct.

[0018] All compositions are described in weight percent unless expressly specified otherwise.

[0019] All yield strengths cited herein are measured at >0.2% offset unless expressly specified otherwise.

[0020] According to an exemplary embodiment of the present invention, a solid-solution nickel-based alloy for use in sour gas and oil environments, comprises, in percent by weight: chromium: min. of 21.0 and max. of 24.0%; iron: min. of 17.0 and max. of 21.0%; molybdenum: min. of 6.5 and max. of 8.0%; copper: min. of 1.0 and max. of 2.5%; tungsten: min. of 0.1 and max. of 1.5%; sol. nitrogen: min. of 0.08 and max. of 0.20%; manganese: max. of 4.0%; silicon: max. of 1.0%; carbon: max of. 0.015%; aluminum max of. 0.5%; and a total amount of niobium, titanium, vanadium, tantalum, and zirconium: max of 0.45%; the balance being nickel and incidental impurities.

[0021] The minimum chromium content is preferably 22.0%, more preferably 22.5%. The maximum chromium content is preferably 23.5%, more preferably 23.3%, and more preferably 23.1%.

[0022] The minimum iron content is preferably 18.0%, more preferably 19.0%. The maximum iron content is preferably 20.5%, more preferably 20.0%.

[0023] The minimum molybdenum content is preferably 6.8%, more preferably 7.1%. The maximum molybdenum content is preferably 7.8%, more preferably 7.6%.

[0024] The minimum copper content is preferably 1.5%, more preferably 1.7%, and more preferably 1.9%. The maximum copper content is preferably 2.3%, more preferably 2.1%.

[0025] The minimum tungsten content is preferably 0.50%, more preferably 0.90%. The maximum tungsten content is preferably 1.4%, more preferably 1.3%.

[0026] The minimum sol. nitrogen content is preferably 0.10%, more preferably 0.12%. The maximum sol. nitrogen content is preferably 0.19%, more preferably 0.18%, more preferably 0.17%, and more preferably 0.16%.

[0027] The maximum manganese content is preferably 2.0%, more preferably 1.0%.

[0028] The maximum silicon content is preferably 0.50%, more preferably 0.25%.

[0029] The maximum carbon content is preferably 0.010%, more preferably 0.005%.

[0030] The minimum aluminum content is preferably 0.001%, more preferably 0.010%, and more preferably 0.10%. The maximum aluminum content is preferably 0.40%, more preferably 0.30%.

[0031] The maximum total amount of niobium, titanium, vanadium, tantalum, and zirconium is preferably 0.40%. The maximum niobium content is preferably 0.20%, more preferably 0.10%. The maximum tantalum content is preferably 0.10%, more preferably 0.01%. The maximum vanadium content is preferably 0.15%. The maximum tantalum content is preferably 0.10%. The maximum zirconium content is preferably 0.05%.

[0032] The maximum content of phosphorus is preferably 0.050%, more preferably 0.010%, and more preferably 0.005%.

[0033] The maximum content of sulfur is preferably 0.050%, more preferably 0.010%, and more preferably 0.005%.

[0034] The alloy may further comprise cobalt: maximum of 5.0%, preferably maximum of 2.0%, more preferably maximum of 1.0%.

[0035] The alloy may further comprise one or more rare earth elements: maximum of 0.10%.

[0036] The alloy may further comprise yttrium: maximum of 0.20%.

[0037] The alloy may further comprise magnesium: maximum of 0.10%.

[0038] The alloy may further comprise calcium: maximum of 0.10%.

[0039] Boron, tin, lead, and zinc are each preferably controlled to be a maximum of 0.10% or less, preferably 0.01% or less, more preferably 0.001% or less.

[0040] The minimum nickel content is preferably 40.0%, more preferably 42.0%, and more preferably 44.0%.

[0041] The content of Mo+½ W is preferably controlled to be a minimum of 7.6%, more preferably a minimum of 7.7%, and more preferably a minimum of 7.8%. The content of Mo+½ W is preferably controlled to be a maximum of 8.5%, more preferably a maximum of 8.4%, and more preferably a maximum of 8.3%.

[0042] The soluble nitrogen content is preferably a minimum of 0.08%, more preferably a minimum of 0.10%, more preferably a minimum of 0.12%. The soluble nitrogen content is preferably a maximum of 0.20%, more preferably a maximum of 0.18%, more preferably a maximum of 0.16%.

[0043] The alloy preferably has a low temperature ageability property, $\Delta(YS \times EI)$, of greater than 0 when a yield strength after aging (YS_{aa}) is at least 145 ksi, wherein $\Delta(YS \times EI)$ is the 0.2% Offset Yield Strength (ksi) times Percent Elongation after aging ($YS_{aa} \times EI_{aa}$) minus the 0.2% Offset Yield Strength (ksi) times Percent Elongation before aging ($YS_{ba} \times EI_{ba}$). In SI units, the alloy preferably has a low temperature ageability property, $\Delta(YS \times EI)$, of greater than 0 when a yield strength after aging (YS_{aa}) is at least 1000 MPa, wherein $\Delta(YS \times EI)$ is the 0.2% Offset Yield Strength (MPa) times Percent Elongation after aging ($YS_{aa} \times EI_{aa}$) minus the 0.2% Offset Yield Strength (MPa) times Percent Elongation before aging ($YS_{ba} \times EI_{ba}$).

[0044] The alloy preferably has a low temperature ageability property that satisfies the condition, $\Delta(YS \times EI) \geq 600 - (YS_{aa} - 145) \times 20$, wherein $\Delta(YS \times EI)$ is the 0.2% Offset Yield Strength (ksi) times Percent Elongation after aging ($YS_{aa} \times$

EI_{aa}) minus the 0.2% Offset Yield Strength (ksi) times Percent Elongation before aging ($YS_{ba} \times EI_{ba}$). In SI units, the alloy preferably has a low temperature ageability property that satisfies the condition, $\Delta(YS \times EI) \geq 4138 - (YS_{aa} - 1000) \times 20$, wherein $\Delta(YS \times EI)$ is the 0.2% Offset Yield Strength (MPa) times Percent Elongation after aging ($YS_{aa} \times EI_{aa}$) minus the 0.2% Offset Yield Strength (MPa) times Percent Elongation before aging ($YS_{ba} \times EI_{ba}$).

[0045] In an exemplary embodiment of the present invention, a method of manufacturing an article, includes: providing a billet formed from the alloy that is solution annealed and then cold worked a minimum of 20% to an article of predetermined dimensions; and heat treating the cold worked article at 468°-537° C. (875°-999° F.) for five minutes to eight hours.

[0046] In an exemplary embodiment of the present invention, an article of manufacture formed from the alloy has a cold-worked and aged microstructure, having grain boundaries with no continuous precipitates, wherein upon microstructural examination on a section taken in the longitudinal direction with respect to the direction of cold work, a total area fraction of intermetallic phases, nitrides, and carbides does not exceed 1.0%, and wherein an area fraction of sigma phase does not exceed 0.5%.

[0047] In an exemplary embodiment, the article has a 0.2% offset yield strength of at least 1000 MPa (145 ksi) and at least 12% elongation.

[0048] In another exemplary embodiment, the article has a 0.2% offset yield strength of at least 1069 MPa (155 ksi) and at least 10% elongation.

[0049] In yet another exemplary embodiment, the article has a 0.2% offset yield strength of at least 1138 MPa (165 ksi) and at least 8% elongation.

BRIEF DESCRIPTION OF THE DRAWINGS

[0050] FIG. 1 is a scatter chart showing an improved low temperature ageability property, which is evidenced by an increase of a product of yield strength (YS) times elongation (EI) as a result of a post cold work low temperature heat treatment (x-axis) vs. yield strength after heat treatment (y-axis).

[0051] FIG. 2 is a line chart showing the effect of cold work on yield strength (ksi) for a comparative alloy and an exemplary alloy, before and after salt bath heat treatment.

[0052] FIG. 3 is a line chart showing the effect of cold work on ultimate tensile strength (ksi) for the comparative alloy and the exemplary alloy, before and after salt bath heat treatment.

[0053] FIG. 4 is a line chart showing the effect of cold work on percent elongation as a measurement of ductility for the comparative alloy and the exemplary alloy, before and after salt bath heat treatment.

[0054] FIG. 5 shows a clean microstructure of an exemplary alloy having a nitrogen content of approximately 0.14% and formed as a hot rolled plate followed by heat treating at 1066° C. (1950° F.) for 30 minutes and water cooling.

[0055] FIG. 6 shows a clean microstructure of an exemplary alloy having a nitrogen content of approximately 0.14% and formed as a hot rolled plate followed by heat treating at 1093° C. (2000° F.) for 30 minutes and water cooling. The average grain size of the microstructure of FIG. 8 was determined to be about 78 microns.

[0056] FIGS. 7 and 8 show the phases calculated to be present under equilibrium conditions for a comparative alloy.

[0057] FIGS. 9-11 show the phases calculated to be present under equilibrium conditions for an exemplary alloy.

[0058] FIG. 12 shows a Time-Temperature-Transformation (TTT) diagram for a comparative alloy.

[0059] FIG. 13 shows a Continuous-Cooling-Transformation (CCT) diagram for the comparative alloy of FIG. 12.

[0060] FIG. 14 shows a Time-Temperature-Transformation (TTT) diagram for an exemplary alloy.

[0061] FIG. 15 shows a Continuous-Cooling-Transformation (CCT) diagram for the exemplary alloy of FIG. 14.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0062] Every effort has been made to correctly convert the units of measurement to SI units. To the extent that any discrepancy exists in the conversion, the non-SI units should be understood to be correct.

[0063] This specification describes all compositions in weight percent unless expressly specified otherwise. All yield strengths cited herein are measured at a 0.2% offset, unless expressly specified otherwise.

Composition

[0064] Although the present invention is not limited by theory, the following selected amounts of alloying elements in the solid-solution nickel-based alloy tend towards the following beneficial effects.

Molybdenum (Mo): 6.5 to 8.0 Weight Percent

[0065] Molybdenum greatly contributes to strength development without degrading thermal stability during manufacture. The strengthening effect of molybdenum is primarily achieved by substitutional solid solution strengthening. Substitutional solid solution strengthening occurs by positioning of molybdenum atoms at lattice positions within the matrix of the alloy. Due to a large difference in size between the small molybdenum atoms and the larger nickel, chromium, and iron atoms of the matrix, local stress fields are created around the molybdenum atoms that inhibit the movement of dislocations through the lattice, thus increasing the strength of the alloy. Also, molybdenum tends to improve corrosion resistance, particularly resistance to pitting and crevice corrosion, and molybdenum tends to contribute to stress-corrosion-cracking resistance and hydrogen embrittlement resistance. Accordingly, the molybdenum content is controlled to be at least 6.5%, preferably at least 6.8%, and more preferably at least 7.1%.

[0066] However, excessive levels of molybdenum tend to form undesirable mu phase $[\text{Mo}_7(\text{Ni}, \text{Fe}, \text{Cr})_6]$ and tend to contribute to formation of undesirable sigma phase $(\text{FeMo})_x(\text{Ni}, \text{Co})_4$, both of which negate against satisfying the clean microstructure requirement of the oil and gas industries. Excessive molybdenum also tends to inhibit strength development and impede corrosion resistance. Accordingly, the molybdenum content is controlled to be 8.0% or less, and preferably 7.8% or less, and more preferably 7.6% or less.

Sol. Nitrogen (N): 0.08 to 0.20 Weight Percent

[0067] Nitrogen is the primary element that distinguishes the alloy of the present invention from INCONEL® alloy G-3 (UNS N06985/W. Nr. 2.4619). Conventionally, nitrogen has been added to some types of nickel alloys to improve strength by precipitation of nitrides. However, precipitation of nitrides and other unwanted phases negates against the clean micro-

structure requirement and tends to result in loss of ductility, toughness, and fabricability. For this reason, additions of high levels of nitrogen have generally been avoided.

[0068] However, the present inventors have found that additions of high amounts of nitrogen that are less than the solubility limit surprisingly provide a low-temperature ageability property that unexpectedly achieves an improved combination of strength and ductility after cold working followed by a low temperature aging process. The improved combination of strength and ductility is achieved without precipitating excessive amounts of unwanted phases and without significantly deteriorating toughness, fabricability, or corrosion resistance.

[0069] Although the invention is not limited by theory, it is believed that the high amounts of nitrogen in solid solution increase the strength of the alloy by interstitial solid solution strengthening, and it is believed that soluble nitrogen may, as a result of the low temperature heat treatment, interact with dislocations in the lattice of the alloy that have resulted from cold working to provide an improved combination of strength and ductility. Accordingly, the sol. nitrogen content of the alloy is controlled to be at least 0.08%, preferably at least 0.10%, and more preferably at least 0.12%.

[0070] However, levels of nitrogen exceeding the solubility limit of the alloy tend to precipitate nitrides and/or carbonitrides. Excessive amounts of these precipitates tend to result in loss of ductility, toughness, and fabricability, negate against a clean microstructure, and also rob the matrix of the elements—molybdenum, tungsten, and chromium—thereby reducing the strength and the corrosion resistance of the alloy. Accordingly, the sol. nitrogen content of the alloy is 0.20% or less, preferably 0.19% or less, more preferably 0.18% or less, more preferably 0.17% or less, and more preferably 0.16% or less.

[0071] At slightly beyond the solubility limit of nitrogen, it is possible that a degree of strengthening may result from Cr_2N dispersoids within the matrix grains. However, greater amounts of nitrogen tend to contribute to grain boundary film formation that negates against the clean microstructure requirement and contributes to poor properties as discussed above. Accordingly, the overall nitrogen content of the alloy is preferably 0.20% or less, more preferably 0.19% or less, more preferably 0.18% or less, more preferably 0.17% or less, and more preferably 0.16% or less. The insoluble nitrogen content of the alloy is preferably 0.12% or less, more preferably 0.10% or less, more preferably 0.08% or less, more preferably 0.06% or less, more preferably 0.04% or less, and more preferably 0.02% or less.

[0072] Nitrogen may be added by dissolving nitrogen gas into the molten alloy prior to tapping. The dissolved nitrogen becomes part of the solid solution during cooling and thereby strengthens the alloy by solid solution strengthening. Since the nitrogen remains in solid solution, nitrogen is trapped in the matrix and does not precipitate. To maximize the solid solution strengthening effect of nitrogen, the solubility limit of nitrogen in the alloy is preferably maximized. The solubility limit is affected by the presence of other alloying elements in the nickel alloy. Thus, the selection of alloying elements is preferably optimized to ensure that high levels of nitrogen remain in solid solution. To achieve the intended effect, the maximum solubility of nitrogen in the alloy at 1538° C. (2800° F.) is preferably at least 0.12%, more preferably at least 0.14%, and most preferably at least 0.16%.

[0073] The following Table 1 shows the effect of composition (in percent by weight) on the maximum solubility limit of nitrogen at 1538° C. (2800° F.), which is approximately 93° C. (200° F.) above the temperature of tapping, as well as the compositional effect on the sigma solvus which is discussed later in the application.

TABLE 1

	1A	1B	1C	1D	1E
C	0.007	0.007	0.007	0.007	0.004
Ni	45.8	42.4	44.9	46.9	47.0
Co	0.6	0.6	0.6	0.6	0.0
Al	0.23	0.23	0.23	0.23	0.20
Ti	0.01	0.01	0.01	0.01	0.005
Nb	0.13	0.13	0.13	0.13	0.19
Mo	6.9	6.9	6.9	7.5	7.0
Fe	19.4	19.5	17.0	14.5	19.5
Cr	22.9	22.9	22.9	22.9	22.2
W	0.94	0.94	0.94	0.94	0.92
Si	0.17	0.17	0.17	0.17	0.21
Cu	2.0	2.0	2.0	2.0	2.0
Mn	0.75	4.0	4.0	4.0	0.72
Max. N ₂ solubility at 2800° F.					
Sigma Solvus ° F.	1900	2074	1998	1994	1854

[0074] As shown in the above Table 1, the composition of the alloy may be optimized to achieve a high maximum nitrogen solubility.

Chromium (Cr): 21.0 to 24.0 Weight Percent

[0075] Chromium beneficially increases the solubility limit of nitrogen in the alloy, thereby increasing the amount of nitrogen that may be added. Also, chromium provides resistance to oxidizing environments particularly during manufacture, and chromium provides pitting resistance to chloride-containing environments and contributes to resistance to stress corrosion cracking and hydrogen embrittlement. Accordingly, the chromium content is controlled to be at least 21.0%, preferably at least 22.0%, and most preferably at least 22.5%

[0076] However, chromium has a strong affinity for carbon. In the presence of carbon, chromium forms undesirable carbides and carbonitrides particularly along the grain boundaries, which decreases the amount of nitrogen in solid solution, deters from fabricability, and negates against the requirement for a clean microstructure. Accordingly, the chromium content is controlled to be at most 24.0%, preferably at most 23.5%, more preferably at most 23.3%, and more preferably at most 23.1%.

Carbon (C): 0.015 Weight Percent or Less

[0077] Small amounts of carbon generally remain in the alloy as a result of normal processing conditions. However, excessive amounts of carbon cause the formation of chromium carbides and carbonitrides, particularly along the grain boundaries, which deplete the amount of chromium in solution near the grain boundaries. This grain boundary depletion of chromium causes intergranular corrosion, particularly in weld heat-affected zones. The precipitation of carbides and carbonitrides also prevents the alloy from meeting industry requirements for a clean microstructure. Excessive carbon also robs the matrix of the strengthening elements—molyb-

denum, tungsten, and chromium—thereby reducing the strength and the corrosion resistance of the alloy. Accordingly, the carbon content is controlled to be 0.015% or less, preferably 0.010% or less, and more preferably 0.005% or less.

Tungsten (W): 0.10 to 1.5 Weight Percent

[0078] As explained above, small amounts of carbon generally remain in the alloy as a result of normal processing conditions. Tungsten has a beneficial effect of tying up carbon as intragranular WC and thus minimizing the detrimental formation of chromium carbides and carbonitrides. Also, tungsten is believed to contribute to tensile strength, weldability, pitting resistance, resistance to stress corrosion cracking, and hydrogen embrittlement resistance. To achieve the desired effect, the tungsten content is controlled to be at least 0.1%, preferably at least 0.50%, and more preferably at least 0.90%

[0079] However, tungsten (like molybdenum) detrimentally increases the propensity of mu phase, which negates against the requirement for a clean microstructure and deteriorates strength development and corrosion resistance. Excessive tungsten also adds to the cost of the alloy while saturating the beneficial effects. Accordingly, the tungsten content is controlled to be 1.5% or less, preferably 1.4% or less, and more preferably 1.3% or less.

Copper (Cu): 1.0 to 2.5 Weight Percent

[0080] Copper is beneficial for increasing the resistance to sour gas corrosion, which is particularly important in deep sour wells prone to H₂S environments. Accordingly, the copper content is controlled to be at least 1.0%, preferably at least 1.5%, and more preferably at least 1.7%, and more preferably at least 1.9%.

[0081] However, excessive amounts of copper lower the resistance to pitting corrosion, which is detrimental to the alloy if in the presence of chlorides. Accordingly, the copper content is controlled to be 2.5% or less, preferably 2.3% or less, and more preferably 2.1% or less.

Combined Amount of Molybdenum (Mo) and Tungsten (W): Mo+½ W=7.6 to 8.5 Weight Percent

[0082] As discussed above, both molybdenum and tungsten are effective for increasing the strength of the alloy. To ensure a high level of strength, a combination of molybdenum and tungsten are preferably controlled such that a content of Mo+½ W is high. Accordingly, a content of Mo+½ W is preferably controlled to be at least 7.6%, more preferably at least 7.7%, and most preferably at least 7.8%.

[0083] However, an excess combined amount of molybdenum and tungsten tends to degrade the stability of the alloy by the precipitation of unwanted phases, which negate against the requirement for a clean microstructure and deteriorates strength development and corrosion resistance. Accordingly, the Mo+½ W content is preferably controlled to be 8.5% or less, more preferably 8.4% or less, and most preferably 8.3% or less.

Niobium (Nb), Titanium (Ti), Tantalum (Ta), Zirconium (Zr), and Vanadium (V): Total Combined Amount of 0.45 Weight Percent or Less

[0084] As explained above, nitrogen is added to the alloy to provide a low temperature ageability property. To ensure that nitrogen remains in solid solution during cooling, the addition

of high-temperature nitride forming elements are limited, the presence of which would precipitate detrimental amounts of nitrides, thereby reducing the amount of soluble nitrogen and degrading ductility, toughness, and fabricability. Accordingly, the total combined amount of niobium, titanium, tantalum, zirconium, and vanadium is controlled to be 0.45% or less, preferably 0.40% or less. The niobium content is preferably controlled to be 0.20% or less. The titanium content is preferably controlled to be 0.10% or less, more preferably 0.01% or less. The vanadium content is preferably controlled to be 0.15% or less. The tantalum content is preferably controlled to be 0.10% or less. The zirconium content is preferably controlled to be 0.05% or less.

Iron (Fe): 17.0 to 21.0 Weight Percent

[0085] Chromium and molybdenum may be economically included in the alloy by the addition of ferrochromium and ferromolybdenum to improve the commercial viability of the alloy. Accordingly, the iron content is preferably included at an amount of at least 17.0%, preferably at least 18.0%, and more preferably at least 19.0%.

[0086] However, the addition of excessive amounts of iron favors undesirable sigma phase formation, which negates against the requirement for a clean microstructure. Accordingly, the iron content is controlled to be at most 21.0%, preferably 20.5% or less, and more preferably 20.0% or less.

Phosphorus (P): 0.050 Weight Percent or Less

[0087] Phosphorus may be present in the alloy as an impurity. Excessive amounts of phosphorus may cause susceptibility to hydrogen embrittlement. Accordingly, the phosphorus content is preferably controlled to be 0.050% or less, more preferably 0.010% or less, and most preferably 0.005% or less.

Sulfur (S): 0.050 Weight Percent or Less

[0088] Sulfur may be present in the alloy as an impurity. Excessive amounts of sulfur may deteriorate the hot workability of the alloy. Accordingly, the sulfur content is preferably controlled to be 0.050% or less, more preferably 0.010% or less, and most preferably 0.005% or less.

Aluminum (Al): 0.5 Weight Percent or Less

[0089] Aluminum is beneficial for desulfurizing the alloy. To achieve the desired effect, the aluminum content is preferably controlled to be at least 0.001%, more preferably at least 0.010%, and more preferably at least 0.10%.

[0090] However, excessive amounts of aluminum detrimentally contribute to the formation of undesirable intermetallic phases. Accordingly, the aluminum content is controlled to be at most 0.5%, preferably at most 0.40%, and more preferably at most 0.30%.

Manganese (Mn): 4.0 Weight Percent or Less

[0091] Manganese is beneficial for desulfurizing the alloy, especially in absence of high amounts of aluminum. However, excessive amounts of manganese reduce the resistance of the alloy to acid chlorides. Accordingly, the manganese content is controlled to be 4.0% or less, preferably 2.0% or less, and more preferably 1.0% or less.

Silicon (Si): 1.0 Weight Percent or Less

[0092] Silicon is beneficial for increasing the oxidation resistance of the alloy particularly during manufacture. However, excessive amounts of silicon reduce hot and cold workability of the alloy. Also, silicon is a strong nitride former. Thus, excessive amounts of silicon may reduce the beneficial effect of nitrogen and negate against the clean microstructure requirement. Accordingly, the silicon content is controlled to be 1.0% or less, preferably 0.50% or less, and more preferably 0.25% or less.

Cobalt (Co): 5.0 Weight Percent or Less

[0093] Cobalt may be beneficial for further improving the corrosion resistance of the alloy. Therefore, cobalt may be added when especially high corrosion resistance is required. However, excessive amounts of cobalt greatly add to the cost of the alloy. Accordingly, the cobalt content is preferably controlled to be 5.0% or less, more preferably 2.0% or less, and most preferably 1.0% or less.

Rare Earths, Y, Mg, and Ca

[0094] Rare Earths Y, Mg, and Ca may all be beneficial for improving hot workability. Therefore, when the alloy has to be subjected to severe hot working, it may be desirable to incorporate at least one of these elements in the alloy. However, excessive amounts of these elements may deteriorate the properties of the alloy. Accordingly, the content of rare earths is preferably controlled to be 0.10% or less, the content of Y is preferably controlled to be 0.20% or less, the content of Mg is preferably controlled to be 0.10% or less, and the content of Ca is preferably controlled to be 0.10% or less.

Nickel (Ni)

[0095] The main benefit of nickel is to maintain a stable austenitic single-phase structure and assure stability and cleanliness of the microstructure, which is important for obtaining optimum corrosion resistance capable of being economically produced and fabricated. Accordingly, nickel may be included as the balance of the alloy composition. The nickel content is preferably controlled to be 40.0% or more, more preferably 42.0% or more, and more preferably 44.0% or more.

Incidental Elements

[0096] The alloy may include incidental elements, such as B, Sn, Pb, and Zn. However, excessive amounts of these elements may deteriorate the properties of the alloy. Accordingly, each incidental element is preferably controlled to be 0.10% or less, more preferably 0.01% or less, and more preferably 0.001% or less.

[0097] The above description describes the amounts and effects of the primary elements in the alloy as best understood. While the invention is envisioned to encompass any alloy having amounts of elements within the above-described ranges, the addition of amounts of additional elements that would materially affect the basic and novel characteristics of the present invention should be avoided. In an embodiment of the present invention, the alloy consists essentially of or consists of amounts of elements within the above-described ranges, along with incidental impurities, while ensuring increased strength and without detrimental loss of ductility, toughness, fabricability, and corrosion resistance.

Method of Manufacture

[0098] In an exemplary embodiment of the present invention, there is a method of manufacturing an article formed from a solid solution nickel-chromium-iron-molybdenum corrosion resistant alloy as described above. The alloy is preferably processed in the manner described below. Although the present invention is not limited by theory, it is believed that the following processing steps have the effects described below.

Introduction of Nitrogen Gas Into the Molten Alloy

[0099] Nitrogen may be added by bubbling nitrogen gas into the molten metal alloy prior to tapping. The introduced nitrogen becomes part of the solid solution during solidification. If the amount of nitrogen is less than the solubility limit, nitrogen is trapped in the matrix and does not precipitate. It is believed that nitrogen in solid solution causes interstitial solid solution strengthening of the alloy as previously described. The solubility limit of nitrogen in the alloy is affected by the additions of other alloying elements, which are selected in the alloy of the present invention to ensure that high levels of nitrogen remain in solid solution. For example, chromium, in particular, is believed to substantially increase the solubility limit of nitrogen in the alloy, thereby increasing the amount of nitrogen that may be added without exceeding the solubility limit.

Homogenization Time and Temperature

[0100] Homogenizing has a beneficial effect of dissolving undesirable second phases that may form during cooling as a result of segregation of alloying elements. To achieve the beneficial effect, a temperature of the homogenization is preferably controlled to be at least 1093° C. (2000° F.), and a time of the homogenization is preferably controlled to be at least 20 hours.

[0101] However, an excessively high temperature during homogenization may cause incipient melting of the alloy. Accordingly, a temperature of the homogenization is preferably controlled to be 1232° C. (2250° F.) or lower.

[0102] Also, an excessively high time of homogenization is believed to saturate the effect of the homogenization treatment while raising the processing cost. Accordingly, a time of the homogenization is preferably controlled to be 48 hours or less.

Hot Working Temperature

[0103] Hot working has a beneficial effect of changing the shape of a cast ingot into the general desired shape of the billet and doing so at high temperatures at which the alloy is more easily deformed. Hot working may include extrusion for tube making, forging for bars and flats, and hot rolling for sheets and plates. To achieve the beneficial effect of hot working, a temperature of the hot working is preferably controlled to be 1149° C. (2100° F.) or greater. Excessively low temperatures of hot working may cause an increase of flow stress that exceeds the capacity of hot working equipment.

[0104] However, an excessively high temperature of hot working may cause adiabatic heating that results in incipient melting of the alloy. Accordingly, a temperature of the hot working is preferably controlled to be 1204° C. (2200° F.) or less.

Solution Annealing or Hot Roll Solution Annealing

[0105] Solution annealing is performed to ensure that the constituents of the alloy are in solid solution. Hot roll solution annealing is performed when annealing and substantial reduction of the material is to be accomplished during annealing, and for flow stress reasons one does not want the material to get cold because of the increase in flow stress. The temperature at which the alloys are annealed is preferably chosen to be well above the recrystallization temperature and at a temperature adequate to keep the flow stress low. Experience indicates that solution annealing at 1038° C. (1900° F.) for a minimum of 20 minutes is sufficient to assure the completion of the anneal. The need for a hot roll solution anneal is a function of a number of variables, such as handling time to reach the hot roll press, time on the press, and size.

Cold Working

[0106] Cold working has a beneficial effect of strengthening the alloy by the introduction of defects into the lattice of the alloy. Cold working creates a textured microstructure that is not necessarily homogeneous with regard to mechanical properties in the longitudinal and transverse directions. Cold working may include drawing, pilgering, swaging, roll forming, and cold rolling of flats.

[0107] To achieve the desired level of strengthening, the amount of cold working is preferably controlled to be at least 20%, more preferably at least 25%, and most preferably at least 30%. When the cold working is drawing, the amount of cold working is preferably controlled to be at least 25%, more preferably at least 30%, and most preferably at least 35%.

[0108] However, the ability to cold work a material depends on the capability of the equipment to work the alloy or the capacity of the material to accept the cold working. Accordingly, an amount of cold working is generally less than 80%, preferably less than 70%, and more preferably less than 60%.

Low Temperature Heat Treatment

[0109] For precipitation hardenable nickel alloys, it is common to perform a heat treatment at temperatures ranging from 427° C. (800° F.) to 871° C. (1600° F.) to increase the strength of the alloy by precipitation of a dispersed phase throughout the matrix. This precipitation strengthening effect is caused by the precipitation of submicroscopic particles throughout the matrix, which results in a marked increase in hardness and strength. Principal aging phases in precipitation-hardenable high nickel alloys usually include one or more of gamma prime (Ni_3Al or $\text{Ni}_3\text{Al, Ti}$), eta (Ni_3Ti), and gamma double prime ($\text{bct-Ni}_3\text{Nb}$). Other phases that may be present include carbides (such as M_{23}C_6 , M_7C_3 , M_6C , and MC), nitrides (MN) and carbonitrides (MCN), and borides (M_3B_2), as well as Laves phase (M_2Ti) and delta phase (orthorhombic- Ni_3Nb).

[0110] However, according to the exemplary method of the present invention, the low-temperature heat treatment may be applied to the alloy, which is deemed to be a non-precipitation hardenable alloy. Instead, the low temperature heat treatment is applied to a solid solution strengthened and cold worked alloy. The inventors of the present application have found that the low temperature heat treatment applied to the alloy having high levels of nitrogen in amounts that are less than the solubility limit surprisingly provides a low temperature ageability property that unexpectedly achieves an improved combination of strength and ductility without precipitating

unwanted phases and without deteriorating toughness, fabricability, and corrosion resistance.

[0111] Although the invention is not limited by theory, it is believed that the temperature of the heat treatment, although less than the temperature at which effects of cold working are completely removed, may partially remove the effect of the cold work since the temperature is in the stress relieving temperature range. It is also believed that, as a result of the low temperature heat treatment, nitrogen in solid solution interacts with the dislocations in the lattice of the alloy that were introduced by the cold working step. The exact mechanism explaining why the low temperature heat treatment enhances the mechanical properties is not clear. Although the present invention is not limited by theory, it is also believed that cooling after low temperature aging treatment may create compressive stresses on the alloy resulting in the strengthening.

[0112] In a preferred embodiment, the low temperature heat treatment may be achieved by employing a hot salt bath. When an article is immersed in molten salt, heat is transferred by direct contact from the molten salt to the surface of the article. Also, since articles are immersed in the salt bath, air cannot contact the article and, therefore, scaling, oxidation, and decarburization are thereby avoided. Also, heat transfer into materials by salt bath treatment is very rapid—faster than with radiation methods, thereby reducing the amount of time necessary for the heat treatment.

Time and Temperature of Heat Treatment

[0113] To achieve the desired effect of the low temperature heat treatment, a temperature of the heat treatment is preferably controlled to be 468° C. (875° F.) or greater, more preferably 482° C. (900° F.) or greater, most preferably 496° C. (925° F.) or greater. A time of the heat treatment is controlled to be 5 minutes or greater, preferably controlled to be 15 minutes or greater, more preferably 30 minutes or greater, and most preferably 45 minutes or greater.

[0114] However, excessively high temperatures are believed to decrease the strength enhancement of the heat treatment. Also, the salt bath is not stable at excessively high temperatures. Accordingly, a temperature of the heat treat-

ment is preferably controlled to be 537° C. (999° F.) or less, more preferably 524° C. (975° F.) or less, and more preferably 510° C. (950° F.) or less.

[0115] Additionally, for an excessively long time of heat treatment, the effect is believed to be saturated. Accordingly, a time of heat treatment is preferably controlled to be 8 hours or less, more preferably 4 hours or less, and more preferably 2 hours or less.

Properties

Low Temperature Ageability

[0116] As explained above, low temperature heat treatments are typically applied to precipitation hardenable alloys rather than solid solution strengthened alloys. However, it was surprisingly found that the low temperature heat treatment applied to the solid solution strengthened alloy after cold working unexpectedly achieved an improved combination of strength and ductility. More specifically, the alloys surprisingly exhibited an improved combination of 0.2% offset yield strength (YS) and elongation as a result of the low temperature heat treatment to achieve a high combined amount of yield strength and ductility. This effect can be further understood with reference to the following experimental examples.

[0117] The alloy compositions of Tables 2 and 3 were air cast as 22.7 Kg (50 lbs) heats and alloys 2A, 2B, and 2C were homogenized at 1204° C. (2200° F.) for 36 hours and air cooled, followed by hot rolling at 1177° C. (2150° F.) with a 10:1 ratio to simulate extrusion, followed by a water quench and post hot rolling anneal at 1010° C. (1850° F.) for 1 hour followed by water quench for subsequent cold reduction trials as specified in Table 4. Alloys 3A and 3B were similarly homogenized at 1204° C. (2200° F.) for 24 hours and air cooled. Alloys 3A and 3B were then hot rolled at 1190° C. (2175° F.) to 11.4 mm (0.45 inch) plate and air cooled. A post hot rolled solution anneal was conducted at 1066° C. (1951° F.) for 30 minutes and subsequently water quenched. The alloys of Tables 2 and 3 were then cold reduced by rolling at specified amounts listed in Tables 4 and 5 and a portion of the rolled plate was heat treated at 500° C. (932° F.) in a salt bath for 45 minutes followed by air cooling.

TABLE 2

Three Comparative Compositions												
Heat	C	Mn	Fe	Si	Cu	Ni	Cr	Al	Ti	Mo	W	N
2A	0.003	0.71	19.1	0.20	1.96	49.7	22.0	0.15	0.004	6.02	0.02	0.020
2B	0.004	0.72	19.5	0.21	2.02	47.0	22.2	0.19	0.005	6.99	0.92	0.020
2C	0.002	0.70	19.6	0.18	1.97	46.0	22.6	0.22	0.000	7.03	1.01	0.023

TABLE 3

Two Exemplary Compositions												
Heat	C	Mn	Fe	Si	Cu	Ni	Cr	Al	Ti	Mo	W	N
3A	0.004	0.7	18.8	0.16	1.99	45.7	22.9	0.16	<0.001	7.52	1.26	0.134
3B	0.003	0.73	19.5	0.19	2.01	45.5	22.9	0.19	0.0013	7.19	1.08	0.15

TABLE 4

Lists the key tensile properties and hardness of the comparative compositions

Heat	% Cold Work	0.2% Yield Strength MPa/ksi	% Elongation	HRC	0.2% Yield Strength after Heat Treatment MPa/ksi	% Elongation after Heat Treatment	HRC
2A	20	807/117.0	20.5	29	810/117.5	21	29
	40	1069/155.0	8.7	33	1165/169.0	7.1	36
2B	20	876/127.0	15.8	31	903/131.0	16.2	33
	40	1124/163.0	8.5	36	1248/181.0	5.2	41
2C	30	875/126.9	17.2	31	952/138.0	17.8	34

TABLE 5

Lists the key tensile properties and hardness of the composition within the scope of this invention

Heat	% Cold Work	0.2% Yield Strength MPa/ksi	% Elong.	HRC	0.2% Yield Strength after Heat Treatment MPa/ksi	% Elongation after Heat Treatment	HRC
3A	30	999/144.9	18.1	36	1039/150.7	21.5	37
	35	1034/149.9	14.8	34	1085/157.4	17.4	37
	40	1071/155.4	13.5	34	1145/166.1	17.1	39

Heat	% Cold Work	0.2% Yield Strength MPa/ksi	% Elong.	Charpy Impact Ft. Lbs.*	HRC	0.2% Yield Strength after Heat Treatment MPa/ksi	% Elong. after Heat Treatment	Charpy Impact after Heat Treatment Ft. Lbs./J/cm ² *	HRC after Heat Treatment
3B	30	1076/156	15.5	32	33	158	18.4	32/108.5	32
	35	1089/158	11.0	29	35	158	15.5	28/94.9	32
	40	1096/159	8.0	25	37	172	8.0	23/78.0	35

*Charpy impact values are reported for half-size samples at a test temperature of 14° F. For conversion into SI unites, the value reported in Ft. Lbs. is multiplied by 3.39 to find the value on Joules/cm² at -10° C.

[0118] FIG. 1 shows an improved low temperature ageability property of the exemplary alloys 3A and 3B from Tables 3 and 5 relative to comparative alloys 2A, 2B, and 2C from Tables 2 and 4. More specifically, FIG. 1 plots a change in the product of 0.2% offset yield strength (ksi) and elongation (El) as a result of aging, i.e., $\Delta(YS \times El)$, vs. the yield strength (ksi) after aging (YS_{aa}), wherein $\Delta(YS \times El)$ is the 0.2% Offset Yield Strength (ksi) times Percent Elongation after aging ($YS_{aa} \times El_{aa}$) minus the 0.2% Offset Yield Strength (ksi) times Percent Elongation before aging ($YS_{ba} \times El_{ba}$).

[0119] As can be understood from FIG. 1, the high sol. nitrogen exemplary alloys 3A and 3B of the present invention have an excellent improvement in the combination of yield strength and elongation as a result of the low temperature aging process when the alloys are cold worked a sufficient amount to have a high yield strength of at least 145 ksi in the heat treated condition, relative to the low nitrogen-containing comparable alloys 2A, 2B, and 2C.

[0120] As shown by FIG. 1, the change in product of yield strength (ksi) and elongation as a result of aging $\Delta(YS \times El)$ is greater than 0 when a final yield strength after aging (YS_{aa}) of the alloy is at least 145 ksi. Thus, the alloys of the present invention show the ability to improve the combined yield strength and elongation of high yield strength alloys by applying a low temperature heat treatment after cold working.

[0121] Furthermore, as represented in FIG. 1, the above-described low temperature ageability property of the alloys can be alternatively expressed by the following formula: $\Delta(YS \times El) \geq 600 - (YS_{aa} - 145) \times 20$, wherein $\Delta(YS \times El)$ is the 0.2% Offset Yield Strength (ksi) times Percent Elongation after aging ($YS_{aa} \times El_{aa}$) minus the 0.2% Offset Yield Strength (ksi) times Percent Elongation before aging ($YS_{ba} \times El_{ba}$). This formula expresses a distinction between the exemplary alloys and the comparative alloys—the exemplary alloys have a better combined yield strength and elongation for a given final yield strength.

[0122] In contrast to the exemplary alloys, the comparative alloys, when cold worked enough to have a high final yield strength of at least 145 ksi, have a decreased product of yield strength and elongation as a result of aging, and the comparative alloys only achieve the improved combination of yield strength and elongation when cold worked a low amount such that a low final yield strength of less than 145 ksi is achieved.

[0123] Although the present invention is not limited by theory, it is believed that, after heat treatment, the soluble nitrogen may interact with dislocations that result from cold working to provide an improved combination of strength and ductility. Thus, a high amount of cold working is believed to contribute to the beneficial interaction between the nitrogen in solid solution and the cold worked structure.

Mechanical Properties—Strength, Ductility, and Toughness

[0124] In an exemplary embodiment, the alloys, after cold working and application of the low temperature heat treatment, achieve a minimum 0.2% offset yield strength of at least 1000 MPa (145 ksi), preferably 1069 MPa (155 ksi), and more preferably 1138 MPa (165 ksi). The alloys also achieve a minimum elongation of 8.0%, preferably at least 10.0%, more preferably at least 12.0%, more preferably at least 14.0%, more preferably at least 16.0%, and more preferably 19.0%.

[0125] The alloys also target combinations of mechanical properties including:

[0126] (i) a 0.2% offset yield strength of at least 1000 MPa (145 ksi) with at least 12% elongation, preferably at least 15%, and more preferably at least 19%;

[0127] (ii) a 0.2% offset yield strength of at least 1069 MPa (155 ksi) with at least 10% elongation, preferably at least 13%, and more preferably at least 16%; and

[0128] (iii) a 0.2% offset yield strength of at least 1138 MPa (165 ksi) with at least 8.0% elongation, preferably at least 10%, and more preferably at least 12%.

[0129] For comparative alloys 2A, 2B, and 2C, it is observed as shown in Table 4 that when the % cold work achieves the target 0.2% yield strength of 1000 MPa (145 ksi), the ductility as measured by the % elongation is below the acceptable minimum of 12%, and when the % cold work achieves the target 0.2% yield strength of 1069 MPa (155 ksi), the ductility as measured by the % elongation is below the acceptable minimum of 10%, and when the % cold work achieves the target 0.2% yield strength of 1138 MPa (165 ksi), the ductility as measured by the % elongation is below the acceptable minimum of 8%.

[0130] Thus, comparative alloys 2A, 2B, and 2C do not achieve any of the target combinations of properties listed in the paragraph above. The deficient mechanical properties of comparative alloys 2A, 2B, and 2C are attributed to the lack of nitrogen for solid solution strengthening in the composition. As seen in Table 4, the use of a low temperature heat treatment for the low nitrogen alloys 2A, 2B, and 2C does not resolve the problem and in fact exacerbates the problem by decreasing the combination of yield strength and elongation when the comparative alloys are cold worked to yield strength exceeding 1000 MPa (145 ksi).

[0131] This problem with the comparative alloys is resolved by the addition of nitrogen as shown in Table 5, thereby achieving the targeted combinations of mechanical properties outlined above. More specifically, a 0.2% offset yield strength of at least 1000 MPa (145 ksi) with an elongation of at least 12% is achieved, preferably at least 15%, more preferably at least 19%. Also, a 0.2% offset yield strength of at least 1069 MPa (155 ksi) with an elongation of at least 10% is achieved, preferably at least 13%, more preferably at least 16%. Additionally, a 0.2% offset yield strength of at least 1138 MPa (165 ksi) with an elongation of at least 8% is achieved, preferably at least 10%, more preferably at least 12%.

[0132] In addition to meeting the targeted combination of final mechanical properties, the exemplary alloys also preferably meet the property requirements of ANSI/NACE MR0175/ISO15156-3 for Type 4e alloys. For cold work reductions of 40%, the property requirements of ANSI/NACE MR0175/ISO15156-3 for Type 4e alloys requires that a 0.2% offset yield strength does not exceed 1240 MPa (180 ksi) and that hardness does not exceed HRC 45. Thus, the alloys

advantageously meet the mechanical properties of Type 4e while advantageously having the more cost-effective composition of Type 4d alloys. Type 4d alloys are required to have a minimum 19.0wt. % Cr, a minimum Ni+Cr of 45wt %, and a minimum Mo+W of 6wt %, whereas Type 4e alloys are required to have a minimum 14.5wt % Cr, a minimum Ni+Cr of 52wt %, and a minimum Mo of 12wt %. Thus, Type 4e alloys require greater amounts of Ni+Cr and greater Mo contents, thereby substantially increasing the cost of Type 4e alloys relative to Type 4d alloys. The alloys of the present invention preferably advantageously have the composition of a Type 4d alloy while meeting the mechanical property requirements of a Type 4e alloy. This results in a substantial cost advantage because oil and gas companies can use the improved alloy where high strength and good corrosion resistance are required. This is particularly beneficial for HPHT (high pressure high temperature) wells which are currently commonly developed since shallow wells are generally depleted.

[0133] The improved strength of the alloys as a result of the low temperature heat treatment is additionally important because ANSI/NACE MR0175/ISO 15156-3 requires that Type 4d alloys have a maximum yield strength of 150 ksi (1034 MPa) and maximum 40 HRC in the annealed and cold-worked condition when the alloy is given cold-work reductions of 30 and 35%. Additionally, ANSI/NACE MR0175/ISO 15156-3 requires that Type 4e alloys have a maximum yield strength of 180 ksi (1240 MPa) and a maximum 45 HRC in the annealed and cold-worked condition when the alloy is given a cold-work reduction of 40%. Accordingly, the alloys are able to remain below the required maximum yield strengths and hardness values in the annealed and cold worked condition, and then subsequently increase the yield strength beyond the maximum amounts as a result of the low temperature heat treatment.

[0134] The following additional experimental examples of Table 6 and FIGS. 2-4 further illustrate the advantageous mechanical properties of the alloys. The following examples relate to mechanical properties of cold worked vs. cold worked plus heat treated samples for comparative alloy 6A having a low nitrogen content of less than 0.03% vs. an exemplary alloy 6B having a high nitrogen content (0.15%).

TABLE 6

Chemical composition of 100 lbs Alloy 6A and 6B		
ALLOY	6A	6B
C	0.004	0.003
Mn	0.73	0.73
Fe	19.5	19.5
S	0.0016	0.0017
Si	0.17	0.19
Cu	2	2
Ni	45.6	45.5
Cr	22.8	22.9
Al	0.22	0.19
Ti	0	0.0013
Mg	0.006	0.011
Co	0.46	0.46
Mo	7.1	7.2
Nb	0.15	0.15
Ta	0.003	0.003
P	0.0041	0.0044
Ca	0.0001	0.0001
N	0.027	0.15

TABLE 6-continued

Chemical composition of 100 lbs Alloy 6A and 6B		
ALLOY	6A	6B
V	0.012	0.014
W	1.07	1.08

[0135] FIGS. 2-4 illustrate a comparison of mechanical properties of flat cold-rolled comparative alloy 6A and exemplary alloy 6B with and without salt bath treatment. As can be understood from FIGS. 2-4, exemplary alloy 6B results in significantly higher yield strength and higher tensile strength, without a significant decrease in elongation compared to comparative alloy 6A.

Microstructure

[0136] The microstructure of the exemplary alloys has an austenitic matrix and a cleanliness that satisfies the requirements of the oil and gas industries. The clean microstructure is believed to be especially important for ensuring the manufacture of a cracking-resistant material.

[0137] The clean microstructure requirement is determined after an article formed from the alloy is cold worked and subjected to a low temperature heat treatment as described previously above. A clean microstructure is deemed to be a microstructure having, upon microstructural examination on a section taken in the longitudinal direction with respect to the direction of cold work, grain boundaries with no continuous precipitates, with intermetallic phases, nitrides and carbides not exceeding 1.0% in total area, and with sigma phase not exceeding 0.5% in total area. Failure to achieve a clean microstructure may result in continuous grain boundary precipitation or excessive amounts of intermetallic phases, nitrides, carbides, or sigma phase, which may adversely affect the impact and corrosion properties of the alloy, and an article formed from the alloy may be more susceptible to intergranular corrosion.

[0138] The exemplary alloys preferably have a microstructure that satisfies the cleanliness requirement both before and after salt bath treatment. Examples of microstructures satisfying the cleanliness requirement are shown in FIGS. 5 and 6. More specifically, FIGS. 5 and 6 show an exemplary alloy having a nitrogen content of approximately 0.14% and formed as a hot-rolled plate followed by heat treating and water cooling. The microstructure of FIG. 5 was heat treated at 1066° C. (1950° F.) for 30 minutes, and the microstructure of FIG. 6 was heat treated at 1093° C. (2000° F.) for 30 minutes. The average grain size of the microstructure of FIG. 6 was determined to be about 78 microns. The microstructures of FIGS. 5 and 6 are representative of the alloys of the present invention.

[0139] As shown, there are grain boundaries with no continuous precipitates and a total area fraction of intermetallic phases, nitrides, and carbides does not exceed 1.0% in total area and an area fraction of sigma phase does not exceed 0.5%. Microstructural examination was made on a section taken in the longitudinal direction with respect to the direction of cold work. The examination of the alloys microstructure was carried out in accordance with ASTM E562 with a minimum of 30 fields measured. The microstructure had grain boundaries with no continuous precipitates. Intermetallic phases, nitrides, and carbides did not exceed 1.0% in total area. Sigma phase did not exceed 0.5% in total area.

[0140] It is believed that the low nitrogen content of the comparative alloys may result in the formation of excess grain boundary precipitation of carbides and sigma phase that may negate against the requirement for a clean microstructure and may reduce ductility and toughness. This problem is resolved by the addition of high amounts of nitrogen but less than the solubility limit.

[0141] FIGS. 7-11 show calculated weight percentages of various phases expected to be present at equilibrium conditions for the following compositions indicated in Table 7 below, which includes comparative alloy 7A and exemplary alloy 7B.

TABLE 7

ALLOY	7A	7B
Al	0.217	0.217
Co	0.4584	0.4584
Cr	22.82	22.82
Cu	2.01	2.01
Fe	19.5	19.5
Mn	0.73	0.73
Mo	7.12	7.12
Nb	0.152	0.152
Si	0.174	0.174
Ta	0.003	0.003
W	1.07	1.07
C	0.003	0.003
N	0.027	0.14
Ni	bal.	bal.

[0142] As shown in FIGS. 7 and 9, cooling alloys 7A and 7B from a molten state under equilibrium conditions is expected to initially result in the formation of a single-phase austenitic gamma phase. At temperatures less than about 980° C. (1800° F.), the undesirable sigma phase becomes stable, and at temperatures less than about 650° C. (1200° F.), the undesirable laves phase becomes stable. As shown in FIGS. 8 and 10, small amounts of carbides and nitrides, as well as p-phase, become stable at lower temperatures in alloys 7A and 7B.

[0143] Although the present invention is not limited by theory, it is believed that, based on a comparison of alloy 7A with alloy 7B, the M6C and M23C6 phases may be destabilized for alloy 7B. Likewise the sigma solvus is beneficially dropped from ~985° C. (~1805° F.) for alloy 7A to 960° C. (1760° F.) for alloy 7B. Thus, based on this equilibrium data, it is expected that alloy 7B may tend to result in reduced precipitation of carbides and sigma phase.

[0144] Additionally, FIGS. 12 and 13 show Time-Temperature-Transformation (TTT) and Continuous-Cooling-Transformation (CCT) diagrams for alloy 7A, and FIGS. 14 and 15 show TTT and CCT diagrams for alloy 7B. As shown in FIGS. 12 and 13, a sigma nose is calculated to be present at 3.63 hours (TTT) and 3.33 hours (CCT) for alloy 7A, while a sigma nose is calculated to be present at 6.45 hours (TTT) and 5.92 hours (CCT) for alloy 7B. Thus, a comparison of the sigma noses for alloy 7A with the sigma noses for alloy 7B shows that avoidance of sigma phase would be expected to be facilitated by using the composition of alloy 7B having the higher nitrogen content as long as the temperature and time of transformation is controlled to be below the ranges shown in FIGS. 14 and 15, thus resulting in a clean microstructure.

[0145] However, levels of nitrogen exceeding the solubility limit of the alloy during cooling tend to precipitate nitrides and/or carbonitrides, which results in loss of ductility, tough-

ness, and fabricability, negates against a clean microstructure, and also robs the matrix of the strengthening elements—molybdenum, tungsten, and chromium—thereby reducing the strength and the corrosion resistance of the alloy. At slightly beyond the solubility limit of nitrogen, a degree of strengthening may result from Cr₂N dispersoids within the matrix grains. However, higher amounts of nitrogen contribute to grain boundary film formation that negates a clean microstructure and contributes to loss of ductility and toughness. Thus, amounts of nitrogen significantly above the solubility limit should be avoided.

Corrosion Resistance

[0146] The alloy of the present application has good corrosion resistance to sour gas and oil atmospheres as well as resistance to stress-corrosion-cracking and hydrogen embrittlement in sulfur-containing H₂S—CO₂—Cl⁻ environments. The alloy preferably has broad resistance to sensitization, which causes intergranular corrosion of weld heat affected zones.

[0147] Table 8 below shows corrosion data for an exemplary alloy 6B, showing very low corrosion rates with and without salt bath treatment, thus evidencing the good corrosion resistance.

TABLE 8

Corrosion Results for Comparison of as Cold Worked and as Cold Worked + Salt Bath Exposed Samples of Alloy 6B. Environment: ASTM A262-C (Huey Test) at Boiling for a Period of 240 Hours					
Heat	Anneal Prior to Cold Working	Corrosion Rate @ 48 Hours (mpy)	Corrosion Rate @ 96 Hours (mpy)	Corrosion Rate @ 96 Hours (mpy)	Average Corrosion Rate (mpy)
30% Cold Worked Samples					
6B	1950° F./1 Hr/WQ	9	6	5	7
35% Cold Worked Samples					
6B	1950° F./1 Hr/WQ	9	6	5	7
40% Cold Worked Samples					
6B	1950° F./1 Hr/WQ	10	6	6	7
45% Cold Worked Samples					
6B	1950° F./1 Hr/WQ	10	5	5	7
60% Cold Worked Samples					
6B	1950° F./1 Hr/WQ	9	5	5	7
Cold Worked + Salt Bath Huey Results					
30% Cold Worked Samples + Salt Bath Exposure					
6B	1950° F./1 Hr/WQ	10	5	5	7
35% Cold Worked Samples + Salt Bath Exposure					
6B	1950° F./1 Hr/WQ	9	5	5	6
40% Cold Worked Samples + Salt Bath Exposure					
6B	1950° F./1 Hr/WQ	9	6	5	7

TABLE 8-continued

Corrosion Results for Comparison of as Cold Worked and as Cold Worked + Salt Bath Exposed Samples of Alloy 6B. Environment: ASTM A262-C (Huey Test) at Boiling for a Period of 240 Hours					
Heat	Anneal Prior to Cold Working	Corrosion Rate @ 48 Hours (mpy)	Corrosion Rate @ 96 Hours (mpy)	Corrosion Rate @ 96 Hours (mpy)	Average Corrosion Rate (mpy)
45% Cold Worked Samples + Salt Bath Exposure					
6B	1950° F./1 Hr/WQ	9	6	5	7
60% Cold Worked Samples + Salt Bath Exposure					
6B	1950° F./1 Hr/WQ	8	5	5	6

[0148] Although the invention has been described in detail for the purpose of illustration based on what is currently considered to be the most practical and preferred embodiments, it is to be understood that such detail is solely for that purpose and that the invention is not limited to the disclosed embodiments but, on the contrary, is intended to cover modifications and equivalent arrangements that are within the spirit and scope of the appended claims. For example, it is to be understood that the present invention contemplates that, to the extent possible, one or more features of any embodiment can be combined with one or more features of any other embodiment.

The invention claimed is:

1. A solid-solution nickel-based alloy for use in sour gas and oil environments, comprising, in percent by weight: chromium: min. of 21.0 and max. of 24.0%; iron: min. of 17.0 and max. of 21.0%; molybdenum: min. of 6.5 and max. of 8.0%; copper: min. of 1.0 and max. of 2.5%; tungsten: min. of 0.1 and max. of 1.5%; sol. nitrogen: min. of 0.08 and max. of 0.20%; manganese: max. of 4.0%; silicon: max. of 1.0%; carbon: max. of 0.015%; aluminum max. of 0.5%; and a total amount of niobium, titanium, vanadium, tantalum and zirconium: max. of 0.45%; the balance being nickel and incidental impurities.
2. The alloy of claim 1, wherein the maximum chromium content is 23.5%.
3. The alloy of claim 1, wherein the minimum molybdenum content is 6.8%.
4. The alloy of claim 1, wherein the maximum molybdenum content is 7.8%.
5. The alloy of claim 1, wherein the minimum copper content is 1.5%.
6. The alloy of claim 1, wherein the minimum tungsten content is 0.50%.
7. The alloy of claim 1, wherein the minimum sol. nitrogen content is 0.10%.
8. The alloy of claim 1, wherein the maximum sol. nitrogen content is 0.19%.
9. The alloy of claim 1, wherein a content of Mo+½ W is controlled to be a minimum of 7.6%.
10. The alloy of claim 1, wherein a content of Mo+½ W is controlled to be a maximum of 8.5%.
11. The alloy of claim 1, wherein an overall nitrogen content is a maximum of 0.20%.

12. The alloy of claim **1**, wherein the alloy has a low temperature ageability property, $\Delta(\text{YS}\times\text{El})$, of greater than 0 when a yield strength after aging (YS_{aa}) is at least 145 ksi, wherein $\Delta(\text{YS}\times\text{El})$ is the 0.2% Offset Yield Strength (ksi) times Percent Elongation after aging ($\text{YS}_{aa}\times\text{El}_{aa}$) minus the 0.2% Offset Yield Strength (ksi) times Percent Elongation before aging ($\text{YS}_{ba}\times\text{El}_{ba}$).

13. The alloy of claim **1**, wherein a low temperature ageability property satisfies the condition, $\Delta(\text{YS}\times\text{El})\leq 600-(\text{YS}_{aa}-145)\times 20$, wherein $\Delta(\text{YS}\times\text{El})$ is the 0.2% Offset Yield Strength (ksi) times Percent Elongation after aging ($\text{YS}_{aa}\times\text{El}_{aa}$) minus the 0.2% Offset Yield Strength (ksi) times Percent Elongation before aging ($\text{YS}_{ba}\times\text{El}_{ba}$).

14. A method of manufacturing an article, comprising:
 providing a billet formed from the alloy of claim **1** that is solution annealed and then cold worked a minimum of 20% to an article of predetermined dimensions; and
 heat treating the cold worked article at 468°-537° C. (875°-999° F.) for five minutes to eight hours.

15. An article of manufacture formed from an alloy of claim **1**, wherein the article has a cold-worked and aged microstructure, having grain boundaries with no continuous precipitates, wherein upon microstructural examination on a section taken in the longitudinal direction with respect to the direction of cold work, a total area fraction of intermetallic phases, nitrides, and carbides does not exceed 1.0%, and wherein an area fraction of sigma phase does not exceed 0.5%.

16. The article of claim **15**, wherein the article has a 0.2% offset yield strength of at least 1000 MPa (145 ksi) and at least 12% elongation.

17. The article of claim **15**, wherein the article has a 0.2% offset yield strength of at least 1069 MPa (155 ksi) and at least 10% elongation.

18. The article of claim **15**, wherein the article has a 0.2% offset yield strength of at least 1138 MPa (165 ksi) and at least 8% elongation.

19. A solid-solution nickel-based alloy for use in sour gas and oil environments, comprising, in percent by weight:

chromium: min. of 21.0 and max. of 23.5%;

iron: min. of 17.0 and max. of 21.0%;

molybdenum: min. of 6.5 and max. of 8.0%;

copper: min. of 1.5 and max. of 2.5%;

tungsten: min. of 0.1 and max. of 1.5%;

sol. nitrogen: min. of 0.08 and max. of 0.20%;

manganese: max. of 4.0%;

silicon: max. of 1.0%;

carbon: max of. 0.015%;

aluminum max of. 0.5%; and

a total amount of niobium, titanium, vanadium, tantalum and zirconium: max of 0.45%;

the balance being nickel and incidental impurities.

* * * * *