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**Description**

This invention relates to a nickel-base alloy and more particularly to such an alloy and products made therefrom having a unique combination of corrosion resistance and age or precipitation hardenability properties in the heat treated condition and without requiring working below the alloy's recrystallization temperature.

The ever-widening search for fossil fuels has resulted in increasing demands for an alloy having improved corrosion resistance and yield strength to overcome the conditions encountered by equipment required to explore and then exploit sour wells. Particularly in deep sour wells, the conditions usually encountered are such that good pitting and crevice corrosion resistance and stress corrosion cracking resistance are required combined with high strength and ductility. In such environments  $Cl^-$ ,  $H_2S$  and  $CO_2$  are present at elevated pressure and temperature. The strengths required are greater than 100 ksi (689.5 MN/m<sup>2</sup>) 0.2% yield strength (YS), preferably greater than 120 ksi (827.4 MN/m<sup>2</sup>), in the age hardened rather than cold worked condition because the parts do not lend themselves to being cold worked and, if at all, only with difficulty and excessive expense. An alloy capable of meeting such rigorous requirements has long been desired for use in the manufacture of components for use in sour wells. Such material would also be well suited for use in other applications involving exposure of members of complex shape or relatively large section to environments requiring outstanding resistance to chlorides and/or sulfides under high stress such as in the chemical process industry or in other industries requiring outstanding stress cracking resistance.

US-A-3,160,500 relates to a matrix-stiffened alloy described as having high strength containing 55-62% Ni, 7 to 11% Mo, 3 to 4.5% Nb, 20-24% Cr, up to 8% W, 0.1% Max. C, 0.5% Max. Si, 0.5% Max. Mn, 0.015% Max. B, 0.40% Max of a deoxidizer selected from the group consisting of Al and Ti and the balance essentially Fe but not more than 20%. Here and elsewhere throughout this application, percent is given as weight percent (w/o) unless otherwise indicated. The alloy is further characterized as having at least about 60 ksi 0.2% YS (414 MN/m<sup>2</sup>) at room temperature and being essentially non-age hardenable, non-age hardenable being defined in US-A-3,160,500 as a maximum increase in yield strength of 20 ksi (138 MN/m<sup>2</sup>) when subjected to a heat treatment at a temperature of about 1100 to 1300 F (593.3 - 704.4 °C) as compared to the yield strength of the alloy in the annealed condition. According to the patent, the total amount of aluminum plus titanium present in the alloy is not to exceed 0.4% "as otherwise the alloys tend to become age hardenable" (Col. 2, lines 45-49). Alloys 1-3 exemplifying the claimed subject matter of the patent and two alloys (identified here as Alloys A and B) described as outside the patented invention, are set forth in Table I where the 0.2% YS (ksi, MN/m<sup>2</sup>) at room temperature in the annealed condition (1900 F (1037.7 °C), 1 hour) as reported in the patent are also given.

TABLE I

	<u>1</u>	<u>2</u>	<u>3</u>	<u>A</u>	<u>B</u>
C	0.02	0.02	0.03		0.04
Mn	0.12	0.11	0.12		0.15
Si	0.05	0.04	0.11		
Cr	21.68	21.41	21.44	21.76	21.4
Mo	9.10	8.83	8.99	9.07	5.1
W	-	5.32	-	-	-
Nb	4.30	4.27	4.19	4.37	1.2
Ti	0.15	0.13	0.20		0.67
Al	0.23	0.20	0.16		0.6
Ni	57.46	Bal.	Bal.	50.8	Bal.
Fe	Bal.	1.92	3.30	Bal.	17.1
.2% YS (ksi)	73.3	92	75.2	66.5	49.5
(MN/m <sup>2</sup> )	505.4	634.3	518.5	458.5	341.3

With regard to Table I it is to be noted that tungsten was reported only in connection with Alloy 2. Alloy A was described as being "similar in composition" to Alloy 1 except as indicated (Pat., col. 4, lines 10 & 11). Alloy B was characterized as having "age hardened strongly but had a yield strength at room temperature

of only 49,500 psi, (341.3 MN/m<sup>2</sup>) . . . when tested after a 1900 F anneal."

A commercial alloy has long been on sale by us under our trademark Pyromet 625 with the composition set forth in Table IA.

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TABLE IA

	<u>w/o</u>		<u>w/o</u>
	C 0.10 Max.	Fe	5.00 Max.
10	Mn 0.50 Max	Ti	0.40 Max.
	Si 0.50 Max.	Co	1.00 Max.
	P 0.015 Max.	Nb (+Ta)	3.15-4.15
	S 0.015 Max.	Al	0.40 Max.
	Cr 20.0-23.0	Ni	Bal.
15	Mo 8.0-10.0		

Thus, while Type 625 alloy as well as other compositions of US-A-3,160,500 are characterized by outstanding corrosion resistance particularly resistance to chlorides, sulfides and carbon dioxide, combined with stability at elevated temperatures, this combination of properties was achieved by eliminating age or precipitation hardening for all practical purposes because of the prohibitively long time required at the elevated temperature required for age hardening.

US-A-3,046,108 describes an age-hardenable nickel alloy containing 0.2 Max. C, 1% Max. Mn, 0.5% Max. Si, 10-25% Cr, 2-5% or 7% Max. Mo, 3-9% Nb + Ta, 0.2-2% Ti, 0.2-2% Al, (Ti + Al  $\leq$  2.5%) 0.02% Max. B, 0.5% Max. Zr, 40% Max. Co, 40% Max. Fe and 45-80% Ni + Co with nickel  $\geq$  30% and Co  $\leq$  40%. A preferred composition contains 0.03% C, 0.18% Mn, 0.27% Si, 21% Cr, 0.6% Al, 0.6% Ti, 4% Nb, 3% Mo, 0.009% B, 53% Ni and balance Fe. In a further variation, iron is limited to 20% Max. with 60-75% Ni + Co, Co  $\leq$  40%. While an alloy within the range of this patent has been available as Pyromet 718 (trademark of the applicant) characterized by high strength, stress rupture life and ductility at elevated temperatures, it and other compositions of US-A-3,046,108 have not provided the desired corrosion resistance in environments containing chlorides, sulfides and carbon dioxide at elevated temperatures required for use in sour wells.

European Patent Application No. 92,397 on the other hand is expressly directed to providing an alloy suitable for use in sour gas wells where corrosion resistance is required to sulfides, carbon dioxide, methane and brine (chlorides) at temperatures up to 300 C. This publication suggests that the most likely causes of failure under such conditions are sulfide stress corrosion cracking, chloride stress corrosion cracking, pitting and general corrosion. The application goes on to propose an alloy having the required corrosion resistance and high yield strength, which is cold workable but not age-hardening containing 15-30% Cr, 5-15% Mo (Cr + Mo = 29-40%) 5-15% Fe (Cr + Mo + Fe  $\leq$  46%), C  $\leq$  0.06%, Al and/or Ti  $\leq$  1%, Si  $\leq$  1%, Nb  $\leq$  0.5%, Mn  $\leq$  0.3%, Bal. Ni. The preferred alloy of this publication asserted to have a yield strength in excess of 1000 MN/m<sup>2</sup> (>145 ksi) is said to consist of 20-30% Cr, 7-12% Mo, (Cr + Mo = 29-40% and Cr - 2  $\times$  Mo = 2-12%), 5-15% Fe, Cr + Mo + Fe  $\leq$  46%, 0.05-0.5% Al and/or Ti, C  $\leq$  0.06%, Nb  $\leq$  0.5%, Si  $\leq$  0.5%, Mn  $\leq$  0.2%, Bal. Ni. Among Alloys A-X, there are six compositions outside the claimed subject matter of the European application 92,397, Alloys F-L, containing 1.9-3.1% Nb but only Alloy K contains a significant amount of Ti for consideration here. Thus, Alloy K in addition to Ni and the usual incidental elements is reported in the publication as containing 0.034% C, 24.7% Cr, 10.1% Mo, 0% Fe, 0.25% Al, 1.40% Ti and 3.1% Nb. Apart from Table I, the only reference to Alloy K to be found in the 92,397 publication is in Table IV where, in the results of chloride stress corrosion tests, Alloy K is reported to have failed in 62 days when exposed to a temperature of 288 C in the U-bend test, the outer fiber stress of the U-bend specimen being 1310 MN/m<sup>2</sup> (190 ksi). Alloy H containing 18.8% Cr, 7.9% Mo, 16.8% Fe, 0.007% C, 0.11% Al, 0.11% Ti, 3.1% Nb and the Bal. Ni according to Table II passed the NACE H<sub>2</sub>S stress corrosion test with an applied stress level of 1200 MN/m<sup>2</sup> (174 ksi) but according to Table IV, Alloy H failed the chloride stress corrosion test in 28 days. Thus, the European patent application 92,397 leads to the conclusion that to achieve high yield strength and resistance to corrosion including stress corrosion in environments encountered in sour wells requires a non-age-hardenable alloy with no more than 0.5% niobium.

US-A-4,400,210 and US-A-4,400,211 and Japanese Publication No. 82-203740 December 1982 relate to alloys for making high strength well casing and tubing having improved resistance to stress corrosion

cracking in media containing sulfides, chlorides and carbon dioxide such as is encountered in deep wells. US-A-4,400,210 and US-A-4,400,211 (Col. 2) assert that "cold working seriously decreases resistance to stress corrosion cracking" but seek to overcome the adverse effect of cold working by the presence of Cr, Ni, Mo and W in the surface layer of a casing or tubing. These two U.S. patents and the Japanese publication specify the composition set forth therein as containing 0.5-4% of at least one of Nb, Ti, Zr, Ta, and V. US-A-4,400,210 and US-A-4,400,211 (Col. 6) and presumably also the Japanese publication state the elements Nb, Ti, Zr, Ta and V are equivalent to each other in providing precipitation (age) hardening due to the formation of an intermetallic compound with Ni.

European patent application 82-56480 relates to a nickel base alloy having resistance to stress corrosion cracking in contact with water at elevated temperature as in boiling water nuclear reactors or pressurized water reactors. The proposed alloy is described as consisting essentially of 15-25% Cr, 1-8% Mo, 0.4-2% Al, 0.7-3% Ti, 0.7-4.5% Nb and the balance Ni, strengthened by gamma prime and/or gamma double prime. The gamma prime phase is defined as an intermetallic compound of Ni<sub>3</sub>(Al, Ti) and the gamma double prime phase as an intermetallic compound of Ni<sub>3</sub>Nb. This publication directly contradicts the assertions of US-A-4,400,210 and US-A-4,400,211 regarding the equivalence of the elements Nb, Ti, Zr, Ta and V in providing age hardening. The European patent application 82-56480 (page 7) states that the addition of Nb is essential for obtaining high hardenability but must be combined with at least 0.4% Al and more than 0.7% Ti to obtain an appreciable age hardenability. Of the many alloys for which specific analyses are given only one, Alloy K, a reference alloy in Table 2, contains more than 4.2% Mo. As set forth in Table 2, Alloy K contains 23.3% Cr, 8.8% Mo, 4.9% Fe, 0.04% C, 0.5% Al, 1.2% Ti, 2.4% Nb and Bal. Ni. Alloy K is noted as having cracked during forging.

There is in addition a considerable quantity of publications including patents both domestic and foreign containing broad composition ranges which overlap in varying degrees with the composition ranges set forth hereinabove but none appears to come any closer to the alloy and articles made therefrom of the present application or, more particularly, to providing a composition suitable for use in sour wells. Nevertheless, there has been an increasing need for an alloy and products made therefrom having a better combination of strength and corrosion resistance, especially an alloy and products made therefrom suitable for use in environments containing sulfides, chlorides and carbon dioxide under high stress without requiring warm or cold working. It is a significant drawback of such prior compositions as disclosed in said US-A-3 160 500 and said European patent application 92 397 that substantial cold reduction is required to reach the level of strength at which parts made therefrom are intended to be used especially in the case of large or massive parts. On the other hand, age-hardenable compositions are exemplified by said US-A-3 046 108 though age hardenable to a desirable high strength, leave much to be desired with regard to corrosion resistance, particularly resistance to cracking under stress in media containing sulfides, chlorides and carbon dioxide as encountered in sour wells.

EP-A-0 066 361 is directed to an age-hardenable nickel-base alloy containing, in weight percent:

C	0-0.1	Cr	15-22	Al	0-1
Mn	0-0.35	Mo	6-9	B	0-0.01
Si	0-0.25/35	Fe	10-28	Cu	0-0.5
P	0-0.015	Nb	2.5-5		
S	0-0.15/0.15	Ti	1-2		

in which the balance is 45-55% nickel. The alloy is described as being good for wrought products, that is, cold rolled strip and extruded tubing for use in tapping deep hydrocarbon fuel reservoirs.

FR-A-2 277 901 discloses an age-hardenable nickel-base alloy containing, in weight percent:

C	0.01-0.2	S	0-0.01	Ti	0.5-1.5
Mn	0-0.35	Cr	15-25	Al	0.3-1.5
Si	0-0.35	Mo	2.5-9	B	0-0.01
P	0-0.01	Nb	1.5-6.5	Fe	15-25

in which the balance is nickel and is directed to a thermal treatment for the alloy defined in time and temperature as a function of the alloy composition so as to control the resulting microstructure.

The problem to which the application is directed is to provide an age-hardenable nickel-base chromium-molybdenum-containing alloy and articles made therefrom which without being warm or cold worked will

have a unique combination of strength and corrosion resistance particularly to pitting and crevice corrosion and resistance to stress corrosion cracking under high stress in severely corrosive environments. The alloy and articles made therefrom should have high resistance to pitting and crevice corrosion and to stress corrosion cracking in the presence of chlorides, sulfides and/or carbon dioxide at elevated pressures and temperatures while being hardenable by heat treatment to a 0.2% yield strength greater than 100 ksi (690MN/m<sup>2</sup>) without the need for working below the recrystallization temperature, that is warm or cold working.

The alloy and articles made therefrom are moreover to be highly resistant to such corrosion in the chloride-, sulfide-, and carbon dioxide- bearing media at the elevated pressures and temperatures, e.g. up to 500 F (260 C) encountered in deep sour oil and/or gas wells.

The foregoing problem is solved in accordance with the invention by providing a nickel base, chromium-molybdenum-containing alloy which in weight percent consists essentially of the composition set forth in Table II below.

**TABLE II**

	<u>Broad (w/o)</u>	<u>Preferred (w/o)</u>
C	0.1 Max.	0.03 Max.
Mn	5 Max.	2 Max.
Si	1 Max.	0.5 Max.
P	0.03 Max.	0.015 Max.
S	0.03 Max.	0.010 Max.
Cr	16-24	18-22
Mo	7-12	7.5-11
Nb	2-6	2.75-4.25
Ti	0.50-2.5	0.75-1.5
Al	Trace-1	0.05-0.35
B	0.02 Max.	0.001-0.006
Zr	0.50 Max.	0.08 Max.
W	4 Max.	-
Co	5 Max.	-
Cu	0-3	0.5 Max.
N	0.04 Max.	0.01 Max.
Fe	20 Max.	2-14

The balance of the composition are incidental impurities and at least 57% nickel, the sum of the percent chromium and molybdenum being not greater than 31, and the sum of the percent niobium, titanium and aluminum being such that the total atomic percent thereof is about 3.5 a/o to 5 a/o when calculated as 0.64(w/o Nb) + 1.24(w/o Ti) + 2.20(w/o Al).

For the composition as specified in Table II and those in Tables III and IIIA hereinbelow, hardener content in weight percent can be converted to atomic percent hardener with reasonable accuracy using the following simplified relationship: Hardener a/o = 0.64 (w/o Nb) + 1.24 (w/o Ti) + 2.20 (w/o Al). And nickel weight percent is so close to atomic percent that they are interchangeable for the purposes of this application. Other elements can be present which aid in making and processing the alloy or which do not objectionably detract from the desired properties. The broad range of one or more elements may be used with the preferred ranges of other elements. Also the stated broad maximum or minimum of one or more elements can be used with their preferred maximums or minimums respectively in Table II and hereinafter. Here and throughout this application it is intended by reference to niobium to include the usual amount of tantalum found in commercially available niobium bearing alloys used in making alloying additions of niobium to commercial alloys.

In this nickel-base composition, in addition to nickel the essential elements are chromium, molybdenum, niobium, titanium and aluminum. Optional elements and the usual incidental impurities may also be present.

Carbon and nitrogen are not considered to be desirable additions in this composition because each can have an adverse effect upon corrosion resistance and because each interferes with the desired hardening reaction, carbon by tying up niobium and titanium, and nitrogen by tying up titanium. Thus, carbon is

limited to no more than 0.1% and preferably to no more than 0.03% or better yet to no more than 0.02%. Nitrogen is limited to no more than 0.04% or even to a maximum of 0.03% and is preferably limited to no more than 0.01%. To offset the adverse effect on the hardening reaction particularly when the carbon content is 0.06% or more, the hardener elements, niobium and titanium, are present in the larger amounts indicated by their ranges. While better results can be attained with extremely low levels of carbon present, e.g. less than 0.005% or less than 0.003%, the cost of reducing carbon below 0.01% makes that a practical minimum for carbon when the added cost would not be warranted.

Manganese may be present in amounts up to 5% but it is preferably kept low, to no more than 2%, better yet to no more than 0.5% or even no more than 0.2%, because manganese increases the tendency for grain boundary precipitation and reduces intergranular corrosion resistance, and pitting and crevice corrosion resistance. Preferably, the larger amounts of manganese when present are at the expense of the larger amounts of iron contemplated in this alloy.

While silicon may be present it is preferably kept low because it promotes the formation of unwanted Laves phase and excessive amounts of silicon can affect weldability and hot workability. Thus, silicon is limited to no more than 1%, preferably no more than 0.5% and better yet no more than 0.2%. Phosphorus and sulfur are considered impurities in this alloy because both adversely affect hot workability and cleanliness of the alloy and promote hydrogen embrittlement. Therefore, phosphorus and sulfur are kept low, less than 0.03% each. Preferably phosphorus is limited to 0.015% Max. and sulfur to 0.010% Max.

Other elements may also be present in relatively small amounts which contribute to a desired property. For example, cobalt contributes to corrosion resistance when present in this composition and to that end may replace nickel on a weight-for-weight basis. However, the cost of cobalt is now and is expected to continue to be greater than nickel so that the extent of the benefit gained from a given addition of cobalt must be weighed against the cost thereof. For that reason, cobalt is limited to a maximum of 5% and nickel is at least 57%, better yet at least 59% nickel is present. Also, up to 4% tungsten can be substituted for its equivalent percent molybdenum, that is 2% by weight tungsten for each 1% by weight molybdenum replaced, when it may be beneficial but at least 7% molybdenum must be present.

Boron up to a maximum of 0.02% may be present in this alloy. Even though many of the advantages of the present alloy can be attained without a boron addition, it is preferred for consistent best results that a small amount of boron of 0.001% to 0.006% Max. be present. Also to aid in refining the alloy, up to 0.50% Max. preferably not more than 0.08% Max. zirconium may be present and from a few hundredths up to about a tenth of a percent of other elements such as magnesium, calcium or one or more of the rare earths may be added.

Copper may be present in this alloy when it may be exposed to sulfuric acid-bearing media or it is desired to ensure maximum resistance to chloride and sulfide stress corrosion cracking at elevated temperature when its adverse effect, if any, on pitting, crevice and intergranular corrosion resistance can be tolerated. To that end, up to 3%, preferably no more than 2.0%, copper may be present.

Iron also is not an essential element in this composition and, if desired, may be omitted. Because commercially available alloying materials contain iron it is preferred to reduce melting costs by using them. It is also believed that iron contributes to resistance to room temperature sulfide stress-cracking. Thus, up to 20% Max. iron may be present but 2% to no more than 14% is preferred.

Chromium, molybdenum, niobium, titanium, aluminum and nickel are critically balanced to provide the uniquely outstanding combination of strength and corrosion resistance properties characteristic of the alloy provided by the present invention. The larger amounts of chromium and molybdenum in their stated ranges of 16-24% Cr and 7-12% molybdenum detract from the hot workability of this composition and, in accordance with this invention, the percent chromium plus the percent molybdenum is not to exceed 31, that is:

$$\% \text{ Cr} + \% \text{ Mo} \leq 31 \quad \text{Eq. 1}$$

In other words, as the chromium content of this composition is increased above 19% to 24%, the maximum tolerable molybdenum is proportionately reduced on a one-for-one weight percent basis from 12% to 7%. Because the larger amounts of chromium ( $\geq 22\%$ ) or molybdenum ( $>11\%$ ) may result in the precipitation of deleterious phases, they are preferably avoided with 57% nickel or better yet 59% nickel is preferred.

The elements niobium, titanium, and aluminum take part in the age hardening reaction by which the present composition is strengthened by heat treatment and without requiring warm or cold working. This invention in part stems from the discovery that the elements niobium and titanium together with smaller amounts of aluminum in the critical proportions specified herein in relation to each other and to the elements chromium, molybdenum and nickel provide a high 0.2% yield strength combined with a high level

of corrosion resistance suitable for use under a wide variety of conditions and, when balanced as indicated to be preferred herein, provide a composition suitable for use under the rigorous conditions to be encountered in deep sour wells. This unique combination of high strength and corrosion resistance is obtained while attempts to strengthen such nickel base chromium-molybdenum compositions with titanium or with titanium and aluminum resulted in lower strength and a reduction in corrosion resistance together with excessive intergranular carbide precipitation during aging. Compositions strengthened primarily with niobium and titanium, in accordance with the present invention differ from those strengthened with titanium or titanium and aluminum in that the titanium and the titanium plus aluminum strengthened material showed extensive intergranular precipitation of chromium-rich carbides ( $M_{23}C_6$ ) during aging which occurred independent of the chromium and molybdenum content.

As in the case of the elements chromium and molybdenum, the hardener elements niobium, titanium and aluminum must be carefully balanced if the high strength of this composition provided by the age hardening reaction is not to result in an unwanted reduction in corrosion resistance. While the broad range for niobium has been stated as 2-6% and for titanium 0.50-2.5%, for better corrosion resistance a preferred niobium range is 2.5-5% or better yet 2.75-4.25% and a preferred titanium range is 0.6 to 2% or even better yet 0.7 to 2.0%. It has been found that in this composition for better crevice corrosion resistance at 55 C as measured in 6%  $FeCl_3$  + 1% HCl for 72 hours the preferred minimum for titanium is again 0.6% while a minimum of 2.75% niobium and at least 1.1% titanium is used for best crevice corrosion resistance.

In this composition the total hardener content should range from 3.5 a/o up to 5 a/o and better yet should not exceed 4.5 a/o for a better all around combination of properties as described herein. When adjusting the balance of a particular composition, increasing the level of niobium and titanium present results in higher strength but because nickel takes part in the strengthening reaction to form the desired intragranular precipitate, nickel should be increased whenever the hardener content is increased with the ratio of the atomic percent increase in nickel to the atomic percent increase in hardener content being 3 to 1 to compensate for the additional nickel removed from the alloy matrix. In this way, the adverse effect of undesired phases, such as sigma phase, and their attendant adverse effect can be avoided. On the other hand, aluminum is beneficial in stabilizing the desired intragranular precipitate and relatively small amounts are found advantageous. It has also been noted that above 0.25%, that is at 0.35% and above, aluminum does not appear to add to but rather to detract from the yield strength at room temperature. Therefore, while up to about 1% aluminum can be present, for better results, particularly higher yield strength, aluminum is limited to no more than 0.5%. In this regard, it is also to be noted that when the larger amounts of aluminum objectionably affect the room temperature yield strength, the strength of the composition can be increased by using a lower solution or a higher primary aging temperature. Also, if the tolerable maximum amounts of niobium and/or titanium are not already present then one or both may be increased. Therefore, aluminum amounts in excess of 0.35% (0.77 a/o) are not to be included in atomic percent determinations throughout this specification but only insofar as room temperature yield strength is concerned.

The alloy of this invention can be melted and hot worked using techniques that are well known and conventionally used in the commercial production of nickel-base alloys. A double melting practice is preferred such as melting in the electric arc furnace plus argon-oxygen decarburization or vacuum induction melting, to prepare a remelt electrode followed by remelting, e.g. consumable remelting. Deoxidation and desulfurization with magnesium and/or calcium when used contributes to hot workability. Additions of rare earths, e.g. in the form of misch metal which is primarily a mixture of cerium and lanthanum, or yttrium may also be beneficial. Small amounts of boron and/or zirconium also stabilize grain boundaries and may contribute to hot workability.

The elements present in this composition are balanced to provide an austenitic microstructure in which the strengthening elements niobium, titanium and aluminum react during appropriate heat treatment with nickel to form one or more strengthening phases in the form of an intragranular precipitate by age or precipitation hardening. The composition of those phases is generalized as  $Ni_3(Nb,Ti,Al)$  and may include gamma prime and/or gamma double prime.

The age-hardenable corrosion resistant nickel-base chromium, molybdenum, niobium, titanium and aluminum alloy of the present invention is readily fabricated into a wide variety of parts following practices utilized in connection with other nickel base alloys. It is well suited to be produced in the form of billets, bars, rod, strip and plate as well as a variety of semi-finished and finished articles for use where its outstanding combination of strength and corrosion resistance in the heat treated condition is desired without requiring working below the recrystallization temperature. Homogenization and hot working is carried out from a temperature of 2050-2200 F (about 1120-1200 C). When required following hot working, solutioning and recrystallization is carried out by heating to a solution treating temperature of 1800-2200 F (980 - 1200

C). An optimum solution treating temperature is 1900 F (1038 C) and preferably should be no higher than 1950 F (1065 C) because higher temperature tends to reduce strength and pitting and crevice corrosion resistance, and to increase intergranular precipitation during the aging heat treatment. Lower solution treating temperatures than the recrystallization temperature are preferably not used to avoid an adverse effect on corrosion resistance and microstructure though higher strength may result. While care is to be exercised in selecting the solution and aging treating temperatures, the temperatures to be used for optimum results are readily determined. A single step age hardening heat treatment may be used if desired but to provide optimum strength and corrosion resistance a two-step aging treatment is preferred. The initial or primary aging treatment can be at 1250 F (677 C) to 1450 F (788 C), preferably between 1300 and 1400 F (700 - 760 C), e.g. 1350 F (732 C), followed by secondary aging at 1100 - 1250 F (590 - 675 C). It is to be noted that in this composition, the use of higher primary aging temperatures result in increased strength but contributes to intergranular precipitation.

The examples set forth in Table III are exemplary of the present invention and in addition to the amounts indicated under each element contained from 0.001-0.006% boron. Other elements when present in more than what is considered a residual or incidental amount in keeping with good commercial practice are indicated in the footnote to the table.

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TABLE III

Ex. No.	C	Cr	Ni	Mo	Nb	Ti	Al	Fe	Hdnr. (= Hardener) (a/o)
5									
10									
1	0.017	16.09	58.94	11.71	3.04	1.23	0.27	8.07	4.1
2	0.016	16.36	63.19	11.85	3.11	1.22	0.27	4.13	4.1
3	0.018	16.40	66.47	12.12	3.06	1.31	0.24	0.21	4.1
4	0.016	18.93	63.87	11.92	3.17	1.37	0.24	0.33	4.3
5	0.018	19.02	63.23	9.03	3.87	1.71	0.28	3.04	5.2
6	0.013	18.79	62.92	8.11	3.08	1.25	0.25	3.21	4.1*
15									
7	0.014	19.00	59.10	9.07	3.11	1.19	0.28	7.84	4.1
8	0.014	18.97	63.30	9.16	3.07	1.23	0.28	4.07	4.1
9	0.015	21.57	63.40	9.04	3.04	1.31	0.26	1.30	4.1
10	0.015	21.82	59.37	9.04	3.15	1.24	0.24	5.09	4.1
20									
11	0.015	21.97	64.02	9.05	3.09	1.26	0.26	0.24	4.1
12	0.014	16.40	58.70	9.10	3.05	1.25	0.21	11.20	4.0
13	0.018	18.81	60.07	8.95	2.54	1.46	0.24	7.37	4.0
14	0.013	18.78	60.21	8.91	3.03	1.26	0.23	7.11	4.0
25									
15	0.010	19.03	60.25	8.90	3.52	0.96	0.23	7.05	3.9
16	0.010	18.88	60.32	8.94	3.02	1.66	0.24	6.79	4.5
17	0.010	18.90	60.24	8.91	3.52	1.39	0.24	6.57	4.5
18	0.011	18.97	60.45	8.93	3.53	1.39	0.11	6.78	4.2
19	0.010	18.99	60.57	8.94	4.00	1.15	0.26	6.41	4.6
30									
20	0.012	18.99	60.33	8.93	4.43	0.84	0.29	6.16	4.5
21	0.010	18.95	58.83	8.83	3.09	1.21	0.22	8.37	4.0
22	0.030	18.99	59.14	8.94	3.05	1.28	0.22	8.51	4.0
23	0.055	18.99	59.01	8.89	3.11	1.22	0.25	8.19	4.1
24	0.012	23.50	58.95	6.59	3.08	1.25	0.24	6.50	4.0
35									
25	0.011	20.48	59.07	7.04	3.12	1.24	0.25	8.63	4.1
26	0.011	23.51	58.97	7.29	3.12	1.26	0.24	5.49	4.1
27	0.014	19.02	59.17	7.52	3.08	1.20	0.25	9.50	4.0
28	0.012	21.97	59.04	7.93	3.10	1.28	0.24	6.25	4.1
29	0.013	20.52	59.15	8.15	3.07	1.26	0.23	7.59	4.0
40									
30	0.010	17.63	59.33	8.94	3.10	1.26	0.23	9.40	4.1
31	0.014	19.01	57.13	8.97	3.14	1.28	0.26	10.33	4.2
32	0.011	20.27	59.07	8.87	3.06	1.27	0.24	7.04	4.1
33	0.012	19.25	59.01	10.57	3.06	1.28	0.21	6.72	4.0
45									
34	0.011	20.47	58.91	10.61	3.03	1.26	0.21	5.31	4.0
50									
55									

TABLE III (Cont.)

Ex. No.	C	Cr	Ni	Mo	Nb	Ti	Al	Fe	Hdnr. (a/o)
35	0.011	20.50	62.96	10.51	3.05	1.27	0.20	1.41	4.0
36	0.012	17.59	59.28	11.92	3.02	1.23	0.23	6.42	4.0
37	0.014	18.93	58.80	8.98	3.07	1.21	0.18	7.15	3.9*
38	0.012	19.03	60.06	9.04	3.05	0.90	0.24	7.75	3.6
39	0.014	19.18	59.92	8.82	3.94	0.50	0.23	7.31	3.6
40	0.017	18.97	60.02	8.98	3.08	1.28	0.05	7.85	3.7
41	0.012	19.02	59.84	8.89	3.49	1.26	0.19	7.02	4.2
42	0.011	19.13	59.64	8.83	3.49	1.37	0.21	5.83	4.4*
43	0.013	19.22	61.27	8.86	3.51	1.41	0.20	5.36	4.4
44	0.010	21.86	61.63	8.89	3.54	1.42	0.22	2.28	4.5
45	0.013	19.20	63.36	8.81	4.20	1.44	0.22	2.93	5.0

\* The following additional quantities were present:  
2.28% W Ex. 6, 1.42% Cu

Ex. ~~44~~, 1.47% Cu Ex. 42.  
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Examples 1-45 were vacuum induction melted as small laboratory heats and, unless otherwise noted, contained <0.2% manganese, <0.2% silicon, <0.015% phosphorus, <0.010% sulfur, and <0.01% nitrogen. An addition of 0.05% magnesium was made to each to complete desulphurization and/or deoxidation before being cast as an ingot. The ingots were homogenized at 2185 F (1195 C) for an extended period (60-70 hours) and then forged from a starting temperature of 2100 F (1150 C), with intermediate reheats as required, to bars 0.75 in x 1.25 or 1.5 in (1.9 x 3.2 or 3.8 cm). Sections of forged bar from each example were then formed into 0.125 in (0.32 cm) thick strip.

Each heat (Ht.) listed in Table IIIA is outside the scope of the present invention and was prepared and processed as described in connection with Examples 1-45 and, in addition to the small amounts of incidental elements as described in connection with Table III, Heat 936 contained tungsten in the footnote to Table IIIA.

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TABLE IIIA

Ht. No.	C	Cr	Ni	Mo	Nb	Ti	Al	Fe	Hdnr. (a/o)
317	0.022	18.84	59.27	4.64	3.17	1.28	0.24	11.39	4.1
318	0.017	16.00	57.74	5.84	3.06	1.28	0.25	15.21	4.1
321	0.016	21.80	59.33	5.85	3.08	1.28	0.25	7.52	4.1
322	0.015	21.82	52.14	6.04	3.15	1.24	0.25	14.71	4.1
324	0.010	19.00	56.59	8.83	0.02	2.75	0.33	12.12	4.1
348	0.050	19.07	52.22	3.03	5.12	1.02	0.59	18.27	5.8
349	0.046	21.87	61.84	8.98	3.78	0.21	0.23	2.54	3.2
394	0.015	16.00	63.01	12.05	0.08	3.52	0.24	4.94	4.9
401	0.018	19.13	63.19	9.00	0.07	3.00	0.24	5.25	4.3
402	0.013	21.99	63.33	8.83	0.06	3.52	0.17	1.99	4.8
406	0.017	15.85	55.29	6.01	3.03	1.26	0.23	18.24	4.0
407	0.017	18.69	54.66	6.01	3.05	1.28	0.24	15.00	4.1
408	0.015	18.97	58.67	6.07	3.07	1.23	0.23	11.06	4.0
409	0.015	18.74	62.76	6.09	3.06	1.26	0.20	7.23	4.0
412	0.016	21.74	55.00	4.57	3.04	1.27	0.25	13.69	4.1
413	0.014	21.55	59.06	4.52	3.12	1.28	0.26	9.80	4.2
414	0.015	24.96	58.75	4.48	3.01	1.33	0.22	6.88	4.1
415	0.017	21.99	54.86	6.09	3.11	1.35	0.22	12.17	4.1
422	0.013	21.53	63.05	6.07	3.11	1.27	0.24	4.29	4.1
423	0.008	21.98	63.06	5.93	0.03	3.57	0.24	5.06	5.0
424	0.017	24.93	62.96	6.20	2.96	1.36	0.25	1.36	4.1
587	0.011	19.11	63.48	8.85	4.35	1.71	0.25	2.32	5.5
588	0.012	19.17	63.56	8.87	4.85	1.40	0.24	2.05	5.4
589	0.012	18.70	59.72	9.00	0.35	2.98	0.70	7.44	5.5
590	0.010	18.79	59.62	8.96	0.31	2.46	1.08	7.72	5.6
910	0.011	23.21	59.03	8.88	3.14	1.26	0.24	4.10	4.1
914	0.011	20.53	58.91	11.83	3.06	1.26	0.21	3.81	4.0
918	0.015	18.94	60.00	9.02	3.49	0.53	0.23	7.76	3.4
931	0.029	21.49	61.77	8.66	4.08	0.40	0.31	3.14	3.8
936	0.011	19.00	58.92	6.32	3.08	1.26	0.26	8.14*	4.1
967	0.012	21.95	58.76	10.48	3.08	1.27	0.22	4.49	4.0

\* Additionally, Heat 936 contained 2.78% W.

Tensile and corrosion test specimens were prepared from bar and/or strip material of the examples and heats of Tables III and IIIA and were tested in the solution treated (recrystallized) plus age hardened condition unless otherwise stated. Room temperature tensile and hardness data are set forth in Tables IV and IVA. The 0.2% yield strength ("0.2% YS") is given as the average of two tests in "ksi" and "(MN/m<sup>2</sup>)" as is also the ultimate tensile strength ("UTS"). The percent elongation in four diameters or widths depending on whether from bar or strip specimens is indicated as "El.(%)". The percent reduction in area is indicated as "RA(%)". The average room temperature hardness on the Rockwell C scale is indicated as "HRC". Whether the data was obtained from bar (B) or strip (S) specimens is indicated under "Bar/Strip". The following is a digest of the heat treatment (H.T.) designations used to identify how the individual test specimens were heat treated. The solution treatment at specific temperatures is assigned an identifying letter, e.g. 1800 F for 1 hour is identified by "A" in the following table. The numbers used to identify specific aging treatments are also given in the following table where cooling in the furnace or oven at a rate of 100 F° (55.6 C°)/hour is indicated by "FC", and cooling in air is indicated by "AC".

	<u>(@F) Sol.Treat.</u>		<u>Aging Treatment</u>
	A 1800-1 h/AC	1	1350 F-8h/FC-1150 F-8h/AC
5	B 1900-1 h/AC	2	1375 F-8h/FC-1150 F-8h/AC
	C 1950-1 h/AC	3	1450 F-8h/FC-1150 F-8h/AC
	D 2000-1 h/AC	4	1325 F-8h/FC-1150 F-8h/AC
	E 2050-1/2 h/AC	5	1425 F-8h/AC
	F 2100-1 h/AC	6	1400 F-8h/AC-1200 F-8h/AC

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TABLE IV

	<u>Ex. No.</u>	<u>0.2% YS</u> <u>ksi(MN/m<sup>2</sup>)</u>	<u>UTS</u> <u>ksi(MN/m<sup>2</sup>)</u>	<u>El.</u> <u>(%)</u>	<u>RA</u> <u>(%)</u>	<u>HRC</u>	<u>Bar/Strip</u>	<u>H.T.</u>
20	1	121.8(839.8)	188.0(1296.2)	28.3	-	38	S	B1
		115.8(798.4)	171.7(1183.8)	18.6	-	36	S	E6
	2	128.6(886.7)	193.0(1330.7)	28.2	-	37.5	S	B1
		112.5(775.7)	172.4(1188.7)	22.2	-	35.5	S	E6
	3	138.5(954.9)	198.9(1371.4)	28.1	-	39	S	B1
25		113.3(781.2)	180.6(1245.2)	25.2	-	34.5	S	E6
	4	133.7(921.8)	197.9(1364.5)	28.6	-	39	S	B1
		108.6(748.8)	162.8(1122.5)	24.7	-	33.5	S	F6
	5	137.9(950.8)	197.7(1363.1)	25.3	-	40.5	S	B1
	6	120.2(828.7)	182.2(1256.2)	31.0	-	36	S	B1
30	7	116.4(802.5)	176.2(1214.9)	28.4	-	36	S	B1
	8	114.5(789.4)	176.2(1214.9)	31.1	-	35.5	S	B1
	9	120.2(828.7)	180.8(1246.6)	28.6	-	36	S	B1
	10	120.8(832.9)	178.2(1228.6)	29.4	-	37	S	B1

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	<u>Ex. No.</u>	<u>HRC</u>	<u>B/S</u>	<u>Ex. No.</u>	<u>HRC</u>	<u>B/S</u>	<u>Ex. No.</u>	<u>HRC</u>	<u>B/S</u>
5	24	36.5	B	32	36.5	B	37	36	B
		36	S		37	S		37.5	S
	25	36	B	33	35.8	B	39	37.5	B
		36	S		35.5	S		37.5	S
	26	36	B	34	36	B	43	36.3	B
10		37.5	S		35.5	S		37	S
	27	35.5	B	35	37	B			
		36.5	S		36	S			

TABLE IVA

	<u>Ht. No.</u>	<u>0.2% YS ksi(MN/m<sup>2</sup>)</u>	<u>UTS ksi(MN/m<sup>2</sup>)</u>	<u>El. (%)</u>	<u>RA (%)</u>	<u>HRC</u>	<u>Bar/Strip</u>	<u>H.T.</u>
	317	112.9(778.4)	167.1(1152.1)	27.2	-	34.5	S	B1
20	318	117.5(810.1)	173.4(1195.6)	24.8	52.2	35	S	B1
	321	126.8(874.3)	181.8(1253.5)	25.8	47.4	38	S	B1
		133.7(921.8)	186.8(1287.9)	25.5	51.9	40	S	A1
	322	123.8(853.6)	177.0(1220.4)	27.3	44.9	37	S	B1
	324	99.8(688.1)	169.3(1167.3)	32.3	33.2	34	S	B2
25	348	135.8(936.3)	186.3(1284.5)	27.9	48.9	38.5	B	B5
		155.3(1070.8)	185.1(1276.2)	23.2	48.1	41.5	S	B4
	349	144.8(998.4)	160.6(1107.3)	16.8	54.8	34.5	S	*
		167.8(1156.9)	180.7(1245.9)	9.4	54.5	37.5	S	*
	394	102.1(704.0)	153.4(1057.7)	19.4	-	31.5	S	E6
30	401	109.6(755.7)	169.4(1168.0)	32.0	-	34.5	S	B6
	402	108.2(746.0)	166.1(1145.2)	27.0	-	33.5	S	E6
	406	120.4(830.1)	172.0(1185.9)	26.4	-	36	S	B1
	407	121.3(836.3)	173.4(1195.6)	29.2	-	36.5	S	B1
	408	116.9(806.0)	172.1(1186.6)	27.5	-	36	S	B1
35	409	112.8(777.7)	169.4(1168.0)	30.0	-	35	S	B1
	412	120.2(828.8)	171.1(1179.7)	28.5	-	37	S	B1
	413	120.0(827.4)	172.3(1188.0)	27.6	-	37.5	S	B1
	414	123.4(850.8)	176.0(1213.5)	27.4	-	37	S	B1
	415	119.8(826.0)	175.0(1206.6)	29.3	-	37	S	B1
40	422	123.0(848.1)	177.4(1223.1)	28.3	-	37	S	B1
	423	111.3(767.4)	167.9(1157.6)	32.6	-	34	S	E6
	424	114.7(790.8)	165.1(1138.3)	30.3	-	35.3	S	E6
	587	160.4(1105.9)	209.9(1447.2)	26.7	47.5	43.5	B	D2
	588	168.8(1163.8)	210.1(1448.6)	23.3	45.5	44	B	D2
45	589	117.4(809.4)	187.1(1290.0)	20.9	22.1	36.5	B	D3
		120.4(830.1)	181.3(1250.0)	22.2	23.5	37	S	C3
	590	110.7(763.3)	178.6(1231.4)	24.9	25.5	33.5	B	D3
		109.5(755.0)	172.6(1190.0)	25.0	23.1	35	S	C3
50	910	135.9(937.0)	189.6(1307.3)	27.2	48.0	36.5	B	B1
		-	-	-	-	36.5	S	B1

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TABLE IVA (Cont.)

Ht. No.	0.2% YS ksi(MN/m <sup>2</sup> )	UTS ksi(MN/m <sup>2</sup> )	El. (%)	RA (%)	HRC	Bar/ Strip	H.T.
914	163.8(1129.4)	214.5(1478.9)	19.8	32.9	43	B	B1
	138.6(955.6)	194.3(1339.7)	27.6	36.3	39.5	S	B1
918	102.6(707.4)	157.4(1085.2)	31.9	60.7	29	B	B1
	94.4(650.9)	150.3(1036.3)	41.4	62.3	26.5	S	B1
931	123.3(850.1)	148.5(1023.9)	37.2	52.1	31.5	S	*
	112.5(775.7)	167.0(1151.4)	38.3	54.3	34	B	B1
936	-	-	-	-	35.5	B	B1
	-	-	-	-	37.5	S	B1
967	127.2(877.0)	188.9(1302.4)	28.2	40.3	38.5	B	B1
	-	-	-	-	36	S	B1

\* Ht. 349 is representative of Type 625 alloy tested in the cold rolled condition, 24% reduction giving the lower and 31% reduction giving the higher strength. Ht. 931 was tested in both the cold rolled (21% reduction) condition (\*) and in the B1 heat treated condition.

The alloy of the present invention in the solution treated and age hardened condition is brought to a high yield strength with a minimum hardener content (Nb + Ti + Al) of 3.5 a/o without requiring warm or cold working for that purpose. Yield strengths greater than 100 ksi (690 MN/m<sup>2</sup>), that is at least 105 ksi (723.9 MN/m<sup>2</sup>) are consistently provided with hardener contents greater than 3.5 a/o with niobium  $\geq$  3.0 w/o. As the weight percent niobium is reduced from 3.0 w/o to 2.0 w/o the minimum weight percent titanium is proportionately increased from 0.8 w/o to 2.0 w/o, that is, a reduction of a predetermined amount in the niobium content should be accompanied by 1.2 times that amount of an increase in the weight percent titanium present in the alloy. Preferably in making this and the following adjustments in niobium and titanium with regard to yield strength, only up to 0.35 w/o (0.77 a/o) aluminum is present. When it is desired to provide consistently a minimum 0.2% yield strength of 120 ksi (about 827 MN/m<sup>2</sup>), niobium and titanium are adjusted proportionately in relation to each other so that as the percent by weight niobium is decreased from 3.9 w/o to 3.0 w/o the minimum weight percent titanium is increased proportionately from 0.50 w/o to 1.1 w/o, that is, the ratio of an increase in titanium to a decrease in niobium is equal to 2/3. As the weight percent niobium is decreased from 3.0% to 2.75% the minimum weight percent titanium is increased proportionately from 1.1% to 1.6%, that is, a ratio of an increase in titanium to the accompanying decrease in niobium of 2. And as the weight percent niobium is decreased from 4.5 w/o to 3.5 w/o the weight percent titanium is increased proportionately from 0.50 to 1.5 w/o, then a minimum 0.2% yield strength of 140 ksi (about 965 MN/M<sup>2</sup>) is attainable. When the carbon content exceeds 0.03%, the effect of carbon on strength can be offset by increasing hardener content, particularly niobium, so as to compensate for the amount tied up by carbon and thereby rendered unavailable for the desired hardening reaction. Because carbon tends toward increased intergranular precipitation and an attendant reduction in corrosion resistance, the higher carbon contents contemplated herein, e.g. greater than 0.06% are to be avoided when its affect on corrosion resistance cannot be tolerated. Thus, Example 23 illustrates that with 0.06% carbon the average yield strength was 99.5 (101.0 and 98.0) ksi. The strength of Ex. 23 can be increased by increasing the hardener content or by using a lower solution treating temperature, the Al heat treatment. To ensure attainment of the maximum attainable yield strength, processing of the material should be such as to provide a grain size in the age hardened material of about ASTM 5 or finer.

It is also to be noted that better toughness as measured by Charpy V-notch impact energy, ft-lb (J), is associated with lower amounts of grain boundary (intergranular) precipitation. As was seen hereinabove, the amounts of nickel, chromium and molybdenum are controlled in relation to each other and a minimum of 57%, better yet 59%, nickel is preferred to avoid undesired phases. And also for better microstructure as represented by smaller amounts of grain boundary precipitation, molybdenum is preferably controlled in relation to the chromium content so that with 16.0-20.5% chromium, molybdenum does not exceed 10.0%. As chromium is increased from 20.5% to 24.0%, the maximum molybdenum is proportionately reduced from 10.0% with 20.5% chromium to 7% at 24.0% chromium. Ex. 21 specimens in the B1 heat treated

condition had a Charpy V-notch impact strength (averages of two tests in each instance) of 97 ft-lb (131.5 J) and, when tested after being held at 1500 F for two hours between solutioning and aging (exposed condition to simulate the effect of the slower rate at which larger sections cool down) had 68.5 ft-lb (92.9 J). Ex. 26 specimens had a V-notch Charpy impact strength of 75 ft-lb (101.7 J) as heat treated B1 and 47 ft-lb (63.7 J) exposed. Ex. 32 specimens when tested had an impact strength of 103 ft-lb (139.6 J) in the B1 condition and 58 ft-lb (78.6 J) in the exposed condition. Ex. 34 containing 20.47% Cr and 10.61% Mo had an impact strength of 45 ft-lb (61.0 J) as heat treated B1 and 30 ft-lb (40.7 J) exposed. To ensure a minimum V-notch Charpy impact strength of 40 ft-lb (54.2 J), a maximum of about 11% molybdenum is preferred with about 16-18% chromium. As chromium is increased from 18.0% to 22.0%, the maximum molybdenum is proportionately reduced from 11% to 9%, and as chromium is increased from 22.0% to 24%, %Cr + %Mo  $\leq$  31. Ex. 36 specimens had a V-notch Charpy impact strength of 34.5 ft-lb (46.8 J) as heat treated B1 and 23.5 ft-lb (31.9 J) exposed. On the other hand, Heats 910, 914 and 967 (%Cr + %Mo > 31) as B1 heat treated had impact strengths, respectively, of 66.5 ft-lb (90.2 J), 30.5 ft-lb (41.4 J) and 42 ft-lb (56.9 J), and in the exposed condition they had, respectively, 33.5 ft-lb (45.4 J), 17 ft-lb (23 J) and 24.5 ft-lb (33.2 J). The preferred composition of the present invention as set forth in Table II hereinabove is characterized by a minimum Charpy V-notch impact strength of 40 ft-lb (54.2 J).

Turning now to Tables V and VA, duplicate pitting and crevice corrosion test specimens were prepared and heat treated as indicated. Each specimen was machined to 1 x 2 x 1/8 in (2.5 x 5 x 0.3 cm) 120 grit surface, cleaned and weighed. The pitting temperature specimens were exposed to 150 ml of 6% FeCl<sub>3</sub> plus 1% HCl for a succession of 24 hour periods starting from room temperature with each period 2.5 C higher than the preceding period. After each 24 hour exposure to the test medium, the specimens were removed, cleaned, reweighed and visually examined (up to 20x) for attack. In the case of pitted specimens the temperature was recorded. Unattacked specimens were returned to fresh solution for a further 24 hour exposure. The test was continued until a pitting temperature was determined or the solution began to boil whereupon the test was discontinued.

To each of the crevice corrosion specimens, after cleaning and weighing, an ASTM G-48 type crevice was attached. The specimens were then exposed to 150 ml of 6% FeCl<sub>3</sub> plus 1% HCl for 3 days at 40 C or 55 C, as indicated. Then the specimens were removed, freed of the crevice forming attachments and then cleaned and weighed. The weight loss in mg/cm<sup>2</sup> was then calculated with the results indicated in Tables V and VA. While the data obtained from specimens exposed at 40 C are averaged those obtained from the exposure at 55 C were not averaged. In evaluating the 55 C data only the larger weight loss (worst case) from each example or heat was used in determining the interaction of the significant elements with respect to resistance to pitting and crevice corrosion in this test. The worst case data from each set of duplicate test specimens was used because with the increase in temperature to 55 C a large spread occurred with the duplicate test specimens of a given example or heat - large in that averages in this case would tend to be misleading.

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TABLE V

5	Ex. No.	HT	Pitting Temp. ( C)* (24h Exp.)	Crevice Corrosion Wt. Loss (mg/cm <sup>2</sup> )		
				(40C/72h)	Avg.	(55C/72h)
10	1	E6	46.5,49	3.0,5.0	4.0	-
		B1	96,>98.5	0.6,1.7	1.2	17.2,20.0
	2	E6	67,71	4.5,4.2	4.4	-
		B1	42,>98.5	1.7,1.1	1.4	21.1,17.9
	3	E6	83.5,83.5	1.5,0.3	0.9	-
		B1	>98.5,>98.5	0.3,0.3	0.3	2.9,14.4
15	4	F6	86,92	0,0	0	-
		B1	>98.5,>98.5	0,0	0	0.0,0.1
	5	B1	>101,>101	0.8,0.9	0.9	2.1,0.7
		B1	>101,>101	0.3,0.6	0.5	3.6,13.3
	6	B1	>101,>101	0.2,0.4	0.3	1.1,1.1
		B1	90,>101	0.5,1.0	0.8	3.3,0.9
20	7	B1	>101,>101	1.1,1.1	1.1	8.0,2.8
		B1	>101,>101	<0.1,<0.1	<0.1	6.7,3.5
	8	B1	>101,>101	0.3,0.3	0.3	10.4,2.0
		B1	92,97	0.5,1.0	0.8	2.1,3.8
25	9	B1	>100,>100	-	-	7.7,11.2
		A1	-	-	-	12.8,8.1
	10	B1	>95,>95	-	-	2.7,3.6
		B1	-	-	-	1.4,0.9
	11	B2	-	-	-	3.5
		B1	>95,>95	-	-	0.7,1.8
30	12	A1	-	-	-	4.0,13.6
		B1	>100	-	-	1.6,4.4
	13	A1	-	-	-	3.8,8.5
		B1	>95,>95	-	-	0.9,2.4
35	14	B1	-	-	-	1.2,1.4
		A1	-	-	-	1.0,19.2
	15	B1	>100,>100	-	-	1.2,11.1
		B1	>101,>101	0.0,0.0	0.0	0.3,1.6
	16	B1	>100,>100	0.1,0.0	0.1	1.2,5.3
		B1	>101,>101	0.0,0.2	0.1	3.0,7.1
40	17	B1	94,100	2.5,1.4	2.0	16.9,3.3
		B1	57.5,90.5,86	0.7,3.0	1.9	2.6,9.9
	18	B1	>101,>101	0.0,0.0	0.0	2.9,6.5
		B1	88,88	3.9,1.3	2.6	12.1,6.7
	19	B1	>101,>101	0.0,2.2	1.1	1.5,4.9
		B1	>101,101	0.3,0.2	0.3	2.0,4.9
45	20	B1	>101,>101	1.2,0.1	0.7	6.2,1.1
		B1	>100,>100	0.0,0.0	0.0	12.1,0.8
	21	B1	>101,95	0.0,0.0	0.0	4.3,4.5
		B1	101,>101	0.0,0.0	0.0	14.9,15.7
	22	B1	>101,>101	0.0,0.0	0.0	15.1,16.9
		B1	>101,>101	0.0,0.0	0.0	5.4,0.2
50	23	B1	>101,>101	0.0,0.0	0.0	11.7,12.2
		B1	96,95	0.0,0.0	0.0	

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TABLE V (Cont.)

Ex. No.	HT	Pitting Temp. (C)* (24h Exp.)	Crevice Corrosion Wt. Loss (mg/cm <sup>2</sup> )		
			(40C/72h)	Avg.	(55C/72h)
374	B1	95,92	0.3,1.8	1.1	14.4,22.0
384	B1	95,>101	0.0,0.0	0.0	11.7,12.5
394	B1	>101,81	0.1,0.0	0.1	23.8,14.0
404	B1	>100,>100	0.0,0.1	0.1	4.9,3.0
414	B1	94,>100	0.4,0.0	0.2	2.1,0.9
	A1	>100,>100	1.9,0.0	1.0	5.4,1.3
424	B1	>100,>100	0.0,0.0	0.0	3.0,11.8
434	B1	100,>100	0.1,0.2	0.0	7.9,7.9
444	B1	>100,>100	0.0,0.0	0.0	0.5,5.3
454	B1	>100,>100	0.1,0.0	0.1	2.5,1.0

\* - Exs. 47-54 exposed at temperature indicated for 72h without interruption.

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TABLE VA

Ex. No.	HT	Pitting Temp. (°C) (24h Exp.)	Crevice Corrosion Wt. Loss (mg/cm <sup>2</sup> )		
			(40C/72h)	Avg.	(55C/72h)
317	B1	44.5,36.5	36.7,37.2	37.0	-
318	B1	65,68	14.5,16.4	15.5	-
321	B1	65,78.5	2.6,2.3	2.5	16.8,15.9
322	B1	76,81	2.4,0.5	1.5	-
324	B2	45.5,50.5	6.6,8.6	7.6	-
348	B4	60,65	36.0,37.6	36.8	43.2,41.9
349	*1	>101,>101	0.0,0.2	0.1	9.6,11.1
	*2	>100,>100	-	-	3.1,10.8
401	B6	49,41	8.0,7.1	7.6	-
402	E6	36.5,44.5	2.1,3.6	2.9	-
406	B1	64.5,71	19.7,17.9	18.8	-
407	B1	70,76	6.1,5.3	5.7	-
408	B1	67,73	3.5,6.7	5.1	34.6,30.0
409	B1	67,67	6.0,7.7	6.9	-
412	B1	65,67	12.0,12.3	12.2	-
413	B1	59,61.5	12.5,15.7	14.1	-
414	B1	67,67	6.3,7.2	6.8	-
415	B1	80.5,80.5	1.2,4.2	2.7	-
422	B1	80.5,80.5	3.8,1.0	2.4	-
423	E6	44.5,48	9.5,8.3	8.9	-
424	E6	83,86	4.5,7.3	5.9	-
	B1	82.5,80	1.7,2.7	2.2	16.4,3.2
587	C2	>100,>100	-	-	0.9,1.2
588	C2	>100,>100	-	-	2.7,0.3
910	B1	>101,95	0.0,0.0	0.0	13.7,0.0
914	B1	>101,>101	0.0,0.0	0.0	0.0,11.3

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TABLE VA (Cont.)

Ex. No.	HT	Pitting Temp. (°C) (24h Exp.)	Crevice Corrosion Wt. Loss (mg/cm <sup>2</sup> )		
			(40C/72h)	Avg. (55C/72h)	
918	B1	90.5,88	0.0,0.0	0.0	24.1,46.2
931	*3	>100,>100	0.0,0.1	0.1	11.7,6.7
936	B1	90,100	0.4,1.2	0.8	38.2,2.2
	B1	-	-	-	33.8,31.4
967	B1	>100,>100	0.0,0.0	0.0	0.0,0.0

\*1 - Cold rolled (24% reduction)  
 \*2 - Cold rolled (31% reduction)  
 \*3 - Cold rolled (21% reduction)

From Tables V and VA it is seen that chromium, niobium, titanium, molybdenum and nickel work to improve resistance to pitting and crevice corrosion resistance. Molybdenum is about four times as effective as chromium (in weight percent) in improving pitting and crevice corrosion resistance when tested at 40 C in 6% ferric chloride (FeCl<sub>3</sub>) plus 1% hydrochloric acid (HCl). In accordance with the present invention, a preferred composition provides a higher level of resistance in FeCl<sub>3</sub>-HCl, that is, an average weight loss of no more than 1 mg/cm<sup>2</sup> when tested with a standard crevice (ASTM G-48) at 40 C for 72 hours. In this composition there is preferably a minimum of 17% chromium and the percent chromium plus four times the percent molybdenum is not less than 52%.

$$\% \text{Cr} + 4(\% \text{Mo}) \geq 52 \quad \text{Eq. 2}$$

This preferred composition also consistently provides freedom from the onset of pitting below the temperature at which the test medium boils, 100 C, however, no more than 11% molybdenum should be used with 17% chromium. From the worst case data obtained with the crevice corrosion test specimens exposed at 55 C, it is apparent good pitting and crevice corrosion resistance is preferably maintained with a minimum of 59% nickel and by limiting the molybdenum content to no more than 10%. The molybdenum and chromium contents are also preferably balanced in relation to each other so that at 16% chromium the molybdenum is 8.5-10%. As the weight percent chromium is increased from 16.0% to 20.5%, the minimum weight percent of molybdenum preferred is proportionately reduced to 7.0% but the maximum remains at 10%. As the weight percent chromium is increased from 20.5% to 24%, the preferred weight percent molybdenum is 7-10% but not greater than [31 - (% Cr)]. For best crevice corrosion resistance in FeCl<sub>3</sub>-HCl at 55 C, with a chromium content of 18.0% it is preferred to use a molybdenum content of 8.5 to 9.7%. As the chromium weight percent is increased from 18.0% to 20.5% the preferred minimum weight percent molybdenum is proportionately reduced from 8.5% to 8.0% and the preferred maximum weight percent is proportionately reduced to 9.4%. Further, as the weight percent chromium is increased from 20.5% to a preferred maximum of 22.0% the minimum weight percent molybdenum is proportionately reduced from 8.0 to 7.7% and the maximum weight percent molybdenum is preferably reduced so that with a chromium content of 22.0%, the maximum molybdenum is 8.2%. In this composition, a minimum of 0.8% to 0.9% titanium is required to attain the outstanding crevice corrosion resistance at 55° C. For best crevice corrosion resistance in FeCl<sub>3</sub>-HCl at 55 C, in addition to controlling the chromium and molybdenum a minimum of 1.1% Ti and of 2.75% Nb is preferred.

Room temperature sulfide stress cracking test specimens were prepared from strip which, after heat treatment had been heated at 550 F (287.8 C) for 30 days and air cooled to simulate deep well aging (well aged). Longitudinal U-bend test specimens 3-7/8 × 3/8 × 1/8 in (9.8 × 1 × .3 cm) from well aged strip were machined to a 120 grit surface finish and bent in accordance with ASTM G-30 (Fig. 5) to a 1 in (2.54 cm) inside diameter. A steel bolt was attached to each leg of each U-bend specimen using nuts and washers at each end. As indicated hereinbelow, transverse specimens were also prepared and processed as described in connection with the U-bend test specimens except that the transverse specimens were about 1-3/8 in (3.5 cm) long and while exposed to the test solution each specimen was anchored at its opposite ends in engagement with iron sleeves and bent to a predetermined deflection by a force applied midway between its ends. After cleaning the specimens were exposed to the solution specified in NACE Test Method TM-01-

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77 (approved July 1, 1977). Each specimen was examined at 20x magnification for cracks after intervals of 240, 504, 648, and 1000 hours. The time after which cracking was detected or "NC" for no cracks is indicated in Table VI and VIA under "NACE". The U-bend data is grouped as longitudinal specimens under "Long." and the transverse specimens under "Trans." in Tables VI and VIA. As is well known, "longitudinal" and "transverse" serve to identify the axis of the specimen in relation to the direction in which the parent material, from which the specimen was prepared, was worked.

Chloride stress corrosion cracking U-bend test specimens were machined from well aged strip as described for use in connection with the NACE test method, and then were bent to an inside diameter of 3/4 in (1.9 cm). The U-bend specimens were cleaned, examined at 20x magnification for mechanical defects and then were exposed without iron contact to 45% MgCl<sub>2</sub>, boiling at 155 C, according to ASTM G-36 using Allihn condensers. The specimens were examined at 20x magnification after intervals of 1, 2, 4, 7, 14, 21, 28, 36, and 42 days (1000h) except that after exposure for 1000h to boiling 45% MgCl<sub>2</sub>, all unfailed U-bend specimens of Examples 17-24 and Ht. Nos. 348, 349 and 587-590 were restressed and exposed for an additional 1000h (2000h total). The results of these tests are set forth in Tables VI and VIA.

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TABLE VI

5	Ex. No.	H.T.	NACE (Rm. Temp.)		45% MgCl <sub>2</sub> (1) (155 C)
			Long.	Trans.	
	1	E6	NC,1000		340,340
		B1	NC,NC	230,NC	NC,NC
10	2	E6	504,240		862,670
		B1	NC,NC		NC,NC
	3	E6	240,240		NC,NC
		B1	NC,NC		NC,NC
	4	F6	240,240		862,862
		B1	NC,NC		NC,NC
15	5	B1	NC,NC	230,NC(3)	NC,NC
	6	B1	NC,NC		NC,NC
	7	B1	NC,NC	NC,NC	NC,NC
	8	B1	NC,NC	NC,NC	NC,NC
	9	A1	NC,NC		48,NC
20		B1	NC,NC		NC,NC
	10	A1	NC,NC		NC,NC
		B1	NC,NC		NC,844
	11	A1	NC,NC		NC,NC
		B1	NC,NC	230,230	670,862
25	12	B1	NC,NC		NC,NC
	13	B1	NC,NC	NC,NC	2016,NC
	14	A1	NC,NC	NC,NC	NC,NC
		B1	NC,NC		NC,NC
	15	B1	NC,NC	NC,NC	672,NC
30		B2	NC,NC		NC,NC
	16	B1	NC,NC	NC,NC	168,NC
	17	A1	NC,NC		NC,504
		B1	NC,NC	NC,652	1168,NC
	18	A1	NC,NC		-,1336
		B1	NC,NC	NC,628	-,1168
35	19	B1	NC,NC	NC,67	504,1504
	20	A1	NC,NC		1168,1168
		B1	NC,NC	NC,67	1168,NC
	21	B1		NC,NC	NC,696
	22	B1	-	-	NC,NC(2)
40	23	B1		NC,NC	336,168
	24	B1		NC,NC	504,504
	25	B1		NC,NC	NC,NC
	26	B1		NC,NC	1032,NC
	27	B1		NC,NC	168,504
45	28	B1		NC,NC	168,696
	29	B1		NC,NC	168,168
	30	B1		NC,NC	1032,NC
	31	B1	-	-	1008,NC
	32	B1		NC,NC	NC,NC
	33	B1		489,NC	504,336
50	34	B1		67,NC	1032,NC

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TABLE VI (Cont.)

Ex. No.	H.T.	NACE (Rm. Temp.)		45% MgCl <sub>2</sub> (1) (155 C)
		Long.	Trans.	
35	B1	-	-	168,168
36	B1	-	230,67	336,336
37	B1	-	NC,NC	504,NC
38	B1	-	-	NC,NC(2)
39	B1	-	NC,NC	NC,NC
40	B1	-	-	NC,NC
41	B1	-	628,628	NC,NC
42	A1	-	-	NC,504
42	B1	-	NC,489	NC,NC
43	B1	-	NC,NC	NC,NC
44	B1	-	-	NC,NC
45	B1	-	67,67	168,NC

(1) Exs. exposed for up to 1000h except Ex. Nos. ~~17-24~~ 13-20 exposed for up to 2000h.

(2) Suspicious area found but examination up to 500 x could not confirm presence or absence of cracks.

(3) The 2nd specimen of Ex 518 (Trans.) was discontinued at 230h because of equipment failure, no cracks were found.

NC = No cracking observed.

TABLE VIA

Ht. No.	H.T.	NACE (Rm. Temp.)		45% MgCl <sub>2</sub> (155 C)
		Long	Trans.	
317	B1	NC,NC		NC,NC
318	B1	NC,NC		NC,NC
321	B1	NC,NC	NC,NC	NC,NC
322	B1	NC,NC		306,355
324	B2	NC,NC		NC,NC
348	B5	NC,NC	NC,NC	168,NC
	B4	NC,NC	NC,NC	48,336
349	(1)	NC,NC		NC,NC
	(1)	NC,NC	NC,NC	NC,NC
394	E6	240,240		334,162
401	B6	NC,NC		NC,NC
402	E6	240,1000		862,862
406	B1	NC,NC		NC,NC
407	B1	NC,NC		NC,676
408	B1	NC,NC	NC,NC	NC,NC

TABLE VIA (Cont.)

5	Ex. No.	H.T.	NACE (Rm. Temp.)		45% MgCl <sub>2</sub> (1) (155 C)
			Long.	Trans.	
	409	B1	NC,NC		NC,NC
	412	B1	NC,NC		NC,NC
10	413	B1	NC,NC		NC,NC
	414	B1	NC,NC		NC,NC
	415	B1	NC,NC		NC,168
	422	B1	NC,NC		NC,NC
	423	E6	504,240		NC,NC
15	424	E6	NC,NC		NC,862
		B1	NC,NC		NC,168(2)
	587	C2	NC,570	67,230	NC,NC
	588	C2	240,240		336,336
	589	C3	NC,NC		NC,NC
20	590	C3	NC,NC		336,336
	910	B1		67,67	336,NC
	914	B1			504,504
	931	(3)		NC,NC	NC,NC
	967	B1		67,67	NC,NC(2)

- 25 (1) Cold rolled to 24% and 31% reductions respectively.  
 (2) Suspicious area found but examination up to 500 x  
 could not confirm presence or absence of cracks.  
 (3) Cold rolled to 21% reduction.  
 30 NC = No cracking observed.

The NACE TM-01-77 test data in Tables VI and VIA show that the present composition is resistant to sulfide stress-cracking at room temperature. For best results, the highest levels of molybdenum, niobium and titanium should be avoided. In this regard, 24% chromium is used with 7% molybdenum. As the amount of chromium is decreased from 23%, the maximum amount of molybdenum can be increased from 8%, with the ratio of the reduction in the chromium weight percent to the increase in the tolerable molybdenum weight percent being equal to about 2. For example, a decrease in chromium content from about 22% to 20% results in an increase from 8.5% to about 9.5% in the maximum amount of molybdenum that is preferably used when optimum resistance to sulfide stress-cracking is desired. Also indicated is a reduction to 16% chromium when the molybdenum content is at about 11.5%. While aluminum is held to its preferred range for this purpose, the amount of niobium and titanium should be carefully controlled. With 4.5% niobium present, titanium should not be greater than about 0.50%. As the weight percent niobium is reduced from 4.5% to about 3.0%, the maximum amount of titanium present can be proportionately increased to 2.0%. Preferably, the maximum weight percent of niobium is 4.25% with which no more than 0.50% titanium is used. As niobium is reduced from 4.25% to 3.0%, the maximum weight percent titanium is proportionately increased from 0.50% to 1.75%. Thus, the ratio of an increase in the weight percent of titanium to the accompanying decrease in niobium is 1.0 in both these instances.

The present alloy and age hardened products made therefrom have good resistance to chloride stress-cracking as demonstrated by exposure to the severe environment of boiling 45% MgCl<sub>2</sub>. With nickel below 60%, the lower chromium and molybdenum contents provide better results. Preferably, with a hardener content of 4.0 a/o at least 60% nickel should be present. And as the hardener content is increased above 4.0 a/o or decreased, the minimum nickel to be present is correspondingly increased or decreased above or below 60% with the amount of the change in nickel content being three times the change in hardener content. Thus, for an increase or decrease in the hardener content of 0.5 a/o the nickel content should be correspondingly increased or decreased by 1.5 a/o. In this regard, it should also be noted that copper also contributes to stress-cracking resistance in boiling MgCl<sub>2</sub> and for this purpose it is desirable to include up to 3% copper to compensate for lower nickel than 60% or when the hardener content is greater than 4.0

a/o. Up to 2.0% copper is effectively used in compositions containing 60% nickel and above.

The combined effect of chloride, hydrogen sulfide and sulfur at elevated temperatures and pressure was determined in autoclave tests (elsewhere herein referred to as the autoclave test) at 400 F (204 C), 450 F (232 C) and 500 F (260 C) as a simulation of severe sour well environments. Duplicate U-bend specimens were prepared from strip which had been heated at 550 F (287.8 C) for 30 days (then air cooled) to simulate deep well aging. The U-bend test specimens were 3-7/8 x 3/8 x 0.100-0.125 in (9.8 x .95 x 0.254-0.318 cm) with 17/64 in (.67 cm) diameter holes adjacent to each end. The specimens were ground to 120 grit finish, bent to 1 in (2.54 cm) inside diameter and were stressed. In Tables VII-IX, the number of hours of exposure following which the specimen showed a stress crack or NC for no crack is given. The examples of the present invention and of the heats in Tables VII-IX were exposed to saturated (25%) sodium chloride, 0.5 g/l elemental sulfur and 1300-1440 psig partial pressure of hydrogen sulfide test medium under three different conditions. As indicated in Table VII, the examples and heats there listed were tested for 648h at 400 F (204.4 C) made up of two 160h periods and one period of 328h and if no cracks were observed the test was continued for 328h at 450 F. Specimens from some of the examples and heats were tested for one 328h period at 450 F followed by two 328h periods at 500 F (260 C). In Table VIII the specimens listed were tested for one 328h period at 450 F and one 328h period at 500 F. The data set forth in Table IX was obtained from specimens tested for 328h at 450 F plus two periods each of 328h at 500 F. It should also be noted here that CO<sub>2</sub> was not required to obtain a low pH and elemental sulfur was included in the test environment to increase the severity of the environment commensurate with such a highly alloyed material as the present composition.

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TABLE VII

Ex. No.	H.T.	2x160h+328h@400F +328h@450F	328h@450F +2x328h@500F	
5				
1	E6	NC,NC,NC,NC	656,984	
	B1	-	984,984	
10	2	E6	NC,NC,NC	-
	3	E6	NC,NC,NC	-
		B1	-	656,656
	4	F6	NC,NC,NC	-
		B1	-	NC,NC
15	5	B1	NC,NC,NC	656
	6	B1	NC,NC,NC	-
	7	B1	NC,NC,NC	656,984
	8	B1	NC,NC,NC	984,984
	9	B1	NC,NC,NC	-
20	10	B1	NC,NC,NC	NC,NC
	11	B1	NC,NC,NC	NC,NC
		A1	-	656,984
	12	B1	NC,NC,NC	984,984
25	<u>Ht. No.</u>			
	317	B1	976,976,NC	-
	318	B1	976,976,976	-
30	321	B1	NC,NC,NC	328,656
	322	B1	NC,NC,NC	-
	324	B2	976,NC,NC	-
	348	B5	-	328,328,328,328
		B4	160,160,160	328,-
	349	*	NC,NC,NC	NC,-
35		*	-	328,656,656
	394	E6	160,976,976,NC	-
	401	B6	NC,NC,NC,NC	-
	402	E6	NC,NC,NC,NC	-
	406	B1	320,320,976	-
40	407	B1	976,NC,NC	-
	408	B1	976,NC,NC	-
	409	B1	NC,NC,NC	-
	412	B1	160,648,976	-
	413	B1	648,976,976	-
	414	B1	648,648,976	-
45	415	B1	976,NC,NC	-
	422	B1	976,NC,NC	-
	423	E6	976,976,NC,NC	-
	424	E6	NC,NC,NC	-
		B1	-	656,NC

\*Cold rolled to 24% and 31% reduction, respectively.

TABLE VIII

328h@450F  
+328h@500F

Ex. No.	H.T.		Ht. No.	H.T.	
	14	A1		NC, NC	587
	B1	NC, NC	588	C2	328, 328
15	A1	NC, NC	589	C3	328, 328
	B1	NC, 656			
16	A1	NC, NC			
	B1	NC, NC			
17	A1	NC, NC			
	B1	NC, 656			

TABLE IX

328h@450F  
+2x328h@500F

Ex. No.	H.T.		Ex. No.	H.T.	
	21	B1		984, 984	34
	B1	NC, 984	35	B1	NC, NC
22	B1	984, 984	36	B1	NC, 984
23	B1	984, 984			
24	B1	984, NC	37	B1	NC, NC
25	B1	656, 656	39	B1	656, 984
26	B1	NC, NC	41	B1	NC, NC
27	B1	656, 984		A1	NC, NC
28	B1	NC, NC	42	B1	NC, 984
29	B1	984, NC	43	B1	656, 984
30	B1	NC, 984	44	B1	NC, NC
31	B1	984, 984	45	B1	984, 984

Ht.  
No.

910 B1 NC, 984  
914 B1 NC, NC  
931 \* 984, 984  
936 B1 NC, 984  
967 B1 NC, NC

\*Cold rolled to 21% reduction.

The autoclave test data demonstrate the outstanding resistance to corrosion and stress cracking under extremely severe conditions. Analysis of the data shows that in this composition molybdenum in weight percent is about four times as effective as chromium in improving resistance to stress cracking as measured in the autoclave test in the 400-450 F temperature range. For best resistance to cracking in the 400-450 F range, the percent chromium plus four times the percent molybdenum should not be less than 47%, that is,

$\% \text{ Cr} + 4(\% \text{ Mo}) \geq 47\%$  Eq. 3

For best resistance to cracking in the 450-500 F range, the percent chromium plus four times the percent molybdenum should not be less than 49.5%, that is,

$\% \text{ Cr} + 4(\% \text{ Mo}) \geq 49.5\%$  Eq. 4

To optimize the alloy for resistance to cracking at 500 F, the percent chromium plus the percent molybdenum should not be less than 30%, that is,

$\% \text{ Cr} + \% \text{ Mo} \geq 30\%$  Eq. 5

And for best resistance to stress-cracking at 500 F in the autoclave test the hardener content is preferably no greater than 4.5 a/o. For exposures at temperatures below 500 F a hardener content up to 5 a/o gives good resistance to stress-cracking. When adjusting hardener content for this purpose, aluminum is preferably no more than 0.35% (no more than 0.77 a/o) to maximize strength. Copper also contributes to improved resistance to stress cracking in the autoclave test and for this purpose up to 3% can be used. As hardener content is increased above 4.0 a/o, copper preferably up to 2.0% is used effectively in improving resistance to stress cracking in the autoclave test.

To further exemplify the present invention, Example 46 was prepared using a double melting practice as a heat weighing about 10,000 pounds (4,545.5 kg) and forged to 4 in (10.16 cm) round bar which was heat treated. The composition of Example 46 is set forth in Table X. The composition of Heat A, representative of commercial Type 625 alloy (also about a 10,000 lb heat) is also given in Table X.

TABLE X

<sup>46</sup>  
Ex. 46      Ht. A

	Ex. 46	Ht. A
C	0.021	0.047
Mn	0.03	0.09
Si	0.08	0.12
Cr	19.85	22.10
Ni	61.73	61.57
Mo	8.81	8.79
Ti	1.27	0.27
Al	0.16	0.28
Nb	3.11	3.91
B	0.0037	-
Fe	4.92	2.84

Each contained less than 0.01% phosphorus and less than 0.01% sulfur. Though not indicated, Heat A also contained about 0.004% boron.

Standard room temperature threaded tensile test specimens cut from transverse sections of the Ex. 46 4 in bar material (B1 heat treated except for water quenching from the solution temperature) were prepared. Transverse tensile test specimens were also formed from forged and heat treated 5-1/2 in (14.0 cm) round bar of Heat A. The tensile test data is set forth in Table XI and heat treated hardnesses are also given.

TABLE XI

Ex./ Ht. No.	0.2% YS ksi(MN/m <sup>2</sup> )	UTS ksi(MN/m <sup>2</sup> )	El. (4D) (%)	RA (%)	HRB/C	H.T.
46 (1)	119.5(823.9)	175.6(1210.7)	33.2	44.8	C34	B1(2)
46 (1)	127.9(887.9)	178.2(1228.3)	30.8	42.8	C35.5	B2(2)
10 A	73.1(504.0)	136.1(938.4)	32.8	33.5	B97	B1
A	77.2(532.3)	138.8(957.0)	33.0	37.6	B98	A1

(1) Average of two tests. < 881.87  
 (2) Water quenched after Sol. Treat.

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Comparison of the data in Table XI clearly demonstrates that Type 625 alloy does not respond to practical age hardening treatment. Known alloys as well as that of the present invention and Type 625 may show higher strength when processing includes warm working. Unless cold worked, the strength of Type 625 alloy is far below that of the alloy of the present invention.

The alloy of the present invention by its unusual combination of strength and corrosion resistance properties is well suited for a wide variety of uses in the chemical, petroleum and nuclear industries. The alloy lends itself to the production of a large variety of sizes and shapes. Intermediate products in any desired form such as billets, bars, strip and sheet as well as powder metallurgy products can be provided from which an even wider range of finished products can be made. The compositions set forth herein are advantageously used to provide parts for use in the exploration for, and exploitation of, petroleum products such as those intended for exposure under stress and/or under elevated temperatures. For example to enumerate a few, such parts include subsurface safety valves, hangers, valve and packer components, and other parts used above or below ground.

While the present invention has been described in connection with exemplary embodiments thereof, it is recognized that further modifications are possible within the scope of the invention claimed. For example, when the smaller amounts of aluminum contemplated herein, that is less than 0.35% aluminum, are reduced to less than 0.1% and are replaced by an equivalent atomic percent of titanium and/or niobium added to attain or maintain a minimum yield strength of 105 ksi (724 MN/m<sup>2</sup>), such replacement may result in several tenths of a percent (atomic) less total hardener than if the aluminum content had not been reduced. This may result because the added amount of titanium and/or niobium causes a greater increase in strength than the amount, if any, the strength of the composition is reduced by the decrease in aluminum. It is, therefore, intended to include as little as 3.0 a/o hardener content when all or substantially all of the aluminum contemplated herein is replaced by titanium and/or niobium.

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**Claims**

1. An age hardenable nickel base chromium-molybdenum-containing alloy characterized by the alloy in weight percent consisting of

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	<u>(w/o)</u>
5	Carbon 0.1 Max.
	Manganese 5 Max.
	Silicon 1 Max.
	Phosphorus 0.03 Max.
	Sulfur 0.03 Max.
	Chromium 16-24
	Molybdenum 7-12
10	Tungsten 4 Max.
	Niobium 2-6
	Titanium 0.50-2.5
	Aluminum Trace-1
	Boron 0.02 Max.
	Zirconium 0.50 Max.
15	Cobalt 5 Max.
	Copper 0-3
	Nitrogen 0.04 Max.
	Iron 20 Max.

20 the balance being incidental impurities and at least 57% nickel, the sum of the percent chromium and molybdenum being not greater than 31, and the sum of the percent niobium, titanium and aluminum being such that the total atomic percent thereof is 3.5 a/o to 5 a/o when calculated as 0.64(w/o Nb) + 1.24(w/o Ti) + 2.20(w/o Al), solution treated and age hardened it has a 0.2% yield strength greater than 25 100 ksi (690 MN/m<sup>2</sup>) combined with resistance to pitting and crevice corrosion and to stress corrosion cracking in chloride and sulfide environments at elevated temperatures up to 500 F (260 C) without requiring working below its recrystallization temperature.

2. The alloy of claim 1, characterized by containing

	<u>(w/o)</u>
30	Carbon 0.03 Max.
	Manganese 2 Max.
35	Silicon 0.5 Max.
	Phosphorus 0.015 Max.
	Sulfur 0.010 Max.
	Chromium 18-22
	Molybdenum 7.5-11
40	Niobium 2.75-4.25
	Titanium 0.75-1.5
	Aluminum 0.05-0.35
	Boron 0.001-0.006
	Zirconium 0.08 Max.
45	Copper 0.5 Max.
	Nitrogen 0.01 Max.
	Iron 2-14

50 and at least 59% nickel.

3. The alloy of claim 1, characterized by containing 0.06% Max. carbon, 2% Max. manganese and 0.5% Max. silicon.
- 55 4. The alloy of claim 3, characterized by containing 0.5% Max. manganese and 0.2% Max. silicon and 14% Max. iron.
5. The alloy of claim 4, characterized by containing at least 60% nickel.

6. The alloy of claim 4, characterized by containing 0.03% Max. carbon and 0.2% Max. manganese.
7. The alloy of claim 6, characterized by containing 0.01% Max. carbon and 0.01% Max. nitrogen.
- 5 8. The alloy of any one of the preceding claims, characterized by containing no more than 11% molybdenum, the weight percent chromium and molybdenum being balanced so that with 16.0% chromium there is 7.5-11.0% molybdenum, and as chromium increases from 16.0% to 19.0% the minimum amount of molybdenum decreases to 7.0%.
- 10 9. The alloy of claim 8, characterized by containing a maximum of 0.35% aluminum.
10. The alloy of any one of claims 1 to 7, characterized by containing no more than 10% molybdenum, in which the weight percent chromium and molybdenum are balanced so that with 16% chromium molybdenum is 8.5-10%, as the weight percent chromium is increased from 16.0% to 20.5% the minimum weight percent molybdenum is proportionately reduced to 7.0%, as the weight percent chromium is increased from 20.5% to about 24% the minimum weight percent molybdenum remains 7% and the sum of the weight percent chromium and molybdenum is not greater than 31.
- 15 11. The alloy of claim 10, characterized by containing a minimum of 0.9% titanium.
- 20 12. The alloy of claim 4, characterized by containing a minimum of 17.0% chromium and in which  $\%Cr + 4(\%Mo) \geq 52\%$ .
13. The alloy of claim 11, characterized by containing a maximum of 0.35% aluminum.
- 25 14. The alloy of claim 10, characterized by containing a minimum of 2.75% niobium and a minimum of 1.1% titanium.
15. The alloy of any one of claims 1 to 7, characterized in that the weight percent chromium and molybdenum are balanced so that with 24% chromium there is 7% molybdenum, as the weight percent chromium is reduced from 23% the maximum weight percent molybdenum is increased from 8% with the ratio of the reduction in weight percent chromium to the increase in the maximum weight percent molybdenum being equal to about 2.
- 30 16. The alloy of claim 15, characterized by containing 3.0-4.5% niobium, 0.50-2.0% titanium, the weight percent titanium and niobium being balanced so that with 4.5% niobium there is no more than 0.50% titanium, and as the maximum weight percent niobium is reduced from 4.5% to 3.0% the maximum weight percent titanium is increased to 2.0%.
- 35 17. The alloy of claim 15, characterized by containing 3.0-4.25% niobium, 0.50-1.75% titanium, the weight percent niobium and titanium being balanced so that with 4.25% niobium there is a maximum of 0.50% titanium, and as the weight percent niobium is decreased from 4.25% to 3.0% the maximum titanium is proportionately increased from 0.50% to 1.75%.
- 40 18. The alloy of claim 1, characterized in that the weight percent chromium and molybdenum are balanced so that with 16.0% chromium there is 7.5% molybdenum, and as chromium increases from 16.0% to 19.0% the minimum amount of molybdenum decreases proportionally to 7.0%.
- 45 19. The alloy of claim 1, characterized in that the weight percent chromium and molybdenum are balanced so that with 16% chromium there is a minimum of 8.5% molybdenum, as the weight percent chromium increases from 16.0% to 21.5% the minimum amount of molybdenum decreases from 8.5% to 7%, and containing no more than 4.5 atomic percent of niobium plus titanium and aluminum.
- 50 20. The alloy of claim 1 or 2, characterized in that niobium and titanium are balanced so that with 3.9% niobium there is present a minimum of 0.50% titanium, as the weight percent niobium is decreased from 3.9 w/o to 3.0 w/o the minimum amount of titanium is proportionately increased from 0.50 w/o to 1.1 w/o, as the amount of niobium is decreased from 3.0 w/o to 2.75 w/o the minimum amount of titanium is increased proportionately from 1.1 w/o to 1.6 w/o.
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21. The alloy of claim 1, characterized in that niobium and titanium are balanced so that with 4.5 w/o niobium there is present a minimum of 0.50 w/o titanium, and as the amount of niobium present is decreased from 4.5 w/o to 3.5 w/o the minimum amount of titanium present is increased proportionately from 0.50 w/o to 1.5 w/o.

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22. The alloy of claim 2, characterized in that niobium and titanium are balanced so that with about 4.25 w/o niobium there is present a minimum of 0.75 w/o titanium, and as the amount of niobium present is decreased from 4.25 w/o to about 3.5 w/o the minimum amount of titanium present is increased proportionately from 0.75 w/o to about 1.5 w/o.

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23. The use of the alloy of any one of the preceding claims to make an age hardened corrosion resistant article.

24. The use of claim 23, characterized by having in the as-solution treated and aged condition a minimum 0.2% yield strength of at least 827.4 MN/m<sup>2</sup> (120 ksi).

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25. Method of making a nickel base alloy containing in weight percent

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	<u>(w/o)</u>
Carbon	0.1 Max.
Manganese	5 Max.
Silicon	1 Max.
Phosphorus	0.03 Max.
25 Sulfur	0.03 Max.
Chromium	16-24
Molybdenum	7-12
Tungsten	4 Max.
Niobium	2-6
30 Titanium	0.50-2.5
Aluminum	Trace-1
Boron	0.02 Max.
Zirconium	0.50 Max.
35 Cobalt	5 Max.
Copper	0-3
Nitrogen	0.04 Max.
Iron	20 Max.

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the balance being incidental impurities and at least 57% nickel, characterized by adjusting the sum of the percent chromium and the percent molybdenum so that the combined weight percent thereof is not greater than 31, and adjusting the sum of the weight percent niobium plus the weight percent titanium and plus the weight percent aluminum so that the combined total atomic percent of the elements niobium, titanium and aluminum is 3.5 a/o to 5 a/o when calculated as 0.64(w/o Nb) + 1.24(w/o Ti) + 2.20(w/o Al).

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26. The method of claim 25, characterized by age hardening said nickel base alloy to provide an article having a 0.2% yield strength greater than 100 ksi (690 MN/m<sup>2</sup>) combined with resistance to pitting and crevice corrosion and to stress corrosion cracking in chloride and sulfide environments at elevated temperatures up to 500F (260C) without requiring working below its recrystallization temperature.

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27. The method of claim 26, characterized by hot working said nickel base alloy before said age hardening thereof.

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28. Method of claim 27, characterized by solution treating said nickel base alloy after said hot working and before said age hardening.

29. Method of any one of claims 26 to 28, characterized in that a two step aging treatment is used in the temperature range of 1100F to 1450F (590-790C).

5 30. The use of an age hardenable nickel base alloy according to claim 1 or 2, for making articles for sour well application.

**Revendications**

10 1. Alliage à base de nickel contenant du chrome et du molybdène, durcissable par vieillissement, caractérisé en ce qu'il comprend, en pourcentage en poids

		<u>% en poids</u>
15	Carbone	0,1 Max.
	Manganèse	5 Max.
	Silicium	1 Max.
	Phosphore	0,03 Max.
	Soufre	0,03 Max.
	Chrome	16-24
20	Molybdène	7-12
	Tungstène	4 Max.
	Niobium	2-6
	Titane	0,50-2,5
	Aluminium	Traces-1
25	Bore	0,02 Max.
	Zirconium	0,50 Max.
	Cobalt	5 Max.
	Cuivre	0-3
	Azote	0,04 Max.
30	Fer	20 Max.

35 le reste étant constitué des impuretés accidentelles et d'au moins 57% de nickel, la somme des pourcentages de chrome et de molybdène étant non supérieure à 31% et la somme des pourcentages de niobium, de titane et d'aluminium étant choisie de manière que le pourcentage atomique total de ces éléments soit de 3,5% at. à 5% at. lors du calcul sur la base de la somme 0,64 (% en poids de Nb) + 1,24 (% en poids de Ti) + 2,20 (% en poids de Al), et il possède, après traitement en solution et durcissement par vieillissement, une limite d'élasticité à 0,2% supérieure à 100 ksi (690 MN/m<sup>2</sup>) associée à une résistance à la formation de piqûres et à la corrosion par formation de crevasses ainsi qu'à la fissuration par corrosion sous contrainte dans des milieux renfermant des chlorures et des sulfures à des températures élevées allant jusqu'à 500 °F (260 °C) sans nécessiter de travail à une température inférieure à sa température de recristallisation.

45 2. Alliage suivant la revendication 1, caractérisé en ce qu'il contient

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		<u>% en poids</u>
	<b>Carbone</b>	<b>0,03 Max.</b>
	<b>Manganèse</b>	<b>2 Max.</b>
5	<b>Silicium</b>	<b>0,5 Max.</b>
	<b>Phosphore</b>	<b>0,015 Max.</b>
	<b>Soufre</b>	<b>0,010 Max.</b>
	<b>Chrome</b>	<b>18-22</b>
	<b>Molybdène</b>	<b>7,5-11</b>
10	<b>Niobium</b>	<b>2,75-4,25</b>
	<b>Titane</b>	<b>0,75-1,5</b>
	<b>Aluminium</b>	<b>0,05-0,35</b>
	<b>Bore</b>	<b>0,001-0,006</b>
	<b>Zirconium</b>	<b>0,08 Max.</b>
15	<b>Cuivre</b>	<b>0,5 Max.</b>
	<b>Azote</b>	<b>0,01 Max.</b>
	<b>Fer</b>	<b>2-14</b>

20 et au moins 59% de nickel.

3. Alliage suivant la revendication 1, caractérisé en ce qu'il contient 0,06% Max. de carbone, 2% Max. de manganèse et 0,5% Max. de silicium.
- 25 4. Alliage suivant la revendication 3, caractérisé en ce qu'il contient 0,5% Max. de manganèse et 0,2% Max. de silicium ainsi que 14% Max. de fer.
5. Alliage suivant la revendication 4, caractérisé en ce qu'il contient au moins 60% de nickel.
- 30 6. Alliage suivant la revendication 4, caractérisé en ce qu'il contient 0,03% Max. de carbone et 0,2% Max. de manganèse.
7. Alliage suivant la revendication 6, caractérisé en ce qu'il contient 0,01% Max. de carbone et 0,01% Max. d'azote.
- 35 8. Alliage suivant l'une quelconque des revendications précédentes, caractérisé en ce qu'il ne contient pas plus de 11% de molybdène, les pourcentages en poids de chrome et de molybdène étant équilibrés de sorte qu'avec 16,0% de chrome, 7,5 à 11,0% de molybdène soient présents et, lorsque la teneur en chrome augmente de 16,0% à 19,0%, la quantité minimale de molybdène s'abaisse à 7,0%.
- 40 9. Alliage suivant la revendication 8, caractérisé en ce qu'il contient un maximum de 0,35% d'aluminium.
10. Alliage suivant l'une quelconque des revendications 1 à 7, caractérisé en ce qu'il ne contient pas plus de 10% de molybdène, les pourcentages en poids de chrome et de molybdène étant équilibrés de sorte qu'avec 16% de chrome, 8,5 à 10% de molybdène soient présents et, lorsque le pourcentage en poids de chrome est de 16,0% à 20,5%, le pourcentage minimal en poids de molybdène soit réduit en proportion à 7,0%, lorsque le pourcentage en poids de chrome est accru de 20,5% à environ 24%, le pourcentage minimum en poids de molybdène reste égal à 7% et la somme des pourcentages en poids de chrome et de molybdène soit non supérieure à 31%.
- 45 11. Alliage suivant la revendication 10, caractérisé en ce qu'il contient un minimum de 0,9% de titane.
12. Alliage suivant la revendication 4, caractérisé en ce qu'il contient un minimum de 17,0% de chrome, et la somme %Cr + 4(%Mo) est supérieure ou égale à 52%.
- 55 13. Alliage suivant la revendication 11, caractérisé en ce qu'il contient un maximum de 0,35% d'aluminium.
14. Alliage suivant la revendication 10, caractérisé en ce qu'il contient un minimum de 2,75% de niobium

et un minimum de 1,1% de titane.

- 5 15. Alliage suivant l'une quelconque des revendications 1 à 7, caractérisé en ce que les pourcentages en poids de chrome et de molybdène sont équilibrés de sorte qu'avec 24% de chrome, 7% de molybdène soient présents et, lorsque le pourcentage en poids de chrome est réduit à partir de 23%, le pourcentage maximal en poids de molybdène soit accru à partir de 8%, le rapport de la réduction du pourcentage en poids de chrome à l'accroissement du pourcentage maximal en poids de molybdène étant égal à environ 2.
- 10 16. Alliage suivant la revendication 15, caractérisé en ce qu'il contient 3,0 à 4,5% de niobium, 0,50 à 2,0% de titane, les pourcentages en poids de titane et de niobium étant équilibrés de sorte qu'avec 4,5% de niobium, il n'existe pas plus de 0,50% de titane, et, lorsque le pourcentage maximal en poids de niobium est réduit de 4,5% à 3,0%, le pourcentage maximal en poids de titane soit accru à 2,0%.
- 15 17. Alliage suivant la revendication 15, caractérisé en ce qu'il contient 3,0 à 4,25% de niobium, 0,50 à 1,75% de titane, les pourcentages en poids de niobium et de titane étant équilibrés de sorte qu'avec 4,25% de niobium, il existe un maximum de 0,50% de titane, et, lorsque le pourcentage en poids de niobium est réduit de 4,25% à 3,0%, le pourcentage maximal de titane soit accru en proportion de 0,50% à 1,75%.
- 20 18. Alliage suivant la revendication 1, caractérisé en ce que les pourcentages en poids de chrome et de molybdène sont équilibrés de sorte qu'avec 16,0% de chrome, 7,5% de molybdène soient présents, et, lorsque le pourcentage de chrome augmente de 16,0% à 19,0%, la quantité minimale de molybdène diminue en proportion à 7,0%.
- 25 19. Alliage suivant la revendication 1, caractérisé en ce que les pourcentages en poids de chrome et de molybdène sont équilibrés de sorte qu'avec 16% de chrome, il existe un minimum de 8,5% de molybdène, et, lorsque le pourcentage en poids de chrome augmente de 16,0% à 21,5%, la quantité minimale de molybdène diminue de 8,5% à 7%, et contenant une quantité totale de niobium, de titane et d'aluminium non supérieure à 4,5% atomiques.
- 30 20. Alliage suivant la revendication 1 ou 2, caractérisé en ce que le niobium et le titane sont équilibrés de sorte qu'avec 3,9% de niobium, un minimum de 0,50% de titane soit présent, et, lorsque le pourcentage en poids de niobium est réduit de 3,9% en poids à 3,0% en poids, la quantité minimale de titane soit accrue en proportion de 0,50% en poids à 1,1% en poids, lorsque la quantité de niobium est réduite de 3,0% en poids à 2,75% en poids, la quantité minimale de titane soit accrue en proportion de 1,1% en poids à 1,6% en poids.
- 35 21. Alliage suivant la revendication 1, caractérisé en ce que le niobium et le titane sont équilibrés de sorte qu'avec 4,5% en poids de niobium, un minimum de 0,50% en poids de titane soit présent, et, lorsque la quantité de niobium présente est réduite de 4,5% en poids à 3,5% en poids, la quantité minimale de titane présente soit accrue en proportion de 0,50% en poids à 1,5% en poids.
- 40 22. Alliage suivant la revendication 2, caractérisé en ce que le niobium et le titane sont équilibrés de sorte qu'avec environ 4,25% en poids de niobium, un minimum de 0,75% en poids de titane soit présent, et, lorsque la quantité de niobium présente est réduite de 4,25% en poids à environ 3,5% en poids, la quantité minimale de titane présente soit accrue en proportion de 0,75% en poids à environ 1,5% en poids.
- 45 23. Utilisation d'alliage suivant l'une quelconque des revendications précédentes pour la production d'un article durci par vieillissement, résistant à la corrosion.
- 50 24. Utilisation suivant la revendication 23, caractérisée par la présence, après traitement en solution et vieillissement, d'une limite minimale d'élasticité à 0,2% au moins égale à 827,4 MN/m<sup>2</sup> (120 ksi).
- 55 25. Procédé de production d'un alliage à base de nickel contenant, en pourcentage en poids

		<u>% en poids</u>
	<b>Carbone</b>	<b>0,1 Max.</b>
	<b>Manganèse</b>	<b>5 Max.</b>
5	<b>Silicium</b>	<b>1 Max.</b>
	<b>Phosphore</b>	<b>0,03 Max.</b>
	<b>Soufre</b>	<b>0,03 Max.</b>
	<b>Chrome</b>	<b>16-24</b>
	<b>Molybdène</b>	<b>7-12</b>
10	<b>Tungstène</b>	<b>4 Max.</b>
	<b>Niobium</b>	<b>2-6</b>
	<b>Titane</b>	<b>0,50-2,5</b>
	<b>Aluminium</b>	<b>Traces-1</b>
	<b>Bore</b>	<b>0,02 Max.</b>
15	<b>Zirconium</b>	<b>0,50 Max.</b>
	<b>Cobalt</b>	<b>5 Max.</b>
	<b>Cuivre</b>	<b>0-3</b>
	<b>Azote</b>	<b>0,04 Max.</b>
20	<b>Fer</b>	<b>20 Max.</b>

le reste étant constitué des impuretés accidentelles et d'au moins 57% de nickel, caractérisé en ce qu'il consiste à ajuster la somme du pourcentage de chrome et du pourcentage de molybdène de sorte que la somme des pourcentages en poids de ces éléments soit non supérieure à 31, et à ajuster la somme du pourcentage en poids de niobium, du pourcentage en poids de titane et du pourcentage en poids d'aluminium de sorte que la somme des pourcentages atomiques totaux des éléments niobium, titane et aluminium soit de 3,5% atomiques à 5% atomiques, lors d'un calcul sur la base de la somme 0,64(% en poids de Nb) + 1,24 (% en poids de Ti) + 2,20 (% en poids de Al).

26. Procédé suivant la revendication 25, caractérisé en ce qu'il consiste à soumettre à un durcissement par vieillissement l'alliage à base de nickel pour obtenir un article ayant une limite d'élasticité à 0,2% supérieure à 100 ksi (690 MN/m<sup>2</sup>) associée à une résistance à la formation de piqûres et à la corrosion par formation de crevasses, ainsi qu'à la fissuration par corrosion sous contrainte dans des milieux renfermant des chlorures et des sulfures à des températures élevées allant jusqu'à 500 ° F (260 ° C), sans nécessiter un travail à une température inférieure à la température de recristallisation de cet alliage.

27. Procédé suivant la revendication 26, caractérisé en ce qu'il consiste à soumettre à un travail à chaud l'alliage à base de nickel avant de le soumettre à un durcissement par vieillissement.

28. Procédé suivant la revendication 27, caractérisé en ce qu'il consiste à soumettre à un traitement en solution l'alliage à base de nickel après le travail à chaud et avant le durcissement par vieillissement.

29. Procédé suivant l'une quelconque des revendications 26 à 28, caractérisé en ce qu'un traitement de vieillissement en deux étapes est utilisé dans la plage de températures de 1100 ° F à 1450 ° F (590 ° C à 790 ° C).

30. Utilisation d'un alliage à base de nickel apte à un durcissement par vieillissement, suivant la revendication 1 ou 2, pour la production d'articles destinés à des applications concernant des puits de liquides corrosifs.

### Patentansprüche

1. Aushärtbare Chrom und Molybdän enthaltende Legierung auf Nickelbasis, dadurch gekennzeichnet, daß die Legierung, in Gew.-%, aus

			<u>Gew.-%</u>
	Kohlenstoff	maximal	0,1
5	Mangan	maximal	5
	Silicium	maximal	1
	Phosphor	maximal	0,03
	Schwefel	maximal	0,03
10	Chrom		16-24
	Molybdän		7-12
	Wolfram	maximal	4
15	Niob		2-6
	Titan		0,50-2,5
	Aluminium		Spur bis 1
20	Bor	maximal	0,02
	Zirkonium	maximal	0,50
	Kobalt	maximal	5
	Kupfer		0-3
25	Stickstoff	maximal	0,04
	Eisen	maximal	20

30 besteht, wobei der Rest aus zufälligen Verunreinigungen und mindestens 57% Nickel besteht, die Summe der Prozentsätze von Chrom und Molybdän nicht größer als 31 ist und die Summe der  
 35 Prozentsätze von Niob, Titan und Aluminium so bemessen ist, daß deren gesamter Atom-Gewichtspro-  
 zentsatz 3,5 bis 5 Atom%, berechnet als  $0,64(\text{Gew.-% Nb}) + 1,24(\text{Gew.-% Ti}) + 2,20(\text{Gew.-% Al})$ ,  
 beträgt, und in lösungsbehandelter und ausgehärteter Form eine 0,2% Dehngrenze von mehr als 100  
 40 ksi (690 MN/m<sup>2</sup>), kombiniert mit einer Beständigkeit gegen Lochfraß und Rißkorrosion sowie gegen  
 Spannungskorrosionsriß in einer Chlorid- und Sulfidumgebung bei erhöhten Temperaturen bis zu  
 500 ° F (260 ° C) aufweist, ohne ein Arbeiten unterhalb ihrer Umkristallisationstemperatur zu erfordern.

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 50  
 55  
 2. Legierung gemäß Anspruch 1, dadurch gekennzeichnet, daß sie

			<u>Gew. -%</u>
	Kohlenstoff	maximal	0,03
5	Mangan	maximal	2
	Silicium	maximal	0,5
	Phosphor	maximal	0,015
	Schwefel	maximal	0,010
10	Chrom		18-22
	Molybdän		7,5-11
	Niob		2,75-4,25
15	Titan		0,75-1,5
	Aluminium		0,05-0,35
	Bor	maximal	0,001-0,006
20	Zirkonium	maximal	0,08
	Kupfer	maximal	0,5
	Stickstoff	maximal	0,01
25	Eisen		2-14

und mindestens 59 % Nickel enthält.

- 30 **3.** Legierung gemäß Anspruch 1, dadurch gekennzeichnet, daß sie maximal 0,06% Kohlenstoff, maximal 2% Mangan und maximal 0,5% Silicium enthält.
- 4.** Legierung gemäß Anspruch 3, dadurch gekennzeichnet, daß sie maximal 0,5% Mangan und maximal 0,2% Silicium sowie maximal 14% Eisen enthält.
- 35 **5.** Legierung gemäß Anspruch 4, dadurch gekennzeichnet, daß sie mindestens 60% Nickel enthält.
- 6.** Legierung gemäß Anspruch 4, dadurch gekennzeichnet, daß sie maximal 0,03% Kohlenstoff und maximal 0,2% Mangan enthält.
- 40 **7.** Legierung gemäß Anspruch 6, dadurch gekennzeichnet, daß sie maximal 0,01% Kohlenstoff und maximal 0,01% Stickstoff enthält.
- 8.** Legierung gemäß irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß sie nicht mehr als 11% Molybdän enthält, wobei die Gewichtsprozensätze von Chrom und Molybdän so ausgeglichen sind, daß mit 16,0% Chrom 7,5-11,0% Molybdän vorliegen, und wenn Chrom von 16,0% auf 19,0% erhöht wird, sich die Molybdänmindestmenge auf 7,0 % verringert.
- 45 **9.** Legierung gemäß Anspruch 8, dadurch gekennzeichnet, daß sie maximal 0,35% Aluminium enthält.
- 50 **10.** Legierung gemäß irgendeinem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß sie nicht mehr als 10% Molybdän enthält, in der die Gewichtsprozensätze von Chrom und Molybdän so ausgeglichen sind, daß mit 16% Chrom 8,5-10% Molybdän vorliegen, wenn der Gewichtsprozensatz von Chrom von 16,0% auf 20,5% erhöht wird, der Mindestgewichtsprozensatz von Molybdän entsprechend auf 7,0% verringert wird, wenn der Gewichtsprozensatz von Chrom von 20,5% auf 24% erhöht wird, der Mindestgewichtsprozensatz von Molybdän 7% bleibt und die Summe der Gewichtsprozensätze von Chrom und Molybdän nicht größer als 31 ist.
- 55

11. Legierung gemäß Anspruch 10, dadurch gekennzeichnet, daß sie mindestens 0,9% Titan enthält.
12. Legierung gemäß Anspruch 4, dadurch gekennzeichnet, daß sie mindestens 17,0% Chrom enthält und daß in ihr  $\%Cr + 4(\% Mo) \geq 52\%$  ist.
- 5 13. Legierung gemäß Anspruch 11, dadurch gekennzeichnet, daß sie maximal 0,35% Aluminium enthält.
14. Legierung gemäß Anspruch 10, dadurch gekennzeichnet, daß sie mindestens 2,75% Niob und mindestens 1,1% Titan enthält.
- 10 15. Legierung gemäß irgendeinem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß die Gewichtsprozentsätze von Chrom und Molybdän so ausgeglichen sind, daß mit 24% Chlor 7% Molybdän vorliegen, wenn der Gewichtsprozentsatz von Chrom von 23% verringert wird, der maximale Gewichtsprozentsatz von Molybdän von 8% erhöht wird, wobei das Verhältnis der Verringerung des Gewichtsprozentsatzes von Chrom zur Erhöhung des maximalen Gewichtsprozentsatzes von Molybdän etwa gleich 2 ist.
- 15 16. Legierung gemäß Anspruch 15, dadurch gekennzeichnet, daß sie 3,0-4,5% Niob und 0,50-2,0% Titan enthält, wobei die Gewichtsprozentsätze von Titan und Niob so ausgeglichen sind, daß mit 4,5% Niob nicht mehr als 0,50% Titan vorliegen, und wenn der maximale Gewichtsprozentsatz von Niob von 4,5% auf 3,0% verringert wird, der maximale Gewichtsprozentsatz von Titan auf 2,0% erhöht wird.
- 20 17. Legierung gemäß Anspruch 15, dadurch gekennzeichnet, daß sie 3,0-4,25% Niob und 0,50-1,75% Titan enthält, wobei die Gewichtsprozentsätze von Niob und Titan so ausgeglichen sind, daß mit 4,25% Niob maximal 0,50% Titan vorliegen, und wenn der Gewichtsprozentsatz von Niob von 4,25% auf 3,0% verringert wird, das Maximum an Titan entsprechend von 0,50% auf 1,75% erhöht wird.
- 25 18. Legierung gemäß Anspruch 1, dadurch gekennzeichnet, daß die Gewichtsprozentsätze von Chrom und Molybdän so ausgeglichen sind, daß mit 16,0% Chrom 7,5% Molybdän vorliegen, und wenn sich Chrom von 16,0% auf 19,0% erhöht, sich die Mindestmenge an Molybdän entsprechend auf 7,0% verringert.
- 30 19. Legierung gemäß Anspruch 1, dadurch gekennzeichnet, daß die Gewichtsprozentsätze von Chrom und Molybdän so ausgeglichen sind, daß mit 16,0% Chrom mindestens 8,5% Molybdän vorliegen, wenn sich der Gewichtsprozentsatz von Chrom von 16,0% auf 21,5% erhöht, sich die Mindestmenge an Molybdän von 8,5% auf 7% verringert, und sie nicht mehr als 4,5 Atom-% Niob plus Titan und Aluminium enthält.
- 35 20. Legierung gemäß Anspruch 1 oder 2, dadurch gekennzeichnet, daß Niob und Titan so ausgeglichen sind, daß mit 3,9% Niob mindestens 0,50% Titan vorliegen, wenn sich der Gewichtsprozentsatz von Niob von 3,9 Gew.-% auf 3,0 Gew.-% verringert, die Mindestmenge an Titan entsprechend von 0,50 Gew.-% auf 1,1 Gew.-% erhöht wird, und wenn die Niobmenge von 3,0 Gew.-% auf 2,75 Gew.-% verringert wird, die Mindestmenge an Titan entsprechend von 1,1 Gew.-% auf 1,6 Gew.-% erhöht wird.
- 40 21. Legierung gemäß Anspruch 1, dadurch gekennzeichnet, daß Niob und Titan so ausgeglichen sind, daß mit 4,5 Gew.-% Niob mindestens 0,50 Gew.-% Titan vorliegen, und wenn die vorliegende Niobmenge von 4,5 Gew.-% auf 3,5 Gew.-% verringert wird, die vorliegende Titanmindestmenge entsprechend von 0,50 Gew.-% auf 1,5 Gew.-% erhöht wird.
- 45 22. Legierung gemäß Anspruch 2, dadurch gekennzeichnet, daß Niob und Titan so ausgeglichen sind, daß mit 4,25 Gew.-% Niob mindestens 0,75 Gew.-% Titan vorliegen, und wenn die vorliegende Niobmenge von 4,25 Gew.-% auf 3,5 Gew.-% verringert wird, die vorliegende Titanmindestmenge entsprechend von 0,75 Gew.-% auf 1,5 Gew.-% erhöht wird.
- 50 23. Die Verwendung der Legierung gemäß irgendeinem der vorhergehenden Ansprüche zur Herstellung eines ausgehärteten, korrosionsbeständigen Gegenstandes.
- 55 24. Die Verwendung gemäß Anspruch 23, dadurch gekennzeichnet, daß der Gegenstand in lösungsbehandelter Form und in ausgehärtetem Zustand eine 0,2% Mindestdehngrenze von mindestens 120 ksi

(827,4 MN/m<sup>2</sup>) aufweist.

25. Verfahren zur Herstellung einer Legierung auf Nickelbasis, die in Gew.-%

5			<u>Gew.-%</u>
	Kohlensstoff	maximal	0,1
	Mangen	maximal	5
10	Silicium	maximal	1
	Phosphor	maximal	0,03
	Schwefel	maximal	0,03
15	Chrom		16-24
	Molybdän		7-12
	Wolfram	maximal	4
	Niob		2-6
20	Titan		0,50-2,5
	Aluminium		Spur bis 1
	Bor	maximal	0,02
25	Zirkonium	maximal	0,05
	Kobalt	maximal	5
	Kupfer		0-3
30	Stickstoff	maximal	0,04
	Eisen	maximal	20

enthält, wobei der Rest aus zufälligen Verunreinigungen und mindestens 57 % Nickel besteht, dadurch gekennzeichnet, daß die Summe der Prozentsätze von Chrom und Molybdän so eingestellt wird, daß deren kombinierter Gewichtsprozentsatz nicht größer als 31 ist, und daß die Summe aus dem Gewichtsprozentsatz von Niob, plus dem Gewichtsprozentsatz von Titan und plus dem Gewichtsprozentsatz von Aluminium so eingestellt wird, daß der kombinierte Atom-Gesamtprozentsatz der Elemente Niob, Titan und Aluminium 3,5 Atom-% bis 5 Atom-%, berechnet als  $0,64(\text{Gew.-% Nb}) + 1,24(\text{Gew.-% Ti}) + 2,20(\text{Gew.-% Al})$ , beträgt.

26. Verfahren gemäß Anspruch 25, dadurch gekennzeichnet, daß die Legierung auf Nickelbasis ausgehärtet wird, um einen Gegenstand mit einer 0,2% Dehngrenze von mehr als 100 ksi (690 MN/m<sup>2</sup>), kombiniert mit Beständigkeit gegen Lochfraß und Ribkorrosion sowie Spannungskorrosionsriß in einer Chlorid- und Sulfidumgebung bei erhöhten Temperaturen bis zu 500 °F (260 °C) zu ergeben, ohne ein Arbeiten unterhalb deren Umkristallisationstemperatur zu erfordern.

27. Verfahren gemäß Anspruch 26, dadurch gekennzeichnet, daß die Legierung auf Nickelbasis vor ihrer Aushärtung heiß bearbeitet wird.

28. Verfahren gemäß Anspruch 27, dadurch gekennzeichnet, daß die Legierung auf Nickelbasis nach der Heißbearbeitung und vor der Aushärtung lösungsbehandelt wird.

29. Verfahren gemäß irgendeinem der Ansprüche 26 bis 28, dadurch gekennzeichnet, daß eine zweistufige Aushärtungsbehandlung im Temperaturbereich von 1100 bis 1450 °F (590-790 °C) angewendet wird.

30. Die Verwendung der aushärtbaren Legierung auf Nickelbasis gemäß Anspruch 1 oder 2 zur Herstellung von Gegenständen zur Verwendung in sauren Bohrlöchern.