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NICKEL BASED ALLOY IN THE QUATERNARY Ni-Fe-Cr-Mo SYSTEM HARDENED BY PRECIPITATION OF THE GAMMA PRIME PHASE AND WITHSTANDING MODES OF CORROSION TO BE FOUND, IN PARTICULAR, IN THE OIL INDUSTRY

The invention relates to improving the composition of a nickel based alloy that is hardened by precipitation of the gamma prime phase and that withstands corrosion, and also to forming said alloy by thermomechanical transformation and heat treatment.

The invention applies typically to making components for the oil industry when the surrounding medium is rendered highly aggressive by the presence of chemical species such as H_2S, CO_2, and S^{--}, H^+, and Cl^- ions, and by very high operating temperatures and pressures.

Thus, components manufactured in the alloy mentioned above must simultaneously present characteristics of great mechanical strength and of high resistance to corrosion, in particular to the forms of corrosion that take place under stress, possibly with the help of mechanisms of degradation by protonic hydrogen.

The most highly aggressive environments encountered during oil exploration and production contain a high percentage of the above-mentioned chemical species, together with some of their compounds, and they are particularly active against conventional metals whose strengths fall off with increasing operating temperature and pressure.

In such environments, risks of severe damage or even of catastrophic failure arise as a consequence of the very rapid development of electrochemical phenomena that may be listed as follows:

localized corrosion by pitting and cracking;

intergranular and/or transgranular type corrosion under stress;

intergranular corrosion; and

degradation induced by protonic hydrogen (brittleness, premature breakage, ...).

The effects of corrosion inhibitors, and in particular organic inhibitors are severely limited at high temperatures, and they become ineffective above 120°C to 150°C.

Strong steels cannot be used under such conditions and they must be replaced with stainless materials that withstand the various kinds of corrosion mentioned.

Possible candidates include austenitic stainless steels for which characteristics of mechanical strength are obtained by work hardening at ambient temperature or at medium hot temperature, sometimes to the detriment of ductility; such steels having a moderate nickel content may present a degree of susceptibility to corrosion under stress in chloride-containing environments.

High mechanical strength "duplex" (austeno-ferritic) steels can be used safely in environments containing H_2S and CINa at relatively high concentrations, so long as the temperature is close to ambient; in contrast, once the temperature rises, e.g. up to 80°C or above, that type of steel is subject to corrosion under stress in a sulfur-containing environment, even at low concentrations of chloride ions.

A quaternary Ni-Fe-Cr-Mo nickel based alloy composition has now been found having high mechanical characteristics under difficult conditions and capable of withstanding environments that give rise to corrosion under stress, and that is more particularly adapted to oil environments that are rich in chlorides, and carbon dioxide, and that are saturated in hydrogen sulfide, and which may also contain ions of protonic hydrogen.

More precisely, this alloy composition presents excellent properties with respect to:

withstanding corrosion under stress;

withstanding localized corrosion and corrosion under tension, by stabilization of passive films on the surfaces of components, in oxidizing environments and in reducing environments;

withstanding generalized corrosion in reducing environments;

hardening by precipitation of gamma prime or gamma double prime phases using a suitable sequence of heat treatments;

minimizing the precipitation of carbides that fix the elements of the austenitic solid solution, which elements are essential for participating in the provision of resistance to corrosion or of hardening by precipitation;

minimizing brittleness of the alloy and reduction in its corrosion resistance due to sulfur and to phosphorus;

minimizing segregation during solidification of billets, in particular segregation that would give rise to the formation of non-dispersed phases that are undesirable for the mechanical transformation properties of the alloys; and

minimizing precipitation of embrittling inter-metallic phases during the manufacturing process, in particular the formation of the sigma phase during hardening heat treatments performed at around 600°C to 900°C.

To this end, in a first aspect the present invention provides an alloy composition comprising, expressed in percentages by weight:

42% to 49% nickel;
3.8% to 5% molybdenum;
19.5% to 22.5% chromium;
1.0% to 1.5% copper;
less than 0.020% carbon;
1.5% to 2.5% titanium;
0.5% to 1% aluminum;
less than 0.1% manganese;
less than 0.1% silicon;
less than 0.010% sulfur;
less than 0.020% phosphorus

the remainder being constituted by iron and by impurities.

Although the content by weight of carbon must not exceed 0.020% under any circumstances, it is important to reduce it as much as possible below said value.

Preferably, the composition of the invention comprises, expressed in percentages by weight:

46% to 48% nickel;
3.8% to 4.5% molybdenum;
20% to 22% chromium;
1% to 1.5% copper;
less than 0.020% carbon;
1.7% to 2.2% titanium;
0.5% to 0.8% aluminum;
less than 0.1% manganese;
less than 0.1% silicon;
less than 0.010% sulfur;
less than 0.020% phosphorus

the remainder being constituted by iron and by impurities.

In a variant, the composition of the invention further comprises tungsten and/or niobium in quantities by weight that do not exceed 0.5%.

In a second aspect, the present invention provides a method of transforming an alloy of the above-defined composition prior to use, in which:

in a first variant the alloy is put into solution between 980°C and 1050°C, it is cooled rapidly to ambient temperature, and then hardened by aging between 760°C and 620°C, the latter cooling taking place sufficiently slowly (in about 5 hours); or

in a second variant, the alloy is put into solution at a temperature in the range 980°C to 1050°C, it is cooled in controlled manner down to 760°C, it is optionally maintained at said temperature, it is cooled to 620°C at a rate of cooling that does not exceed 100°C

per hour, it is maintained at 620°C, and then it is cooled to ambient temperature; or

in a third variant, the alloy is put into solution at a temperature in the range 980°C to 1050°C, it is cooled down to ambient temperature, and it is then subjected to one or more aging treatments at temperatures lying in the range 760°C to 620°C.

In the transformation method described above, the alloy is preferably put into solution with the temperature of the alloy being maintained for 2 minutes per mm of alloy thicknesses, it is cooled rapidly with water, oil, or air depending on the size of the component, with the lengths of time it is maintained at the plateaus for aging in stages or in separate cycles with return to ambient temperature between successive cycles lying in the range 2 hours to 24 hours.

The alloy is advantageously formed under a vacuum, and is then remelted by means of a consumable electrode under a vacuum or under slag.

In a third aspect, the present invention provides a component made of an alloy having the composition of claim 1, in particular a component designed to form all or a portion of tubing, of a wellhead, or of some other apparatus for the oil industry.

Finally, the invention also provides the use of the alloy of the composition of claim 1 in environments that provoke degradation mechanisms by corrosion under stress, in particular in the manufacture of components for the oil industry. In this type of use, the present alloy particularly excels by its resistance to corrosion and by maintaining high mechanical properties in spite of spending long periods in corrosive environments.

The invention is now illustrated by the following examples.

EXAMPLE

Three test casts referenced A, B, and C were made having the compositions given in the following table

where they are expressed in terms of percentage by weight:

Cast	A	B	C
C	0.022	0.013	0.005
Si	0.08	0.08	0.08
Mn	0.035	0.035	0.035
S	0.0046	0.0047	0.0035
Ni	41.5	41.4	43.3
Cr	22.1	22.35	19.8
Mo	3.73	2.27	3.93
Al	0.22	0.27	0.67
Cu	1.11	2.85	1.11
Ti	0.70	0.70	2.11
Nb	3.63	3.7	--
Fe	remainder	remainder	remainder

Only the alloy composition of cast C complies with the present invention.

Casts A and B differ essentially in their contents of molybdenum and of copper.

Casts A and C differ in the nature of the added hardening elements (niobium, titanium, aluminum).

Those alloys, formed under a vacuum, were transformed by a thermomechanical method having the following sequence of operations:

homogenization at 1165°C for 8 hours (h);

transformation into bars of section 40 mm by 40 mm at a temperature below 1100°C; and

heat treatment including putting into solution at 980°C, cooling by means of air or water, followed by various aging treatments in the range 760°C to 620°C.

Forged products were characterized according to four main criteria:

1. For corrosion under stress, ring-shaped test pieces (of the C-ring type specified by ASTM G 38) were subjected to constant stress in environments suitable for causing corrosion under stress, of which the best known is an environment containing 44% $MgCl_2$-$6H_2O$ boiling at

154°C (test in accordance with ASTM G 36), or in an environment for testing breakage differed by hydrogen, of which the best known is a solution of NaCl at 50 g/l, buffered to a pH of 3 by acetic acid and saturated with H_2S at ambient temperature (test in accordance with NACE TM 01-77).

The test pieces, stretched to within 2/3 of the elastic limit $Rp_{0.2}$ showed no cracking after 720 hours of testing in either of the environments.

2. To evaluate resistance to corrosion by cracking, the so-called "depassivation pH" test was used in a 2M aqueous solution of NaCl de-aired acidified by adding hydrochloric acid (the depassivation pH or pH_d being determined by using the criterion of the dissolution current density of the sample being equal to 10 $\mu A.cm^{-2}$).

The best result in this test was obtained by cast A ($pH_d \approx 0.3 \pm 0.1$), while casts B and C behave similarly ($pH_d \approx 0.4 \pm 0.1$), which places them very favorably amongst alloys that withstand cracking corrosion, having a pH_d lower than that of the alloy Inconel® 925 and greater than that of Inconel® 625 (see Figure 1).

3. With respect to mechanical characteristics, cast C stood out clearly from the other two (see the table below):

casts A and B were characterized by relative brittleness in the aged state: the breaking energy absorbed by KV test pieces in an impact test under bending (KV impact energy) did not exceed 30 J, regardless of the strength level above 1000 MPa; those two casts had the greatest hardening potential.

In contrast, cast C absorbed a large amount of energy in an impact test under bending, with the quantity of energy decreasing progressively with increasing strength level: it is thus possible to accurately adjust the compromise of elastic limit $Rp_{0.2}$ to breaking energy absorbed in an impact test under bending.

For an elastic limit $Rp_{0.2}$ of 650 MPa, the breaking energy absorbed by a KV test piece on impact under bending was still 70 J. Isothermal aging performed at 620°C, 650°C, 680°C, 720°C, and 760°C has shown that hardening takes place most quickly at 760°C. And at that temperature, the rate of hardening is still sufficiently slow (several hours) for it to be possible to select the level of mechanical strength and to optimize the $Rp_{0.2}$/impact breaking energy compromise for treatment under industrial conditions.

Following the plateau at 760°C, cooling in an oven followed by being maintained isothermally in a range below precipitation of the gamma prime phase (≈ 620°C) made it possible to increase the total amount of precipitation.

In temperature ranges below ambient, the bending energy absorbed by the alloy on impact is relatively insensitive to temperature: in particular it should be observed that there is no ductile/brittle transition.

4. Observation of their microstructures shows that casts A and B are marked by major segregation, particularly of the element niobium, and by structures that are fairly heterogeneous, and difficult to resorb.

In contrast, cast C appears to be completely homogeneous.

TABLE

Mechanical characteristics of test casts, at various thermal states of aging

Cast A			Traction				
Heat treatment	Rm (MPa)	$Rp_{0.2}$ (MPa)	A5d (%)	A4d (%)	Z (%)	KV impact energy (J)	BHN
Min. nec.	≥827	≥621	≥14	≥15	≥20	≥27	
I	1126	769	17.4	18	28	21-22	331
II	1173	852	18.4	19	34	11-12	
III	1093	734	21	21.7	41	19-25	295
IV	1129	792	19.8	20.4	38	23-24	
V	1084	715	21.6	22.3	39	19-19	302
VI	1117	766	20.9	21.6	40	21-29	323

Cast B			Traction				
Heat treatment	Rm (MPa)	$Rp_{0.2}$ (MPa)	A5d (%)	A4d (%)	Z (%)	KV impact energy (J)	BHN
Min. nec.	≥827	≥621	≥14	≥15	≥20	≥27	
I	1115	798	20.4	21	34	20-22	331
II	1175	878	18.4	18.6	38	13-13	
III	1124	803	21	21.7	36	18-18	309
IV	1140	833	21.4	22.1	34	23-23	
V	1079	750	20.2	20.8	37	19-19	298
VI	1140	844	19.8	20.4	35	14-22	321

Cast C			Traction				
Heat treatment	Rm (MPa)	$Rp_{0.2}$ (MPa)	A5d (%)	A4d (%)	Z (%)	KV impact energy (J)	BHN
Min. nec.	≥827	≥621	≥14	≥15	≥20	≥27	
I	1158	673	27.5	28.4	37	67-67	307
II	1144	657	24.4	25.2	38	70-74	
III	1108	571	33	34	47	98-100	
IV	1105	574	29	30	43	110-111	
V	1154	672	26	29.2	39	67-68	307
VI	1116	591	29	30	43	97-99	

Heat treatments

- A = ambient temperature

I 980°C/1½ h/A ⎫
⎬ + 760°C/8 h, at 60°C/h to 620°C/8 h/A
II 1050°C/1 h/A ⎭

III 980°C/1½ h/A ⎫
⎬ + 760°C/3 h/A + 620°C/4 h/A
IV 1050°C/1 h/A ⎭

V 980°C/1½ h/A + 760°C/8 h, at 100°C/h to 620°C/4 h/A

VI 980°C/1½ h/A + 760°C/3 h/A + 650°C/4 h/A

Rm = maximum strength

$Rp_{0.2}$ = conventional 0.2% elastic limit

A5d, A4d = elongation in percentage on bases of 4d and 5d where d = the diameter of the test piece

Z = striction

BHN = Brinell hardness number.

CLAIMS

1/ An alloy composition comprising, in percentage by weight:

42% to 49% nickel;
3.8% to 5% molybdenum;
19.5% to 22.5% chromium;
1.0% to 1.5% copper;
less than 0.020% carbon;
1.5% to 2.5% titanium;
0.5% to 1% aluminum;
less than 0.1% manganese;
less than 0.1% silicon;
less than 0.010% sulfur;
less than 0.020% phosphorus

the remainder being constituted by iron and by impurities.

2/ An alloy composition according to claim 1, comprising, expressed in percentages by weight:

46% to 48% nickel;
3.8% to 4.5% molybdenum;
20% to 22% chromium;
1% to 1.5% copper;
less than 0.020% carbon;
1.7% to 2.2% titanium;
0.5% to 0.8% aluminum;
less than 0.1% manganese;
less than 0.1% silicon;
less than 0.010% sulfur;
less than 0.020% phosphorus

the remainder being constituted by iron and by impurities.

3/ An alloy composition according to claim 1 or claim 2, further comprising tungsten and/or niobium in quantities by weight that do not exceed 0.5%.

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4/ A method of transforming an alloy of the composition according to any one of claims 1 to 3, prior to use, characterized in that the alloy is put into solution at a temperature in range 980°C to 1050°C, it is cooled rapidly to ambient temperature, and is then hardened by aging in the range 760°C to 620°C.

5/ A method of transforming an alloy of the composition according to any one of claims 1 to 3, prior to use, characterized in that the alloy is put into solution at a temperature in range 980°C to 1050°C, it is cooled in controlled manner to 760°C, it is optionally maintained at said temperature, it is cooled to 620°C at a rate of cooling that does not exceed 100°C per hour, it is maintained at 620°C, and it is then cooled to ambient temperature.

6/ A method of transforming an alloy of the composition according to any one of claims 1 to 3, prior to use, characterized in that the alloy is put into solution at a temperature in range 980°C to 1050°C, it is cooled to ambient temperature, and then one or more aging operations are performed at temperatures lying in the range 760°C to 620°C.

7/ A transformation method according to any one of claims 4 to 6, characterized in that the alloy is put into solution with its temperature being maintained for 2 minutes per mm of thickness of the alloy, it is cooled rapidly by means of water, oil, or air, depending on the size of the component, the lengths of time during which the alloy is maintained at plateaus for aging in stages or in separate cycles with return to ambient temperature between successive cycles lying in the range 2 hours to 24 hours.

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8/ A transformation method according to any one of claims 4 to 7, characterized in that it includes a preliminary step of forming the alloy under a vacuum, followed by remelting by means of a consumable electrode under a vacuum or under slag.

9/ A component made of the alloy of the composition of claim 1.

10/ A component according to claim 9, designed to constitute or form a portion of tubing, a wellhead, or other apparatus for the oil industry.

11/ The use of the alloy of the composition of claim 1 in environments that give rise to mechanisms of degradation by corrosion under stress.

12/ A use according to claim 11, in the manufacture of components for the oil industry.

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