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(54) Nickel-chromium-iron-molybdenum alloy

(57) Nickel-chromium-iron-molybdenum alloy, comprising 40 to 48 wt% nickel, 30 to 38 wt% chromium, 4 to 12 wt% molybdenum and iron, wherein the alloy op-

tionally further comprises up to 5 wt% manganese, up to 2 wt% copper and up to 0.6 wt% nitrogen.

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Description

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[0001] The present invention relates to novel nickel-chromium-iron-molybdenum alloys, corresponding products and articles and their uses. The alloys according to the invention allow achieving good mechanical properties combined with a good corrosion resistance in water with high salinity, especially at elevated temperatures. They are thus particularly suited for use in geothermal power plants, e.g. as down-hole-headers.

[0002] Down-hole-headers in geothermal power plants are required to withstand hot geothermal fluids (e.g. above 100°C) containing high concentrations of chloride ions (e.g. above 100 g/l). These conditions are particularly demanding and often lead to pitting and crevice corrosion. Alloys used for these applications are required to have a sufficient corrosion resistance under these conditions.

[0003] Up to now titanium based alloys and nickel based alloys are regularly used for constructing such down-hole-headers. These alloys are generally thought to be the only practical and reliable alternative when it comes to this application. However, the use of these alloys is uneconomical. For example, nickel is one of the most costly constituents in corrosion resistant alloys. A59 is an example of an alloy often used. It contains high amounts not only of nickel, but also of molybdenum, which also strongly contributes to the overall cost of the alloy. Moreover, A59 performs considerably worse under reducing conditions than under oxidizing conditions.

[0004] Austenitic stainless steels, such as 316L, 254SMO or A31 have been proposed as alternatives. Unfortunately these materials are well-known to be prone to crevice corrosion. Even A31, which is the most highly alloyed steel in this group of materials, is not sufficiently resistant to corrosion in some situations. Hence, it is obvious that neither the traditional austenitic steels nor the nickel based alloys are fully satisfactory.

[0005] Corrosion resistant nickel based alloys with lower amounts of nickel than in A59 are proposed in US 5,424,029. However, the alloys disclosed therein still require a relatively high proportion of nickel, rendering them quite costly. In most applications, the costs are a decisive criterion.

[0006] The object of the present invention is to provide alloys combining low material costs and a high corrosion resistance. In particular, the alloys should have a high wet corrosion resistance in water with high salinity, especially at temperatures above 100°C. The alloys should have a good resistance against pitting and crevice corrosion attack. Preferred alloys have a good resistance to reducing conditions (as measured e.g. by ASTM G 28 A) and at the same time to pitting corrosion and chloride ion attack (as measured e.g. by ASTM G 28 B). Advantageous alloys combine a high corrosion resistance with good mechanical properties, e.g. a high strength. Alloys with such properties are particularly suitable for, but not limited to, down-hole-headers in geothermal power plants operating using hot geothermal fluids containing high chloride concentrations.

[0007] This object is solved by a nickel-chromium-iron-molybdenum alloy, comprising 40 to 48 wt% (percent-by-weight) nickel, 30 to 38 wt% chromium, 4 to 12 wt% molybdenum, and iron, wherein the alloy optionally further comprises up to 5 wt% manganese, up to 2 wt% copper and up to 0.6 wt% nitrogen.

[0008] According to a second aspect of the present invention, the object of the invention is solved by a nickel-chromium-iron-molybdenum alloy, consisting of 40 to 48 wt% nickel (Ni), 30 to 38 wt% chromium (Cr), 4 to 12 wt% molybdenum (Mo), optionally manganese (Mn), optionally copper (Cu), optionally nitrogen (N), optionally tungsten (W), optionally niobium (Nb), optionally cobalt (Co), optionally carbon (C), optionally tantalum (Ta), optionally titanium (Ti), optionally silicon (Si), and balance iron (Fe) plus impurities.

[0009] Surprisingly, it was found that it is possible to achieve a high corrosion resistance in spite of reducing the amounts of molybdenum and nickel, which in practice due to their high price are the two primary constituents that determine the overall final cost of a corrosion resistant alloy. In order to obtain a single phase alloy, the inventors have found that it is possible to increase the chromium content at the expense of the molybdenum and nickel instead of following the conventional way of increasing the iron content. It has been found that it is possible to dissolve very high amounts of chromium in an (austenitic) single phase matrix together with an optimal amount of molybdenum and very low amounts of nickel and iron. The alloys according to the invention have the desired good corrosion resistance and allow for achieving favourable mechanical properties. At the same time the amounts of costly materials may be reduced. This way the alloys according to the invention provide an economically viable and robust alternative for demanding applications such as contact with hot fluids having a high salinity (e.g. above 100°C, above 100 g/l chloride ions).

[0010] The indicated ranges of nickel, chromium and molybdenum allow balancing these three main alloying elements in order to achieve the desired favourable properties. Outside the ranges of 40 to 48 wt% nickel, 30 to 38 wt% chromium and 4 to 12 wt% molybdenum, at least one of the following properties cannot be expected to be favourable: corrosion resistance, structural properties (e.g. number of phases) and mechanical properties. Additionally, higher amounts of nickel and/or molybdenum would render the alloy uneconomical.

[0011] Other elements may be additionally added to the alloy according to the invention. Manganese and nitrogen may be useful for stabilizing a desired austenite phase. Tungsten, niobium, tantalum and titanium may be used for optimizing the mechanical properties. Silicon and manganese may improve melting and casting of the alloy. Copper and nitrogen may further improve the corrosion resistance of the alloy. Carbon may be present either as a side effect or as

a deliberate addition. On the one hand carbon affects the corrosion resistance adversely; on the other hand when added in the right amounts carbon improves the mechanical properties. Accordingly it is possible to fine tune the required properties of the alloy according the invention and thus to either add a certain amount of carbon e.g. to improve mechanical strength or to limit it to the minimum amount possible.

[0012] The alloy according to the invention is suitable for use in water with high salinity (also at high temperatures) and in the geothermal, off-shore, chemical, oil and gas industry.

[0013] A preferred alloy according to the inventions consists of 40 to 48 wt% nickel, 30 to 38 wt% chromium, 4 to 12 wt% molybdenum, up to 5 wt% manganese, up to 2 wt% copper, up to 0.6 wt% nitrogen, up to 5 wt% tungsten up to 3 wt% niobium, up to 2 wt% cobalt, up to 0.2 wt% carbon, up to 1 wt% tantalum, up to 1 wt% titanium, up to 1 wt% silicon, and balance iron plus impurities.

[0014] In the context of the alloy according to the invention the term "impurities" preferably refers to unavoidable impurities, i.e. impurities that result automatically when the alloy is made up of the other components. Preferably the term "impurities" refers to unwanted components. It goes without saying that the term "impurities" does not include any of the following elements: nickel, chromium, molybdenum, manganese, copper, nitrogen, tungsten, niobium, cobalt, carbon, tantalum, titanium, silicon and iron. In a preferred alloy according to the invention, the sum of impurities is at most 0.1 wt%, preferably at most 0.05 wt% and more preferably at most 0.02 wt%. This allows controlling the effect the impurities may have on the properties of the alloy.

[0015] A preferred alloy according to the invention as described above contains at least 2 wt%, preferably at least 4 wt% iron.

[0016] According to the invention, an alloy is preferred that contains one or more of the following: (i) 42 to 48 wt% nickel, (ii) 32 to 38 wt% chromium, (iii) 4 to 11.5 wt% molybdenum, (iv) 0.01 to 5 wt% manganese, (v) 0.1 to 2 wt% copper, (vi) 0.01 to 0.6 wt% nitrogen, (vii) up to 2 wt% tungsten, (viii) up to 1 wt% niobium, (ix) up to 1.8 wt% cobalt, (x) 0.002 to 0.2 wt% carbon, (xi) up to 0.5 wt% tantalum, (xii) up to 0.5 wt% titanium, (xiii) 0.01 to 1 wt% silicon.

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[0017] The alloy according the invention accordingly has at least one, several or all of the features described above with reference to points (i) to (xiii), i.e. the amount of one, several or all of the mentioned components is in corresponding ranges.

[0018] More preferred is an alloy to the invention that contains one or more of the following: (i) 43 to 47 wt% nickel, (ii) 33 to 37 wt% chromium, (iii) 4 to 11 wt% molybdenum, (iv) 0.02 to 2 wt% manganese, (v) 1 to 2 wt% copper, (vi) 0.05 to 0.4 wt% nitrogen, (vii) up to 1 wt% tungsten, (viii) up to 0.2 wt% niobium, (ix) up to 1.5 wt% cobalt, (x) 0.005 to 0.1 l wt% carbon, (xi) up to 0.2 wt% tantalum, (xii) up to 0.2 wt% titanium, (xiii) 0.02 to 0.7 wt% silicon.

[0019] Even more preferred is an alloy according to the invention, wherein the alloy contains one or more of the following: (i) 43 to 46.5 wt% nickel, (ii) 33.5 to 37 wt% chromium, (iii) 4.5 to 10.5 wt% molybdenum, (iv) 0.05 to 0.5 wt% manganese, (v) 1.5 to 1.8 wt% copper, (vi) 0.1 to 0.3 wt% nitrogen, (vii) up to 0.5 wt% tungsten, (viii) up to 0.05 wt% niobium, (ix) up to 1 wt% cobalt, (x) 0.01 to 0.02 wt% carbon, (xi) up to 0.05 wt% tantalum, (xii) up to 0.05 wt% titanium, (xiii) 0.05 to 0.4 wt% silicon.

[0020] Preferably the alloy according to the invention has a PREN value, calculated as wt%Cr + 3.3*wt%Mo + 16*wt%N, of at least 40.

[0021] The PREN (pitting resistance equivalent number) value is a measure for the corrosion resistance of an alloy. Generally, the higher the PREN value, the more resistant the alloy is against corrosion. The PREN value of the alloy according to the invention is preferably at least 50, 55, 60, 65 or even 70.

[0022] Preferably the alloy according to the invention is austenitic. Preferably the alloy consists of a single phase. Alternatively the matrix of the alloy may preferably consist of a single phase harbouring precipitates that have a positive influence on the desired properties of the steel.

[0023] According to the invention, an alloy is preferred that is characterized by one or more of the following features (a) to (d) combined with one or more of the following features (e) to (f):

- (a) an $R_{\rm p0.2}$ proof strength measured according to DIN EN 10 002-1:2001-12 of at least 300 MPa at 25°C,
- (b) an R_{p0.2} proof strength measured according to DIN EN 10 002-1:2001-12 of at least 250 MPa at 150°C,
- (c) an $R_{\rm m}$ ultimate tensile strength measured according to DIN EN 10 002-1:2001-12 of at least 450 MPa at 25°C,
- (d) an R_m ultimate tensile strength measured according to DIN EN 10 002-1:2001-12 of at least 400 MPa at 150°C,
- (e) a material loss measured according to ASTM G 28 A of at most 0.5 mm/year,
- (f) a material loss measured according to ASTM G 28 B of at most 2.5 mm/year.

[0024] The alloy accordingly preferably has one, two, three or all of the features listed under points (a) to (d) above and at the same time either or both of the features listed under (e) and (f). These preferred alloys have a combination of a high strength and a high corrosion resistance.

[0025] However according to another embodiment, preferred alloys according to the invention may simply have one or more of the features (a) to (f) as described above.

[0026] Features (a) to (d) relates to the mechanical properties and specifically to mechanical strength. These values are determined according to standard DIN EN 10 002-1:2001-12. Points (e) to (f) refer to corrosion resistance as measured by ASTM G 28 A (reducing conditions: 50% H₂SO4 + 2.7% Fe₂(SO₄)₃) and ASTM G 28 B (pitting corrosion and resistance against chloride attack: 23% H₂SO₄ + 1.2% HCl +1 % FeCl₃ + 1% CuCl₂). Preferably the R_{p0.2} proof strength is at least 325 or 350 MPa at 25°C and/or at least 275 or 300 MPa at 150°C, in each case measured according to DIN 10 002-1: 2001-12. Preferably the R_m ultimate tensile strength is at least 475 or 500 MPa at 25°C and/or at least 425 or 450 MPa at 150°C, in each case measured according to DIN 10 002-1:2001-12. Preferably the material loss is at most 0.4, 0.3 or 0.2 mm/year (measured according to ASTM G 28 A) and/or at most 2, 1.5 or 1 mm/year (measured according to ASTM G 28 B).

[0027] According to another aspect the present invention relates to a product comprising an alloy according to the invention. Preferred products are selected from the group consisting of powders, granules, sheets, plates, bars, wires, pipes, cast products, wrought products, rolled products, forgings and welding materials (e.g. filler materials).

[0028] The present invention according to another aspect also relates to an article for applications in water with high salinity, comprising an alloy according to the invention. The water preferably has a chloride concentration above 100 g/l. Since the alloys according to the invention may withstand water with high salinity, the articles according to the invention are suitable for such applications. Preferred articles are selected from the group consisting of down-hole-headers, pipelines, tubes, valves, pumps and housings.

[0029] According to another aspect the present invention relates to the use of an alloy according to the invention, a product according to the invention or an article according to the invention for applications in water with high salinity, preferably with a chloride concentration above 100 g/l. The present invention also relates to the use of an alloy according to the invention, a product according to the invention or an article according to the invention for applications in the geothermal, off-shore, chemical, oil and gas industry. Applications at high temperature are preferred.

[0030] The following examples further illustrate the invention.

Examples

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Examples 1 to 15: Experimental alloy castings

[0031] A number of experimental melts were cast using either a vacuum furnace and a ceramic mould (examples 1-4), exposed to air using an induction furnace and a Cu-mould (examples 5-7), in production vertical spun-cast tubes with a diameter of 330 mm, a height of 300 mm and a wall thickness of 70 mm (examples 8-10) and horizontally-spun cast tubes with a diameter of 115 mm and a wall thickness of 12 mm (examples 11-13). Example 1 is a comparative example in which the alloy has a very low molybdenum content.

[0032] Example 14 (alloy A31, comparative example) and example 15 (alloy A59, comparative example) were produced horizontally cast in order to allow comparison. The chemical compositions of the castings are listed in Table I, together with the calculated PREN values.

Table I - Chemical analysis

| | | | | | rable | I - Che | micai an | iaiysis | | | | |
|-----|-------|------|------|------|-------|---------|----------|---------|------|------|---------|---------|
| Ex. | С | Cr | Ni | Мо | Fe | Cu | N | Mn | Si | PREN | Melting | Casting |
| 1 | 0.014 | 34.7 | 44.3 | 0.03 | Bal. | 1.79 | 0.19 | 0.43 | 0.24 | 38 | V | СМ |
| 2 | 0.012 | 35.9 | 44.9 | 4.78 | Bal. | 1.50 | 0.16 | 0.46 | 0.29 | 54 | V | СМ |
| 3 | 0.020 | 35.6 | 43.4 | 7.12 | Bal. | 1.68 | 0.23 | 0.35 | 0.36 | 63 | V | СМ |
| 4 | 0.012 | 35.8 | 46.3 | 9.58 | Bal. | 1.51 | 0.27 | 0.40 | 0.23 | 72 | V | СМ |
| 5 | 0.012 | 34.6 | 44.8 | 5.50 | Bal. | 1.79 | 0.20 | 0.38 | 0.08 | 56 | Α | Cu |
| 6 | 0.020 | 34.8 | 45.0 | 7.43 | Bal. | 1.61 | 0.19 | 0.43 | 0.10 | 62 | Α | Cu |
| 7 | 0.020 | 34.0 | 43.3 | 9.44 | Bal. | 1.70 | 0.22 | 0.47 | 0.11 | 69 | Α | Cu |
| 8 | 0.017 | 34.5 | 44.9 | 5.64 | Bal. | 1.77 | 0.19 | 0.37 | 0.08 | 57 | Α | VC |
| 9 | 0.018 | 34.6 | 45.2 | 7.51 | Bal. | 1.63 | 0.18 | 0.41 | 0.11 | 63 | Α | VC |
| 10 | 0.017 | 33.9 | 43.6 | 9.43 | Bal. | 1.67 | 0.20 | 0.46 | 0.13 | 69 | Α | vc |
| 11 | 0.015 | 33.7 | 46.4 | 4.84 | Bal. | 1.59 | 0.27 | 0.07 | 0.07 | 54 | Α | HC |
| 12 | 0.015 | 33.8 | 46.0 | 7.23 | Bal. | 1.48 | 0.19 | 0.10 | 0.07 | 61 | Α | HC |

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(continued)

| Ex. | С | Cr | Ni | Мо | Fe | Cu | N | Mn | Si | PREN | Melting | Casting |
|-----|-------|------|------|------|------|------|------|------|------|------|---------|---------|
| 13 | 0.010 | 36.7 | 46.0 | 9.59 | Bal. | 1.53 | 0.26 | 0.08 | 0.08 | 72 | Α | HC |
| 14 | 0.020 | 26.4 | 30.1 | 6.6 | Bal. | 1.12 | 0.26 | 0.40 | 0.24 | 52 | Α | HC |
| 15 | 0.010 | 22.5 | Bal. | 15.2 | 1.2 | 0.01 | 0.07 | 0.25 | 0.10 | 76 | Α | HC |

[0033] The chemical compositions are given in wt%. The PREN value is calculated as wt%Cr + 3.3*wt%Mo + 16*wt%N. Melting is indicated as V = Vacuum and A = Air. The casting method is indicated as CM = Ceramic mould, Cu = Cumould, VC = Vertical Centrifugally cast (70 mm wall thickness) and HC = Horizontal Centrifugally cast (12 mm wall thickness). Further abbreviations are Ex. = Example, Bal. = Balance.

Example 16: Mechanical properties

[0034] In Table II the mechanical properties for the alloy castings from Examples 1 to 15 are presented. All alloys according to the invention (alloys of Examples 2 to 13) show very good values. The alloys of Example 4, 7, 10 and 13 show particularly good values, the proof strength is 30-40 MPa above that of A59 (alloy of Example 15) at room temperature. At 150 °C, the alloys of Examples 4 and 7 still have a proof strength well above 300 MPa, and the alloy of Example 10 slightly below. The alloys of Examples 2, 3, 5, 6, 8 and 9 have proof strengths roughly equal to A59. The alloy of Example 1, substantially without Mo, exhibits good, but in comparison to the other castings the poorest mechanical values. The impact toughness values for all alloys according to the invention are well above 200, i.e. excellent. The ductility values are as well high, all well above 14%, which is the common limit for pressure vessels.

[0035] The mechanical properties of the alloy according to the invention are significantly better than those of A31 (Example 14) and with a Mo content in the lower range, comparable to those of A59 (Example 15). With a Mo content in the higher range, the alloy becomes superior to both A31 and A59, especially at elevated temperatures (T>100°C).

Table II - Mechanical properties

| Alloy of Example | Room | Temperatui | re | | 150°C | | Room Temperature |
|------------------|-----------------------|--------------------|------------------|-----------------------|--------|------------------|---------------------------------------|
| | R _{p0.2} MPa | R _m MPa | A ₅ % | R _{p0.2} MPa | Rm MPa | A ₅ % | Impact Toughness J/cm ² |
| 1 | 287 | 523 | 51 | 194 | 444 | 56 | 273 |
| 2 | 325 | 547 | 61 | 271 | 487 | 62 | 344 |
| 3 | 338 | 559 | 46 | 297 | 518 | 60 | 250 |
| 4 | 372 | 497 | 37 | 318 | 444 | 52 | 352 |
| 5 | 347 | 592 | 64 | 298 | 526 | 53 | 273 |
| 6 | 338 | 584 | 61 | 272 | 519 | 59 | 264 |
| 7 | 379 | 577 | 40 | 319 | 502 | 44 | 259 |
| 8 | 314 | 580 | 59 | 272 | 513 | 59 | 445 |
| 9 | 335 | 578 | 55 | 290 | 439 | 49 | 256 |
| 10 | 368 | 595 | 64 | 293 | 463 | 50 | 256 |
| 11 | 345 | 588 | 60 | 267 | 511 | 62 | 317 |
| 12 | 349 | 611 | 64 | 273 | 516 | 64 | 303 |
| 13 | 399 | 630 | 64 | 307 | 532 | 61 | 338 |
| 14 | 317 | 614 | 66 | 243 | 516 | 64 | 324 |
| 15 | 326 | 655 | 74 | 272 | 581 | 71 | 359 |
| 14* | ≥ 276 | ≥ 650 | ≥ 40 | - | - | - | ≥ 185 |

(continued)

| Alloy of Example | Room | Temperatu | ·e | | 150°C | | Room Temperature |
|------------------|-----------------------|--------------------|------------------|-----------------------|--------|------------------|---------------------------------------|
| | R _{p0.2} MPa | R _m MPa | A ₅ % | R _{p0.2} MPa | Rm MPa | A ₅ % | Impact Toughness J/cm ² |
| 15* | ≥ 340 | ≥ 690 | ≥ 40 | - | - | - | ≥ 225 |

^{* =} Literature values, rolled sheet material.

 $R_{p0.2}$ = Proof strength

R_m = Ultimate tensile strength

A₅ = Ductility

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--- = not available

Example 17: Corrosion resistance properties

[0036] In Table III the results from the corrosion tests on the alloys according to the invention of Examples 2 to 4 and 8 to 10 according to ASTM G 28 A (reducing conditions), ASTM G 28 B (pitting corrosion and resistance against Clattack) and ASTM A 262 C (oxidizing conditions) are shown. The alloys A31 (Example 14), A59 (Example 15) and the alloy of Example 1, none of which according to the invention, were also tested for comparison.

[0037] The theoretical values for the Critical Pitting Temperature (CPT) and Critical Crevice Temperature are also included as well as the calculated PREN value. The results show that A59 can withstand pitting corrosion and Cl⁻ induced attack (G 28 B) very well, while it performs significantly worse when exposed to reducing conditions (G 28 A). For A31 it is the other way around, and the material loss in the presence of Cl⁻ ions reaches several mm per year. All investigated alloys according to the invention show that these alloy compositions, regardless of their exact Mo content, have excellent corrosion resistance when it comes to both reducing and oxidizing acids. Mo has an effect on the resistance against Cl⁻ induced general corrosion and pitting corrosion. The alloy of Example 1 (comparative example) substantially without Mo suffers from severe material loss as well as from pitting corrosion. As soon Mo in the range according to the invention is added, the corrosion rate is retarded by about a hundredfold. Additional Mo reduces the rate even further and with 9-10 %wt Mo, values close to A59 are reached, but without losing the excellent properties of the alloys according to the invention in reducing acid. In the end the alloy according to the invention allow combining the favourable properties of A31 (corrosion resistance under reducing conditions) and A59 (resistance against pitting corrosion and Cl⁻ induced attack) without suffering from their unfavourable properties.

[0038] The theoretical values have been added in order to allow for a qualitative comparison between the castings and A31 and A59. The CPT and CCT values listed are the calculated starting values for the CPT and CCT test according to the ASTM G 48 standard, which standard however only allows testing up to 85 °C.

[0039] The alloys according to the invention have several benefits compared to the two commercial alloys used as benchmark, A31 (Example 14) and A59 (Example 15). They have a good corrosion resistance against both reducing and oxidizing acids and Cl-induced pitting corrosion. Alloy 31 (A31) can resist reducing conditions but has rather poor pitting resistance, while Alloy 59 (A59) has good pitting corrosion resistance but cannot compete with A31 or the alloys according to the invention in reducing solutions.

Table III - Corrosion resistance

| Alloy of Example | | Experimental | | Theoretical | | | |
|------------------|----------------|----------------|-----------------|-------------|---------|------|--|
| | G 28 A mm/year | G 28 B mm/year | A 262 C mm/year | *CPT °C | *CCT °C | PREN | |
| 1 | 0.11 | 364 | 0.08 | 52 | 32 | 38 | |
| 2 | 0.10 | 2.51 | | 90 | 72 | 54 | |
| 3 | 0.20 | 1.95 | 0.14 | 109 | 89 | 63 | |
| 4 | 0.20 | 0.36 | 0.18 | 130 | 109 | 72 | |
| 5 | | | | 94 | 70 | 56 | |
| 6 | | | | 108 | 89 | 62 | |
| 7 | | | | 123 | 102 | 69 | |
| 8 | 0.16 | 4.2 | 0.04 | 94 | 74 | 57 | |

(continued)

| Alloy of Example | | Experimental | | - | Theoretical | |
|------------------|----------------|----------------|-----------------|---------|-------------|------|
| | G 28 A mm/year | G 28 B mm/year | A 262 C mm/year | *CPT °C | *CCT °C | PREN |
| 9 | 0.23 | 1.2 | 0.05 | 108 | 89 | 63 |
| 10 | 0.15 | 0.08 | 0.07 | 125 | 105 | 69 |
| 11 | | | | 89 | 66 | 54 |
| 12 | | | | 105 | 84 | 61 |
| 13 | | | | 132 | 112 | 72 |
| 14 | 0.15 | 2.8 | | 82 | 57 | 52 |
| 15 | 1.25 | 0.25 | | 138 | 114 | 76 |

G 28 A: 50% $H_2SO4 + 2.7\% Fe_2(SO_4)_3$

G 28 B: 23% H₂SO₄ + 1.2% HCl +1 % FeCl₃ + 1% CuCl₂

A 262: 65% HNO₃

CPT = Critical Pitting Temperature, CCT = Critical Crevice Temperature

* = Values calculated according to ASTM G48 PREN = wt%Cr + 3.3*wt%Mo + 16*wt%N

--- = not available

Claims

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1. Nickel-chromium-iron-molybdenum alloy, comprising

40 to 48 wt% nickel,
30 to 38 wt% chromium,
4 to 12 wt% molybdenum,
and iron,

wherein the alloy optionally further comprises up to 5 wt% manganese, up to 2 wt% copper and up to 0.6 wt% nitrogen.

2. Nickel-chromium-iron-molybdenum alloy, consisting of

| | 40 to 48 wt% | nickel, |
|----|--------------|-----------------------|
| 40 | 30 to 38 wt% | chromium, |
| | 4 to 12 wt% | molybdenum, |
| | optionally | manganese, |
| | optionally | copper, |
| 45 | optionally | nitrogen, |
| | optionally | tungsten, |
| | optionally | niobium, |
| | optionally | cobalt, |
| | optionally | carbon, |
| 50 | optionally | tantalum, |
| | optionally | titanium, |
| | optionally | silicon, and |
| | balance | iron plus impurities. |

3. Alloy according to claim 2, consisting of

| | | 40 t | o 48 wt% | nickel, | |
|-----|----|---|---------------|-----------|---|
| | | 30 t | o 38 wt% | chrom | ium, |
| 5 | | 4 to | 12 wt% | molyb | denum, |
| | | up t | o 5 wt% | manga | anese, |
| | | up t | o 2 wt% | coppe | r, |
| | | up t | o 0.6 wt% | nitroge | en, |
| 10 | | up t | o 5 wt% | tungst | en, |
| ,,, | | up t | o 3 wt% | niobiu | m, |
| | | up t | o 2 wt% | cobalt | , |
| | | up t | o 0.2 wt% | carbor | ٦, |
| | | up t | o 1 wt% | tantalu | ım, |
| 15 | | up t | o 1 wt% | titaniu | m, |
| | | up t | o 1 wt% | silicon | , and |
| | | bala | ance | iron pl | us impurities. |
| | | | | | |
| 20 | 4. | Alloy according to claim 2 or claim 3, whe | rein the sum | n of imp | urities is at most 0.1 wt%, preferably at most 0.05 wt%. |
| | | | | | |
| | 5. | Alloy according to any of the preceding cla | ims, whereir | n the all | by contains at least 2 wt%, preferably at least 4 wt% iron. |
| | _ | AU | | | |
| | 6. | Alloy according to any of the preceding of | claims, wher | ein the | alloy contains one or more of the following: |
| 25 | | | | | |
| | | (i) | 42 to 48 w | t% | nickel, |
| | | (ii) | 32 to 38 w | | chromium, |
| | | (iii) | 4 to 11.5 w | | molybdenum, |
| 30 | | (iv) | 0.01 to 5 w | ∕t% | manganese, |
| | | (v) | 0.1 to 2 wt | % | copper, |
| | | (vi) | 0.01 to 0.6 | wt% | nitrogen, |
| | | (vii) | up to 2 wt% | % | tungsten, |
| 25 | | (viii) | up to 1 wt% | % | niobium, |
| 35 | | (ix) | up to 1.8 w | /t% | cobalt, |
| | | (x) | 0.002 to 0.2 | 2 wt% | carbon, |
| | | (xi) | up to 0.5 w | ∕t% | tantalum, |
| | | (xii) | up to 0.5 w | ∕t% | titanium, |
| 40 | | (xiii) | 0.01 to 1 w | ∕t% | silicon. |
| | | | | | |
| | 7. | Alloy according to claim 6, wherein the a | lloy contains | s one o | r more of the following: |
| | | | | | - |
| 45 | | | | | |
| | | (i) | 43 to 47 w | | nickel, |
| | | (ii) | 33 to 37 w | | chromium, |
| | | (iii) | 4 to 11 wt9 | | molybdenum, |
| | | (iv) | 0.02 to 2 w | | manganese, |
| 50 | | (v) | 1 to 2 wt% | | copper, |
| | | (vi) | 0.05 to 0.4 | | nitrogen, |
| | | (vii) | up to 1 wt9 | | tungsten, |
| | | (viii) | up to 0.2 w | | niobium, |
| 55 | | (ix) | up to 1.5 w | | cobalt, |
| | | (x) | 0.005 to 0. | | carbon, |
| | | (xi) | up to 0.2 w | /t% | tantalum, |
| | | | | | |

titanium,

up to 0.2 wt%

(xii)

(continued)

0.02 to 0.7 wt% (xiii) silicon.

5 8. Alloy according to claim 7, wherein the alloy contains one or more of the following:

| | (i) | 43 to 46.5 wt% | nickel, |
|----|--------|------------------|-------------|
| | (ii) | 33.5 to 37 wt% | chromium, |
| 10 | (iii) | 4.5 to 10.5 wt% | molybdenum, |
| | (iv) | 0.05 to 0.5 wt% | manganese, |
| | (v) | 1.5 to 1.8 wt% | copper, |
| | (vi) | 0.1 to 0.3 wt% | nitrogen, |
| 15 | (vii) | up to 0.5 wt% | tungsten, |
| 10 | (viii) | up to 0.05 wt% | niobium, |
| | (ix) | up to 1 wt% | cobalt, |
| | (x) | 0.01 to 0.02 wt% | carbon, |
| | (xi) | up to 0.05 wt% | tantalum, |
| 20 | (xii) | up to 0.05 wt% | titanium, |
| | (xiii) | 0.05 to 0.4 wt% | silicon. |
| | | | |

- 9. Alloy according to any of the preceding claims, wherein the alloy has a PREN value, calculated as wt%Cr+3.3*wt%Mo + 16*wt%N, of at least 40. 25
 - 10. Alloy according to any of the preceding claims, wherein the alloy is austenitic.
- 11. Alloy according to any of the preceding claims, wherein the alloy is characterized by one or more of (a) to (d) combined with one or more of (e) to (f): 30
 - (a) an R_{p0.2} proof strength measured according to DIN EN 10 002-1-2001-12 of at least 300 MPa at 25°C,
 - (b) an R_{p0.2} proof strength measured according to DIN EN 10 002-1:2001-12 of at least 250 MPa at 150°C,
 - (c) an R_m ultimate tensile strength measured according to DIN EN 10 002-1:2001-12 of at least 450 MPa at 25°C,
 - (d) an R_m ultimate tensile strength measured according to DIN EN 10 002-1:2001-12 of at least 400 MPa at 150°C,
 - (e) a material loss measured according to ASTM G 28 A of at most 0.5 mm/year,
 - (f) a material loss measured according to ASTM G 28 B of at most 2.5 mm/year.
- 12. Product comprising an alloy according to any of the preceding claims, wherein the product is selected from the group consisting of powders, granules, sheets, plates, bars, wires, pipes, cast products, wrought products, rolled 40 products, forgings and welding materials.
 - 13. Article for applications in water with high salinity, comprising an alloy according to any of the preceding claims.
- 14. Article according to claim 13, wherein the article is selected from the group consisting of down-hole-headers, pipe-45 lines, tubes, valves, pumps and housings.
 - 15. Use of an alloy according to any of claims 1 to 11, a product according to claim 12 or an article according to any of claims 13 to 14 for applications in water with high salinity.

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