(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 3 663 422 A1**

(12) # EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:
10.06.2020 Bulletin 2020/24

(21) Application number: **17919968.2**

(22) Date of filing: **29.12.2017**

(51) Int Cl.:
C22C 19/05 *(2006.01)*

(86) International application number:
PCT/RU2017/001014

(87) International publication number:
WO 2019/027347 (07.02.2019 Gazette 2019/06)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
MA MD TN

(30) Priority: **01.08.2017 RU 2017127607**

(71) Applicants:
- **Stock Company "Chepetsky Mechanical Plant"(SC CMP)**
  Glazov, Udmurtskaya Respublika 427622 (RU)
- **Joint Stock Company "Science and Innovations"**
  Moscow 119180 (RU)
- **Shipulin, Sergey Aleksandrovich**
  Udmurtskaya Respublika 427628 (RU)

(72) Inventors:
- **ASEEV, Mikhail Anatol'evich**
  Moscow 123481 (RU)
- **BELIKOV, Sergei Vladimirovich**
  Ekaterinburg 620026 (RU)
- **DEDOV, Kirill Vladimirovich**
  Glazov
  Udmurtskaya Respublika 427628 (RU)
- **KRITSKIY, Aleksandr Aleksandrovich**
  Glazov
  Udmurtskaya Respublika 427628 (RU)
- **MITYUKOV, Rashid Amirovich**
  Glazov
  Udmurtskaya Respublika 427620 (RU)
- **PANTYUKHIN, Aleksandr Pavlovich**
  Reutov
  Moskovskaya obl. 143964 (RU)
- **POLOVOV, Il'ya Borisovich**
  Ekaterinburg 620102 (RU)
- **SKIBA, Konstantin Vladimirovich**
  Glazov
  Udmurtskaya Respublika 427621 (RU)
- **KHARIN, Petr Alekseevich**
  Moscow 117452 (RU)
- **CHINEIKIN, Sergey Vladimirovich**
  Glazov
  Udmurtskaya Respublika 427620 (RU)
- **SHEVAKIN, Aleksandr Fedorovich**
  Moscow 127642 (RU)

(74) Representative: **Friese Goeden Patentanwälte PartGmbB**
Widenmayerstraße 49
80538 München (DE)

(54) **CORROSION-RESISTANT ALLOY**

(57) The invention relates to metallurgy and more particularly to nickel-based alloys intended for use in aggressive oxidising environments. The present nickel-based corrosion-resistant alloy contains: ≤ 0.006 wt.% carbon, ≤ 0.1 wt.% silicon, ≤ 1.0 wt.% manganese, 22.8-24.0 wt.% chromium, ≤ 0.75 wt.% iron, 12.0-14.0 wt.% molybdenum, 0.01-0.03 wt.% niobium, 0.01-0.06 wt.% titanium, 0.1-0.2 wt.% aluminium, 0.005-0.01 wt.% magnesium, ≤ 0.015 wt.% phosphorus and < 0.012 wt.% sulphur, with the remainder being nickel and unavoidable impurities.

EP 3 663 422 A1

Description

[0001] The invention relates to metallurgic engineering, to nickel-based alloys intended for use in aggressive oxidizing environments.

[0002] A corrosion-resistant alloy Nicrofer 6616 hMo alloy C-4 (No. 2.4610), containing wt.%: 14.5-17.5 Cr, 14.0-17.0 Mo, ≤3.0 Fe, ≤0.009 C, ≤1.0 Mn, ≤0.05 Si, ≤2.0 Co, ≤0.7 Ti, ≤0.020 P, ≤0.010 S, nickel and other unavoidable impurities is known from the prior art (Catalogue "Corrosion-resistant, heat-resistant and high-strength steels and alloys", M., Prometey-Splav, 2008, pp. 304 - 306).

[0003] The alloy is used for the manufacture of equipment operated in a wide range of chemical environments, at room and elevated temperatures. In particular, for adsorbers in flue gas desul-phuring; etching baths and acid recovery plants; acetic acid and agrochemicals plants.

[0004] The nearest analogue of the given invention is an alloy XH65MBУ(ЭП760) containing, wt.%: ≤0.02 C, ≤0.1 Si, ≤1.0 Mn, 14.5-16.5 Cr, 15.0-17.0 Mo, 3.0-4.5 W, ≤0.5 Fe, ≤0.012 S, ≤0.015 P, nickel and other unavoidable impurities (GOST 5632-2014 - prototype).

[0005] The alloy is used for the manufacture of welded structures (columns, heat exchangers, reactors) operating under elevated temperatures in aggressive redox environments, in the chemical, petrochemical industry (production of acetic acid, epoxy resins, vinyl acetate, melamine, complex organic compounds) and other industries in the temperature range -70 to 500°C.

[0006] The XH65MB alloy and its welded joints can be used in KCl - AlCl3 - ZrCl4 media only up to 500 °C, because at a temperature above this value, the alloy, in addition to intergranular corrosion and corrosion cracking, sharply decreases the percentage elongation from 48% to 7.3-13% at 550°C and up to 2.5% at 625°C and the embrittlement of the metal appears when deformation is applied.

[0007] The objective of the invention is to create an alloy having a high level of corrosion properties at temperatures up to T = 650°C in the working media of chloride plants (KCl - AlCl3 - ZrCl4).

[0008] The technical result of the invention is to obtain an alloy with a high level of plastic properties for the operation in the temperature range 550°C to 625°C and increased corrosion cracking resistance in chlorides KCl, AlCl3 + (ZrCl4 HfCl4) molten metal, at temperatures up to 650°C.

[0009] The specified technical result is achieved in that the alloy containing carbon, silicon, manganese, chromium, molybdenum, phosphorus, sulphur, iron, nickel and unavoidable impurities, according to the invention additionally contains titanium, aluminium, niobium, magnesium with the following components ratio, wt.% :

Carbon	≤0.006
Silicon	≤0.1
Manganese	≤1.0
Chromium	22.8-24.0
Iron	≤0.75
Molybdenum	12.0-14.0
Niobium	0.01-0.03
Titanium	0.01-0.06
Aluminium	0.1-0.2
Magnesium	0.005-0.01
Phosphorus	≤0.015
Sulphur	≤0.012
Nickel and unavoidable impurities	balance

[0010] To obtain a stable structure and plastic properties, it is preferable that the content of chromium, molybdenum and iron is related by the ratio:

$$\frac{[Cr]+[Ì\ î]}{[Fe]} \geq 46,4 \qquad (1)$$

(the ratio of the total weight percentage of chromium and molybdenum to the percentage of iron is not less than 46.4)

[0011] To obtain a stable structure and high corrosion properties, it is preferable that the content of niobium and carbon is related by the ratio:

$$\frac{[Nb]}{[C]} \geq 1,66 \qquad (2)$$

(the ratio of the weight percentage of niobium to the weight percentage of carbon is not less than 1.66).

[0012] It is preferably that the content of chromium, molybdenum, iron, niobium and carbon is related by the ratios:

$$\frac{[Cr]+[\grave{I}\ \hat{\imath}]}{[Fe]} \geq 46,4 \qquad (1)$$

[0013] At

$$\frac{[Nb]}{[C]} \geq 1,66 \qquad (2).$$

[0014] Comparative analysis with the prototype allows making a conclusion that the claimed alloy differs from the known one with a lower carbon content (≤0.006% instead of ≤0.02), molybdenum (12.0-14.0% instead of 15.0-17.0%), increased chromium content (23.0-24.0% instead of 14.5-16.5%), iron (≤0.75% instead of ≤0.5%) does not contain tungsten, as well as with the additional introduction of elements such as niobium in an amount of 0.01-0.03%, titanium in an amount of 0.01-0.06%, aluminium in an amount of 0.1-0.2% and magnesium in an amount of 0.005-0.01%.

[0015] Moreover, in particular cases of the invention, the claimed ratios of elements are observed:

$$\frac{[Cr]+[\grave{I}\ \hat{\imath}]}{[Fe]} \geq 46,4 \;;$$

or

$$\frac{[Nb]}{[C]} \geq 1,66$$

[0016] Or

$$\frac{[Cr]+[\grave{I}\ \hat{\imath}]}{[Fe]} \geq 46,4 \text{ at } \frac{[Nb]}{[C]} \geq 1,66 \,.$$

[0017] The limits of the content of alloying elements in the invention alloy are specified as a result of a study of alloys properties with different composition options.

[0018] Exceeding the carbon content of more than 0.006% leads to a decrease in corrosion resistance in solutions of zirconium and hafnium salts due to an increase in the carbide formation process at high temperatures (the appearance of undesirable carbide phases).

[0019] The chromium content was found to be 22.8 - 24.0% to ensure the required heat resistance in hafnium and zirconium oxides. When chromium is introduced into the alloy in the amount of less than 22.8%, the required heat resistance is not ensured, and exceeding the content above 24.0% impairs the heat resistance of the alloy.

[0020] The introduction of molybdenum into nickel alloys increases the recrystallization temperature of solid solutions, inhibits their softening, increases heat resistance, and leads to an ductility increase during short and long tests.

[0021] The range of molybdenum content of 12.0-14.0% is selected to provide the required mechanical properties for both short-term and long-term loads and high temperatures. With the introduction of less than 12.0% of molybdenum, the mechanical properties are not met. When the content is above 14.0%, there is a decrease in ductility and, accordingly, a decrease in the processability of the alloy during metallurgical processing.

[0022] Niobium in an amount of 0.01-0.03%, binds residual carbon and nitrogen to carbides, nitrides and carbonitrides, prevents the formation of chromium carbides and carbonitrides along the grain boundaries. The addition of niobium in an amount 6 to 10 times higher than the carbon content in the alloy eliminates intergranular corrosion of the alloys and protects the welds from destruction. When the niobium content is less than 0.01%, its interaction with residual carbon is ineffective, and the niobium content above 0.03% is not reasonable for carbide formation.

[0023] Exceeding the silicon content of more than 0.1% negatively affects the processability of the alloy, as well as leads to embrittlement of the alloy due to an increase of silicon silicates content in it.

[0024] Increase of manganese content over 1.0% leads to the appearance of a fusible eutectic, which leads to the destruction of the ingot during pressure processing and reduces the heat resistance of the alloy, as well as leads to a decrease of local corrosion resistance.

[0025] Nickel is stable in HCl even at boiling point. However, in the presence of chlorides, ions of Fe(III) and other oxidizing agents corrosion of nickel and nickelchrome molybdenum alloys is enhanced, the limitation of the iron content of not more than 0.75% is due to this.

[0026] The introduction of titanium in an amount of 0.01-0.06% increases the corrosion resistance in melts of zirconium and hafnium salts, binds residual carbon to carbides and leads to the formation of a sufficient amount of Ni3Ti type intermetallic compound, which, at an operating temperature of 500-700C, positively affects the heat resistance of the alloy. When the titanium content is less than 0.01%, the requirements for corrosion resistance are not met, and the excess of the titanium content above 0.06% leads to a decrease in the processability of the alloy and the formation of undesirable phases due to the reactivity of titanium.

[0027] Aluminium and magnesium in the amount of 0.1-0.2% and 0.005-0.01% are introduced into the alloy to remove residual oxygen, as well as, with regard to aluminium, to form an intermetallic compound of the Ni3Al type, which positively affects the heat resistance of the alloy. When these elements are introduced in amounts less than specified, the necessary removal of residual oxygen is not achieved. If the content of these elements is exceeded, gross non-metallic inclusions are formed.

[0028] When the sulphur content exceeds 0.012% and phosphorus exceeds 0.015%, coarse non-metallic inclusions are formed that adversely affect the ductility of the alloy.

[0029] Under the condition $\frac{[Cr]+[\grave{I}\ \hat{\imath}]}{[Fe]} \geq 46,4$, when the ratio decreases below 46.4, the alloy structure becomes less stable (sigma phase is released), which has a negative effect on plastic characteristics and corrosion resistance.

[0030] In the condition $\frac{[Nb]}{[C]} \geq 1,66$, with a ratio of less than 1.66, a decrease in the corrosion resistance of the alloy occurs.

[0031] The proposed ratio of the elements in the alloy were found experimentally and are optimal, since they allow obtaining the claimed comprehensive technical result. When breaking the ratios of the elements, the properties of the alloy deteriorate, their instability is observed, and the complex effect is not achieved.

[0032] Examples of the invention implementation.

[0033] Alloy ingots were smelted in vacuum induction furnaces. The change in the plastic properties of the studied alloys under the influence of temperatures of 550°C and 625°C after long exposure in the furnace for more than 1000 hours was controlled by bending samples to an angle of 90 degrees or more according to GOST 14019-2003. Industrial corrosion cracking resistance tests of alloys were carried out in molten chlorides KCl, AlCl3 + (ZrCl4 HfCl4)

[0034] Table 1 shows the chemical composition of alloy ingots with various compositional options, as well as the prototype alloy. Table 2 shows the results of determining the plastic properties of the alloys indicated in table 1 by bending at an angle of 90 degrees according to GOST 14019-2003. Table 3 presents the results of industrial corrosion cracking resistance tests of the alloys indicated in Table 1 in molten chlorides KCl, AlCl3 + (ZrCl4 HfCl4), 100 hours, at T = 650°C.

[0035] As can be seen from tables 1, 2, the plastic properties of alloy at 550 and 625C with the claimed composition (alloys 1, 2) are higher than the properties of the prototype alloy, alloy 3, not satisfying the claimed composition, has lower plastic characteristics than alloys 1, 2, which leads to the formation of cracks as a result of bending tests according to GOST 14019-2003.

[0036] As it can be seen from table 3, the corrosion rate of alloys (alloys 1, 2) that satisfy the claimed composition is lower than the corrosion rate of the prototype alloy, visual inspection did not reveal the cracks, unlike the prototype alloy. The corrosion rate of alloy 3, which does not satisfy the claimed composition, exceeds the corrosion rate of alloys 1, 2 (however, lower than the corrosion rate of the prototype alloy), visual inspection revealed a crack in the sample.

Table 1 - Chemical composition of the investigated alloys

Alloy	C	Mn	Si	Mo	Cr	Nb	S	P	Fe	Ti	Al	W	Ni and unavoidable impurities	Ratio (1)	Ratio (2)
Alloy 1	0.0011	0.55	00.7	13.0	23.3	0.03	0.0028	0,01	0.54	≤0.01	0.1	-	balance	67.2	27.27
Alloy 2	0.005 8	0.31	0,10	13.1	22.9	0.02	0.005	0.005	0.75	0.05	0.1	-	balance	48.0	3.45
Alloy 3	0.009	0.65	0.10	12.5	23.6	0.01	0.008	0.009 1	0.84	0.04	0.1	-	balance	42.98	1.11
Alloy acc.to prototype	0.017	0.63	0.08	16.2	15.6	-	0.006	0.009	0.45	-	-	3.7	balance	-	-

Table 2 - Results of determining plastic properties by bending at an angle of 90 degrees according to GOST 14019-2003

Alloy	Exposure temperature, °C			
	550°C		625°C	
	Exposure time, h	Samples bending result	Exposure Time, h	Sample bending result
Alloy acc.to prototype	720	Sample broken	720	Sample broken
	1000	No cracks	1000	Crack
	2065	Crack	2065	Crack
Alloy 1	720	No cracks	720	No cracks
	1000	No cracks	1000	No cracks
	2065	No cracks	2065	No cracks
Alloy 2	720	No cracks	720	No cracks
	1000	No cracks	1000	No cracks
	2065	No cracks	2065	No cracks
Alloy 3	720	No cracks	720	No cracks
	1000	No cracks	1000	Crack
	2065	Crack	2065	Crack

Table 3 - Results of industrial corrosion cracking resistance tests of alloys in chloride melts

KCl, AlCl3 + (ZrCl4 HfCl4), 100 h, at T = 650 C		
Alloy	**Visual inspection Cracks after testing**	**Corrosion rate, mm/ year**
Alloy acc.to prototype	Crack in sample Pit corrosion in a sample up to 0.1-0.2 mm deep	0.50
Alloy 1	No cracks Pit corrosion in metal sample up to 0.1-0.2 mm deep	0.16
Alloy 2	No cracks Pit corrosion in a sample up to 0.1-0.2 mm deep	0.21
Alloy 3	Crack in sample Pit corrosion in a sample up to 0.1-0.2 mm deep	0.45

Claims

1. A corrosion-resistant nickel-based alloy containing carbon, silicon, manganese, chromium, molybdenum, phosphorus, sulphur, iron, nickel and unavoidable impurities, wherein it additionally contains titanium, aluminium, niobium, magnesium with the following components ratio, wt.% :

Carbon	≤0.006
Silicon	≤0.1
Manganese	≤1.0
Chromium	22.8-24.0
Iron	≤0.75
Molybdenum	12.0-14.0
Niobium	0.01-0.03
Titanium	0.01-0.06

(continued)

Aluminium	0.1-0.2
Magnesium	0.005-0.01
Phosphorus	≤0.015
Sulphur	≤0.012
Nickel and unavoidable impurities	balance.

2. The alloy according to claim 1, wherein the content of chromium, molybdenum and iron is related by the ratio:

$$\frac{[Cr]+[\grave{I}\ \hat{\imath}]}{[Fe]} \geq 46,4 .$$

3. The alloy according to claim 1, wherein the content of niobium and carbon is related by the ratio:

$$\frac{[Nb]}{[C]} \geq 1,66 .$$

4. The alloy according to claim 1, wherein the content of chromium, molybdenum and iron is related by the ratio:

$$\frac{[Cr]+[\grave{I}\ \hat{\imath}]}{[Fe]} \geq 46,4$$

and the content of niobium and carbon is related by the ratio:

$$\frac{[Nb]}{[C]} \geq 1,66 .$$

INTERNATIONAL SEARCH REPORT

International application No.
PCT/RU 2017/001014

A. CLASSIFICATION OF SUBJECT MATTER

C22C19/05 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C 19/00, 19/03, 19/05

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

RUPAT, PatSearch, PAJ, Espacenet, ScienceDirect, WIPO, USPTO

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 20030049155 A1 (LEE M. PIKE JR. et al.) 13.03.2003, paragraphs [0002], the claims, Tables 1, 2	1-4
A	US 5855699 A (DAIDO TOKUSHUKO KABUSHIKI KAISHA et al.) 05.01.1999	1-4
A	US 4906437 A1 (VDM NICKEL-TECHNOLOGIE AKTIENGESELLSCHAFT) 06.03.1990	1-4
A	GB 2405643 A (HAYNES INTERNATIONAL INC) 09.03.2005	1-4
A	RU 2440876 C1 (STARCHENKO EVGENII GRIGOREVICH et al.) 27.01.2012	1-4

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 April 2018 (23.04.2018)	07 June 2018 (07.06.2018)
Name and mailing address of the ISA/	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 1998)

REFERENCES CITED IN THE DESCRIPTION

Non-patent literature cited in the description

- **M., PROMETEY-SPLAV.** Corrosion-resistant, heat-resistant and high-strength steels and alloys. *Catalogue,* 2008, 304-306 **[0002]**