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

(11) Publication number: 0 069 452 A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 82302600.0

(22) Date of filing: 21.05.82

(51) Int. Cl.³: C 22 C 19/05
G 21 C 3/06

(30) Priority: 21.05.81 US 266005

(43) Date of publication of application:
12.01.83 Bulletin 83/2

(84) Designated Contracting States:
DE FR GB IT SE

(71) Applicant: HUNTINGTON ALLOYS, INC.
Huntington West Virginia 25720(US)

(72) Inventor: Floreen, Stephen
12 River Road
Suffern NY 10901(US)

(72) Inventor: Nelson, Joseph Lawrence
High Meadow Drive
Warwick NY 10990(US)

(74) Representative: Lockwood, Barbara Ann et al,
Thames House (Fifth Floor) Millbank
London SW1P 4QF(GB)

(54) Articles or parts resistant to stress corrosion cracking.

(57) Articles or parts which are resistant to stress corrosion cracking for use in aqueous environments such as nuclear reactors comprise an age-hardened nickel-based alloy containing 0.05 to 0.2% zirconium. The invention is particularly usefully applied to springs or bolts which require a yield strength (0.2% offset) of at least 689.47 MN/m² at room temperature.

EP 0 069 452 A1

0069452

Articles or parts resistant to stress corrosion cracking

The present invention relates to articles or parts which are resistant to stress corrosion cracking, for use in aqueous environments such as those encountered in nuclear reactors.

It has been found that highly stressed parts employed in nuclear reactor environments, particularly light water reactors, are subject to stress corrosion cracking and this casuses the part to fail catastrophically. A commercial alloy known as INCONEL alloy X-750 having the nominal composition up to .08% carbon, up to 1% manganese, from 5% to 9% iron, up to 0.01% sulphur, up to 0.5% silicon, up to 0.5% copper, from 14% to 17% chromium, from 0.4% to 1.0% aluminium, from 2.25% to 2.75% titanium, from 0.7% to 1.2% niobium (+ tantalum) and 0.01 to 0.04% zirconium, balance nickel (+ cobalt) has been used for highly stressed parts such as springs, bolts and valve stems in nuclear reactors. This age-hardened alloy, disclosed and claimed in US patents No. 2 570 193 and 2 570 194 has a tensile yield strength in excess of 689.47 MN/m^2 but has been subject to failure, attributed to stress corrosion cracking, in deaerated water to pH 10 at temperatures up to 360°C.

The failures encountered in service were quite unexpected and dismaying. It was known that over-aging heat treatments were beneficial in improving resistance to stress corrosion cracking of age-hardenable alloys and it was postulated that compositional changes in the alloy used could also improve stress corrosion cracking but no leads were available which would indicate the direction in which to proceed or the ingredient in the alloy which should be controlled in order to improve resistance to stress corrosion cracking of age-hardenable alloys heat treated to provide a room-temperature yield strength (0.2% offset) of at least 689.47 MN/m². The problem was further complicated in that not only was it desirable to obtain the property of resistance to stress corrosion cracking but in addition the capability of providing a yield strength of design interest was still to be retained. It was known from testing of wedge opening loading (WOL) stress corrosion specimens made of an essentially non-aging nickel-base alloy containing 15.75% chromium, 8.1% iron, 0.014% carbon, 0.29% aluminium, 0.007% titanium, 0.0005% sulphur, 0.15% silicon, 0.21% copper, 0.006% boron, 0.008% phosphorus, 0.006% nitrogen, 0.21% zirconium, subjected to deaerated, deionized water at pH 10 and a temperature of 360°C that cracking was observed at 7 and 16 weeks in two specimens of material which had been annealed (solution treated) one hour at 1120°C and water quenched but that when the same annealed material was then heated ("L" treatment) for 7 hours at 608°C and air cooled that no cracking was observed in the full 36-week course of the test. However this alloy in the annealed condition has a yield strength at room temperature of only about 275.79 MN/m² or less and therefore it was not possible to draw valid comparison between this alloy and the age-hardenable alloy with high yield strength, of 689.47 MN/m² at room temperature, desirable in the stressed parts of nuclear reactors.

The present invention is based on the discovery that a modification of the INCONEL alloy 750X composition by increasing the zirconium content considerably above the level of the normal commercial alloy provides the alloy with excellent resistance to stress corrosion cracking.

According to the present invention an article or part which is subjected in use to conditions which promote failure by a stress corrosion cracking mechanism, such as in nuclear reactor environments, consists of an age hardened alloy containing 0.05 to 0.2% zirconium, up to 0.08% carbon, up to 1% manganese, up to 0.5% silicon, up to 0.5% copper, up to 0.01% sulphur, from 5 to 9% iron, from 14 to 17% chromium, from 0.4 to 1% aluminium, from 2.25 to 2.75% titanium, from 0.7 to 1.2% niobium, and the balance apart from impurities and incidental elements being nickel. Such alloys provide a yield strength (0.2% offset) of at least 689.47 MN/m² at room temperature and have excellent resistance to stress corrosion cracking in testing at 360°C in deaerated, deionized water containing less than 50 parts per billion of oxygen and saturated with hydrogen.

The alloy preferably contains at least .07% zirconium.

In accordance with a further aspect of the invention an alloy is provided consisting .073 to 2% zirconium, up to 0.08% carbon, up to 1% manganese, up to 0.5% silicon, up to 0.5% copper, up to 0.01% sulphur, from 5 to 9% iron, from 14 to 17% chromium, from 0.4 to 1% aluminium, from 2.25 to 2.75% titanium, from 0.7 to 1.2% niobium, and the balance apart from impurities and incidental elements being nickel.

Incidental alloys and impurities may include those typical in age-hardenable nickel-based alloys. For example the niobium will normally include about 0.1% tantalum, and the nickel will normally incorporate about 1% cobalt. Up to about .05% rare earth alloys such as lanthanum and/or cerium may be present. Impurities may include up to .005% boron, up to .039% magnesium, up to about .30% molybdenum and about 0.05% vanadium.

The invention will now be described by reference to the following examples.

It should be noted that all percentages given in this specification and claims are by weight.

Example 1

Sixteen laboratory size heats of an alloy containing nominally 15% chromium, 7.5% iron, 1% niobium, 0.75% aluminium, and 2.7% titanium with the balance essentially nickel were produced and reduced to 1.27 cm thick by 12.7 cm wide hot rolled plate. Certain of the alloys contained about 0.08% zirconium while the others were essentially zirconium-free. 1.27 cm thick WOL specimens were prepared from each heat. The WOL samples were fatigue pre-cracked at room temperature and bolt loaded to various starting stress intensities determined by a crack opening displacement gauge inserted at the outer edge. Two or three WOL samples were tested from each heat. Prior to machining, specimen blanks of the WOL samples were subjected to a heat treatment comprising a solution at 1093°C for 2 hours followed by water quenching and an aging at 704°C for 20 hours. The WOL samples were tested in deaerated pH 10 water at 360°C. The samples were removed from test at four-week intervals and the crack lengths measured on the sides of the samples. These tests and earlier studies showed that visible crack propagation halted after approximately six weeks of testing. The total test time was 12 weeks. Compositions of the heats are given on Table I and the results of the WOL test are given in Table 2. The stress corrosion cracking resistance is measured in terms of the stress intensity at which stress corrosion crack propagation stopped, as measured on the fracture surfaces of samples that were mechanically broken open at room temperature after the stress corrosion test was completed. The higher the K_{ISCC} value the greater is the resistance to stress corrosion cracking. The yield strength values were determined by tensile tests at room temperature.

The results of Table 2 demonstrate that statistically the alloys containing 0.08% zirconium were significantly higher in K_{ISCC} value than were the low zirconium heats.

TABLE I

COMPOSITIONS OF FIRST SERIES OF HEATS

Heat	Cr	Fe	Nb	Cu	Al	Ti	Si	Mn	Zr	Mg	B	S	N	C
1	15.3	7.61	1.00	0.18	0.73	2.70	0.33	0.24	<0.005	0.0005	0.003	0.003	N.A.	0.018
2	15.2	7.66	0.97	0.19	0.73	2.73	0.32	0.26	<0.005	0.0024	0.003	0.003	N.A.	0.068
3	15.2	7.66	0.94	0.18	0.79	2.71	0.34	0.28	<0.005	0.025	0.005	0.003	N.A.	0.020
4	15.1	7.58	0.92	0.20	0.76	2.68	0.32	0.28	<0.005	0.031	0.002	0.003	N.A.	0.068
5	15.4	7.61	0.99	0.20	0.76	2.59	0.32	0.29	0.085	0.0007	0.003	0.003	N.A.	0.020
6	15.3	7.70	0.92	0.19	0.69	2.62	0.32	0.27	0.083	0.0005	0.002	0.003	N.A.	0.064
7	15.2	7.66	0.92	0.21	0.72	2.63	0.32	0.30	0.092	0.025	0.002	0.003	N.A.	0.024
8	15.1	7.61	0.96	0.20	0.70	2.70	0.32	0.29	0.091	0.028	0.001	0.003	N.A.	0.068
9	15.3	7.43	0.98	0.20	0.68	2.78	0.34	0.28	<0.005	0.0006	0.002	0.005	N.A.	0.022
10	15.2	7.61	0.94	0.19	0.66	2.67	0.30	0.28	<0.005	0.0007	0.001	0.007	N.A.	0.070
11	15.3	7.70	0.93	0.20	0.74	2.62	0.32	0.29	<0.005	0.039	0.002	0.008	N.A.	0.023
12	15.2	7.62	0.98	0.19	0.76	2.60	0.30	0.29	<0.005	0.037	0.001	0.008	N.A.	0.071
13	15.4	7.64	0.97	0.19	0.68	2.68	0.30	0.23	0.083	0.0004	0.001	0.007	N.A.	0.018
14	15.3	7.60	0.96	0.20	0.68	2.66	0.29	0.27	0.085	0.0005	0.002	0.009	0.0012	0.064
15	15.1	7.62	0.96	0.18	0.81	2.70	0.31	0.25	0.073	0.034	0.002	0.008	0.0008	0.019
16	15.1	7.70	0.96	0.20	0.78	2.64	0.28	0.26	0.095	0.033	0.001	0.008	0.0014	0.081

TABLE 2

STRESS CORROSION TEST RESULTS OF THE FIRST SERIES OF HEATS

Heat	Zr	K_{ISCC} MN/m² per cm (360°C Water)			Yield Strength (ksi)
1	L	86.6	93.6		772.2
2	L	115.1	122.4		758.4
3	L	106.1	122.2	112.9	799.8
4	L	141.2	139.3		744.6
5	H	161.8	187.6	163.1	772.2
6	H	149.3	133.8		737.7
7	H	149.3	152.3		792.9
8	H	154.7	158.8		772.2
9	L	141.2	143.9		772.2
10	L	127.6	142.8	132.5	772.2
11	L	143.9	151.7		772.2
12	L	146.9	142.5		772.2
13	H	143.9	153.9		786.0
14	H	142.5	167.8	146.6	758.4
15	H	145.5	165.9	141.2	792.9
16	H	147.9	136.0		786.0

L = Low ∾ 0.005%Zr

H = High ∾ 0.08%Zr

Example II

Seven heats having compositions set forth in Table 3 were produced.

Tensile specimens and WOL test specimens were prepared from each of these seven alloys. All samples were solution treated at 1093°C for two hours and water quenched and were then given an aging treatment at either 704°C for 20 hours followed by air cooling (treatment A) or at 760°C for 96 hours followed by air cooling (treatment B). The results of the tensile and WOL testing are given in Table 4. The test conditions for WOL test were the same as those of Example I.

Again the significance of increasing the zirconium content of the alloy is clearly shown in comparing the K_{ISCC} values given in Table 4.

TABLE 3

COMPOSITION OF SERIES TWO HEATS

Heat	Cr	Fe	Nh	Cu	Al	Ti	Si	Mn	Zr	Mg	B	S	C	Other
17	15.3	7.61	0.96	0.20	0.69	2.65	0.29	0.28	0.005	0.0007	0.002	0.003	0.019	0.025P
18	15.5	7.61	0.96	0.20	0.72	2.64	0.29	0.29	0.005	0.0009	0.002	0.003	0.022	0.010N
19	15.1	7.70	0.98	0.20	0.70	2.70	0.30	0.26	0.020	0.0005	0.003	0.003	0.027	--
20	15.3	7.54	0.98	0.20	0.81	2.70	0.26	0.28	0.15	0.0005	0.002	0.002	0.017	--
21	15.5	6.83	0.85	0.20	0.73	2.40	0.25	0.15	0.020	0.0005	0.002	0.002	0.063	--
22	15.6	7.50	0.96	0.20	0.74	2.66	0.27	0.28	0.020	0.0015	0.002	0.003	0.018	0.03La+ 0.02Ce
23	15.3	7.50	0.96	0.20	0.75	2.58	0.28	0.28	0.02	0.0015	0.003	0.003	0.018	0.05La

TABLE 4

PROPERTIES OF SERIES TWO HEATS

Alloy	Heat Treatment	Yield Strength (ksi)	K_{ISCC} MN/m² per cm		
17	A	765.3	136.5,	107.8,	89.6
18	A	758.4	133.8,	127.6	
19	A	758.4	152.6,	129.8	
20	A	792.9	>169.4		
20	B	703.3	>167.2		
21	A	682.6	>138.2,	166.9	
22	A	868.7	63.5,	93.9	
23	A	854.9	114.5,	130.6	

A = 1093°C /2 hr.WQ + 704°C/20 hr. AC

B = 1093°C/2 hr.WQ + 760°C/96 hr. AC

Example III

Plate stock of commercial origin of an Inconel alloy X750 having the composition shown in Table 5 was obtained.

Tensile specimens and WOL test specimens of the type described in Example I were prepared from the commercial alloy material.

The results of the tensile test on the heat treated alloy specimens together with the K_{ISCC} results obtained for the various heat treatments are shown in Table 6. The heat treatment accorded each specimen is also included in Table 6.

The data of Table 6 demonstrate that the heat treatments produced underaged, peaked aged and overage microstructures. The data of Table 6 indicate however that neither underaging nor overaging produces a distinctively combination of strength and cracking resistance. Only the specimens aged for 96 hours at 760°C appear to possess distinctly better properties. The results of the heat treatment experiments indicate that the flexibility accorded through the heat treatment route is far less than that provided by changes in alloy composition. While it is true that a substantial improvement in properties was produced by a 96-hour aging treatment, such a treatment is not considered to be commercially practical.

TABLE 5

CHEMICAL COMPOSITION OF ALLOY 24
(WEIGHT PERCENT, BALANCE Ni)

Cr	Fe	C	Al	Ti	Nb	Cu	Si	Mn	Mg	Zr	B	S	N
15.2	6.8	0.042	0.66	2.37	0.88	0.23	0.28	0.13	0.012	0.005	0.003	<0.001	0.0034

TABLE 6

PROPERTIES OF ALLOY 24 AS A FUNCTION OF HEAT TREATMENT (All samples originally annealed for 2 hours at 1093°C and water quenched)

Aging Heat Treatment(1)	Yield Strength MN/m²	K_{ISCC} MN/m² per cm	
593°C/20 h	510.2	143.9,	130.3
649°C/20h	682.6	114.0,	111.3
704°C/20 h	723.9	114.0,	130.3
760°C/20 h	655.1	119.4,	127.6
816°C/20 h	530.9	97.7,	135.7
760°C/96 h	620.5	157.4,	165.6

Claims

1. An article or part which is subjected in use to conditions which promote failure by a stress corrosion cracking mechanism such as in nuclear reactor enviroments consisting of an age hardened alloy containing 0.05 to 0.2% zirconium, up to 0.08% carbon, up to 1% manganese, up to 0.5% silicon, up to 0.5% copper, up to 0.01% sulphur, from 5 to 9% iron, from 14 to 17% chromium, from 0.4 to 1% aluminium, from 2.25 to 2.75% titanium, from 0.7 to 1.2% niobium, and the balance apart from impurities and incidental elements being nickel.

2. An article or part as claimed in claim 1 in which the zirconium content is 0.07 to 0.15%.

3. An article or part as claimed in claim 1 or 2 which is a bolt or spring and which has a yield strength (0.2% offset) of at least 689.47 MN/m^2 at room temperature.

4. A nickel based alloy for use in conditions which promote failure by a stress corrosion cracking mechanism such as in nuclear reactor enviroments containing 0.073 to 0.2% zirconium, up to 0.08% carbon, up to 1% manganese, up to 0.5% silicon, up to 0.5% copper, up to 0.01% sulphur, from 5 to 9% iron, from 14 to 17% chromium, from 0.4 to 1% aluminium, from 2.25 to 2.75% titanium, from 0.7 to 1.2% niobium, and the balance apart from impurities and incidental elements being nickel.

5. An age-hardenable nickel based alloy as claimed in any one of the preceding claims and substantially as hereinbefore described as alloys 1 to 23 of the Examples.

European Patent Office

EUROPEAN SEARCH REPORT

0069452
Application number

EP 82 30 2600

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl 3)
A,D	US-A-2 570 193 (BIEBER et al.) *Claim 1*	1	C 22 C 19/05 G 21 C 3/06
A,D	US-A-2 570 194 (BIEBER et al.) *Claim 1*	1	
A	METAL PROGRESS, March 1958, pages 82-86; W.J.PENNINGTON: "Improvement in high-temperature alloys by boron and zirconium". *The whole document*	1	
A	AT-A- 231 737 (BIRMINGHAM SMALL ARMS CY.) *Claim 2*	1	TECHNICAL FIELDS SEARCHED (Int. Cl 3)
A	CHEMICAL ABSTRACTS, vol. 75, 1971, page 408, no. 104178d, Columbus Ohio (USA); P.KNUDSEN: "Review of Danish irradiation experiments in the Halden boiling water reactor". & DAN. AT. ENERGY COMM., RISOE REP. 1971, RISO-M-1350, 32 pp. *Abstract*	1	C 22 C 19/05 C 22 C 19/00 G 21 C 3/06

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	25-10-1982	LIPPENS M.H.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document