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3,811,960

PROCESS OF PRODUCING NICKEL CHROMIUM ALLOY PRODUCTS

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6 Claims

ABSTRACT OF THE DISCLOSURE

Wrought corrosion-resistant nickel-chromium alloy products having high strength and ductility at elevated temperatures are produced by hot-working a two-phase nickel-chromium alloy containing, by weight, from 47 to 65% chromium, from 0 to 12% cobalt, from 0.02 to 0.1% carbon, from 0 to 0.01% boron, one or more of titanium, aluminum, molybdenum, tungsten, tantalum and niobium in amounts in the ranges from 1 to 6% titanium, from 0.5 to 5% aluminum, from 1 to 10% molybdenum, from 2 to 10% tungsten, from 2 to 10% tantalum and from 0.5 to 10% niobium, and such that

$$3 \times (\text{percent Ti}) + 3 \times (\text{percent Al}) + 5 \times (\text{percent Mo}) + 2.5 \times (\text{percent W}) + 2.5 \times (\text{percent Ta}) + 5 \times (\text{percent Nb}) - 12 \geq 0$$

with the provisos that

- (i) the sum of the aluminum and titanium contents does not exceed 6%;
- (ii) the sum of the aluminum, titanium, niobium and tantalum contents does not exceed 15%; and
- (iii) the sum of the tungsten and molybdenum contents does not exceed 10%

and one or more of zirconium, cerium, yttrium and hafnium in a total amount exceeding that required to combine with all the nitrogen present and sufficient to form a eutectic with the nickel, but not exceeding 4%, the balance, except for impurities including nitrogen in an amount not exceeding 0.1%, being nickel in an amount of at least 25%, to break down its cast structure and then solution-heating it at a temperature within the range of 50° C. below its solidus temperature for from ½ to 20 hours.

This invention relates to wrought nickel-chromium alloys for use at elevated temperatures in corrosive environments and which have an improved combination of stress-rupture strength, ductility and corrosion resistance.

Nickel-chromium alloys containing from 45 to 75% chromium are known to have good resistance at elevated temperatures, e.g. 600° C. and above, to corrosion by the combustion products of low-grade fuel oil, which products include highly corrosive compounds of sodium and sulphur, and in particular of vanadium. At these high chromium contents the alloys have a two-phase structure on solidification, consisting of the alpha-chromium and gamma-nickel phases. In the cast form they exhibit moderate strength at such temperatures, but suffer from lack of ductility, and they are not readily workable into wrought products.

Various attempts have been made to improve the properties of nickel-chromium alloys.

The workability and ductility of alloys containing from 28 to 75% chromium, with or without up to 49% iron, and including the two-phase alloys with 45% or more chromium, can be improved, as described and claimed in the specification of our Pat. No. 3,627,511, by incorporating in the alloy one of the eutectic-forming elements zir-

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conium, cerium, yttrium and hafnium in excess of the amount required to combine with nitrogen in the alloy as nitride and adequate to form a eutectic with the nickel. These additions enable the cast alloys to be wrought and the resulting wrought products to be further worked. The ductility of the wrought alloys at temperatures below 600° C. can be further increased by annealing in the temperature range of 600 to 800° C. Whether or not this heat-treatment is used, the stress-rupture strength of the alloys at temperatures above 600° C. remains fairly low, and it is desirable to produce wrought alloys having an improved combination of stress-rupture strength, ductility and corrosion resistance at temperatures in excess of 600° C.

In the specification of our Pat. No. 3,519,419 we have described a process in which nickel-chromium alloys which consist essentially of a single gamma solid solution phase containing precipitable alpha-chromium are subjected to a combined mechanical and thermal treatment to produce a micro-duplex gamma-alpha microstructure, which can be strengthened by the precipitation of inter-metallic gamma prime phases containing titanium, aluminum, niobium or tantalum or by the presence of solid-solution strengthening elements such as molybdenum or tungsten. However the need to obtain a single phase structure limits the amount of chromium that can be present or requires the presence of iron, both of which impair the resistance of the alloys to corrosion by vanadium-containing combustion products of impure hydrocarbon fuels.

The well-known nickel-chromium superalloys containing up to about 35% chromium together with one or more precipitation-hardening or solid solution-strengthening elements also have a single-phase austenitic (gamma-phase) matrix. The heat treatments commonly used to strengthen such alloys comprise a solution heating step followed by an aging treatment, the solution heating being performed at the lowest practical temperature in order to avoid loss of creep ductility at elevated temperatures.

Another proposal for improving the properties of cast nickel-chromium alloys was made by Bloom and Grant in U.S. Specification No. 2,809,139. These patentees postulated the existence in nickel-chromium alloys with more than 40 or 45% chromium of a high-temperature chromium phase which they called the beta-phase, stable above an eutectoid temperature of 1180° C. Their proposed method of improving the stress-rupture strength of the cast alloys at a temperature of 816° C. comprised heating the alloys above the eutectoid temperature followed by cooling, with or without subsequent heating below this temperature to develop a fine-grained high temperature structure. Subsequent work has failed to demonstrate the existence of this beta-phase or of the eutectoid temperature in the nickel-chromium alloy phase diagram, and there is no suggestion in this specification that such a heat-treatment would render the alloys workable or improve their high-temperature properties after hot-working to break down the cast structure.

The present invention is based on the discoveries that certain two-phase nickel-chromium base alloys having compositions within a critically-controlled range can be worked to form wrought products after breaking down their cast structure, and that the resulting wrought products can be heat-treated to develop surprisingly improved stress-rupture strengths at 600° C. and above, while retaining excellent ductility, by solution-heating within a narrow temperature range immediately below the solidus temperature.

According to the invention the alloys contain, by weight, from 47 to 65% chromium, from 0 to 12% cobalt, from 0.02 to 0.1% carbon, from 0 to 0.01% boron, one or more of titanium, aluminum, molybdenum, tungsten, tantalum and niobium in amounts in the ranges from 1 to 6% titanium, from 0.5 to 5% aluminum, from 1 to 10%

molybdenum, from 2 to 10% tungsten, from 2 to 10% tantalum and from 0.5 to 10% niobium, and such that

$$3 \times (\text{percent Ti}) + 3 \times (\text{percent Al}) + 5 \times (\text{percent Mo}) + 2.5 \times (\text{percent W}) + 2.5 \times (\text{percent Ta}) + 5 \times (\text{percent Nb}) - 12 \geq 0$$

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and one or more of zirconium, cerium, yttrium and hafnium in a total amount exceeding that required to combine with all the nitrogen present and sufficient to form a eutectic with the nickel, but not exceeding 4%, the balance, except for impurities including nitrogen in an amount not exceeding 0.1%, being nickel in an amount of at least 25%. The alloys are hot-worked, preferably by extrusion, to break down their cast structure, and then subjected to a solution heat-treatment at a temperature within the range of 50° C. below the alloy solidus temperature for from ½ to 20 hours, if desired after further hot- or cold-working to the desired shape. Advantageously they are subsequently subjected to an aging heat-treatment at a temperature in the range 600 to 900° C. for from 4 to 20 hours. This latter aging will in any event occur when the alloys are heated above 600° C. in service, but preferably it is performed as a separate step before they are put into service.

The resulting alloys have an excellent combination of stress-rupture strength and ductility at temperatures of 600° C. and above combined with excellent resistance to the combustion products of impure fuels containing sodium, sulphur and vanadium. This makes them particularly suitable as materials for load-bearing furnace or turbine parts exposed in use to the combustion products of such low-grade fuels.

The chromium content of the alloys must be at least 47% for adequate resistance to the combustion products of low-grade fuel oil containing vanadium, sodium and sulphur as impurities. However, with more than 65% chromium the hot-workability of the alloys becomes inadequate and there is a tendency for the corrosion resistance to decrease. Increasing the chromium content also lowers the room-temperature ductility, and preferably therefore the chromium content does not exceed 53%. The room-temperature ductility is also adversely affected if the nickel content is reduced below 25%.

Cobalt increases the stress-rupture lives of the alloys. However, more than 12% cobalt leads to inadequate corrosion resistance and preferably the cobalt content does not exceed 5%.

At least 0.02% carbon is required so that the alloys possess good stress-rupture properties but more than 0.1% leads to lower room-temperature ductility, tends to reduce corrosion resistance and can lead to difficulties in working, e.g. by forging.

The elements titanium, aluminum, molybdenum, tungsten, tantalum and niobium make an important contribution to the stress-rupture strength of the alloys, and one or more of these elements must be present in individual amounts of at least 1% titanium, 0.5% aluminum, 1% molybdenum, 2% tungsten, 2% tantalum and 0.5% niobium, the total amount being such that the relationship

$$3 \times (\text{percent Ti}) + 3 \times (\text{percent Al}) + 5 \times (\text{percent Mo}) + 2.5 \times (\text{percent W}) + 2.5 \times (\text{percent Ta}) + 5 \times (\text{percent Nb}) - 12 \geq 0$$

is obeyed. However, the presence of individual amounts of these elements exceeding 6% titanium, 5% aluminum, 10% molybdenum, 10% tungsten, 10% tantalum or 10% niobium embrittles the alloys and reduces their workability, so that they tend to crack, for example when

forged. For the same reasons, the total aluminum and titanium content must not exceed 6%, the total content of aluminum, titanium, niobium and tantalum must not exceed 15% and the sum of tungsten and molybdenum must not exceed 10%.

The presence of uncombined nitrogen in the alloys is highly detrimental as it leads to embrittlement of the alloys during service. The elements zirconium, cerium, yttrium and hafnium each have a very strong affinity for nitrogen, and the alloys must contain one or more of these elements in an amount in excess of that required to combine with all of the nitrogen present but not more than 4% in all by weight. The excess amounts of these elements form a eutectic with nickel which serves to impart good workability to the alloys. The preferred eutectic-forming element is zirconium, but cerium, yttrium or hafnium or a combination of any two or more of these four elements may be used up to the total of 4%, although preferably the total amount does not exceed 2%.

The nitrogen content of the alloys must in any event not exceed 0.1%. Nitrogen is commonly introduced into the alloys by the chromium, as commercial chromium usually contains about 0.1% nitrogen, so that nitrogen is invariably present in alloys of this type as an impurity. To achieve a low nitrogen content it is preferable to make the alloys by vacuum-melting, when nitrogen levels of the order of 0.01 to 0.08% can readily be achieved. Preferably, the nitrogen content does not exceed 0.04%.

The amount of eutectic-forming element in excess of the amount combined with nitrogen as nitride and in excess of any amount which may be dissolved in the nickel or chromium phases of the alloy may conveniently be referred to as the effective zirconium (or cerium, yttrium or hafnium). If there is no eutectic-forming element in solution in the nickel or chromium phases, the effective zirconium is that in excess of 6.5 times the nitrogen content, the effective cerium is that in excess of 9 times the nitrogen content, the effective yttrium is that in excess of 6 times the nitrogen content and the effective hafnium is that in excess of 13 times the nitrogen content. The amounts of impurities present other than nitrogen should also be as small as possible. Thus any silicon, iron and manganese present should not exceed 0.5% each.

A particularly satisfactory combination of properties is exhibited by alloys containing from 48 to 53% chromium, not more than 2% cobalt, and one or more of the elements titanium, aluminum, molybdenum, tungsten, tantalum and niobium in the ranges Ti from 2.5 to 4.0%, Al from 3.0 to 4.0%, Mo from 1.0 to 6.0%, W from 2.0 to 8.0%, Ta from 2.0 to 7.5% and Nb from 0.5 to 7.5%, subject to the relationships set out above. The contents of zirconium, cerium and yttrium preferably do not exceed 1.0% each and the hafnium content preferably does not exceed 1.5%.

Most preferably the alloys contain both titanium and aluminum in the ranges 2.5 to 4.0% titanium and 3.0 to 4.0% aluminum, the combination of 3% titanium and 3.5% aluminum being particularly satisfactory.

Provided the composition of the alloys is within the broad range set forth above, they can be hot- or cold-worked after their duplex cast structure, which comprises the gamma nickel and alpha chromium phases, has been broken down by extrusion or forging. Thus they can be rolled to rod or sheet, swaged, upset, drawn to wire or otherwise shaped to the desired wrought form.

To develop their high-temperature strength properties the wrought alloys must be solution-heated at a temperature within 50° C. below the alloy solidus temperature for from 1 to 20 hours. Depending on the precise composition, the solidus temperature is generally in the range from 1150 to 1348° C. This treatment serves to coarsen the grain structure and thus to reduce the area of the grain boundaries. This effect is surprising in a duplex alloy and is not fully understood, since the two phases would be expected to be in substantial equilibrium so

that there would be no driving force available for massive diffusion. It is important to use a solution temperature as close as practicable to the solidus temperature and in any event not more than 50° C. below it, in order to develop the maximum driving force for grain growth.

After solution-heating the alloys may then be subjected to an aging treatment at a temperature in the range from 600 to 900° C. for from 4 to 20 hours. This is particularly advantageous if the alloys contain at least one of the elements titanium, aluminum, niobium and tantalum which form precipitable inter-metallic phases that further contribute to the stress-rupture strength of the alloys, but it also serves to bring the alloy structure into equilibrium by diffusion of nickel and chromium from the saturated alpha and gamma solid solutions. As already explained, aging will take place during the initial heating in service, but preferably it is performed as a separate step.

If the highest stress-rupture strength is required for service at temperatures exceeding 650 or 700° C., the

I were vacuum-melted and cast as 3 kg. ingots which were enclosed in mold steel cans and extruded to 16 mm. diameter bar at 1120° C. to break down their cast structure.

Test pieces machined from the bars were then subjected to one of the following three heat-treatments, of which numbers 2 and 3 were in accordance with the invention while number 1 was not, because the solution heating temperature employed was more than 50° C. below the solidus temperature of the alloys treated.

- (1) 4 hr./1150° C., air-cool+16 hr./700° C., air-cool.
- (2) 18 hr./1220° C., air-cool+4 hr./1150° C., air-cool; +16 hr./700° C., air-cool.
- (3) 18 hr./1250° C., air-cool+4 hr./1150° C., air-cool; +16 hr./700° C., air-cool.

The results of stress-rupture tests on the alloys under various conditions of stress and temperature are set forth in Table II.

TABLE I
Composition (weight percent)

Alloy	Ti	Al	Nb	Mo	W	Ta	Co	Zr	B	C	N	Cr	Ni
1			5					0.3	0.003	0.04	0.015	50	Balance
2					10			0.3	0.003	0.04	0.015	50	Do.
3				5				0.3	0.003	0.04	0.015	50	Do.
4	1.0	0.5		2.5				0.3	0.003	0.04	0.013	50	Do.
5	1.0	0.5				5		0.3	0.003	0.04	0.015	50	Do.
6	1.5	0.75	0.5	2.5				0.3	0.003	0.04	0.011	50	Do.
7	1.5	0.75	0.5		2.5			0.3	0.003	0.04	0.011	50	Do.
8	2.0	1.0		2.5				0.3	0.003	0.04	0.015	50	Do.
9	2.0	1.0			5			0.3	0.003	0.04	0.015	50	Do.
10	2.0	1.0	0.5	2.5				0.3	0.003	0.04	0.015	50	Do.
11	2.0	1.0	0.5		5			0.3	0.003	0.04	0.015	50	Do.
12	3.0	1.5						0.4	0.003	0.04	0.015	50	Do.

NOTE.—The solidus temperature of Alloys 4, 6 and 7 was approximately 1,290° C. while that of the other alloys was approximately 1,260° C.

aging treatment may follow the solution-heating without any intermediate treatment. However to obtain the maximum ductility with a somewhat lower stress-rupture strength the alloy may be given an intermediate heat-treatment comprising heating in the range 1100 to 1150° C. for from ½ to 8 hours before it is aged.

As explained above, the alloys are preferably vacuum-melted. However alloys free from titanium and aluminum may be melted at atmospheric pressure with the use of an inert gas shield and a dry basic slag cover in order to prevent the ingress of nitrogen.

Some examples will now be given.

Twelve alloys having the compositions shown in Table

The results in Table II show the remarkably good combination of stress-rupture strengths with ductility of the alloys heat-treated according to the invention, at temperatures between 600 and 1050° C. Comparison of the test results for Alloy No. 4 at 900° C. shows the 10-fold increase in stress-rupture life resulting from the use of heat treatment No. 3 according to the invention, while the results for Alloys 6 and 7 at 800 and 850° C. at the same stress of 7.7 hbar shows that even at the higher test temperature these alloys, when heat-treated according to the invention, had stress-rupture lives many times greater than those obtained at the lower temperature of 800° C. after solution-heating more than 50° C. below the solidus temperature.

TABLE II.—STRESS-RUPTURE PROPERTIES

Alloy	54 hbar at 600° C. (1)		54 hbar at 600° C. (2)		7.7 hbar at 800° C. (1)		15.4 hbar at 800° C. (2)		10.8 hbar at 850° C. (2)		7.7 hbar at 850° C. (3)	
	Life, hours	Percent elongation	Life, hours	Percent elongation	Life, hours	Percent elongation	Life, hours	Percent elongation	Life, hours	Percent elongation	Life, hours	Percent elongation
1							24	8	25	9		
2							23	34	15	38		
3							44	51	14	53		
4	323	39			74	131					188	42
5							46	19	80	13		
6	178	28			74	115					261	8
7	110	7			34	86					371	13
8							90	36	23	39		
9							75	35	25	41		
10			>1,600	ND					97	23		
11			2,160	8			77	29	97	52		
12			137	7			40	16	49	24		
Alloy	4.6 hbar at 900° C. (1)		6.2 hbar at 900° C. (2)		4.6 hbar at 900° C. (3)		3.1 hbar at 1,000° C. (2)		1.54 hbar at 1,050° C. (1)		1.54 hbar at 1,050° C. (2)	
	Life, hours	Percent elongation	Life, hours	Percent elongation	Life, hours	Percent elongation	Life, hours	Percent elongation	Life, hours	Percent elongation	Life, hours	Percent elongation
1			51	6			24	15			52	22
2			22	39			10	110			13	114
3			27	63			7	87			66	126
4	11	147			111	38						
5			96	20			82	19				
6									2	175		
7					402	42						
8			71	73			69	64			45	80
9			18	84			8	123			15	146
10			26	107			20	84			27	144
11			76	82			39	84			22	105
12			33	25			8	59				

NOTE.—ND=Not determined.

The excellent properties of the alloys according to the invention may be compared with those of two commercially-available wrought nickel-chromium alloys. The first of these, which nominally contained 1% zirconium, 50% chromium, balance nickel, was solution-treated for 2 hours at 1140° C., which was within 30° C. of its solidus temperature of 1170° C. The second alloy, which nominally contained 0.7% titanium, 0.6% aluminum, 0.4% zirconium, balance nickel, was not heat-treated. Each of these alloys had a stress-rupture life of less than 1 hour under a stress of 4.6 hbar at 900° C.

The excellent corrosion-resistance of two typical alloys of the invention, Nos. 13 and 14, are shown by tests in which specimens of these alloys and of the first of the commercially-available alloys mentioned above were half-immersed in a molten salt mixture consisting of 80% vanadium pentoxide and 20% sodium sulphate at 900° C. for 300 hours. The compositions of the alloys and the loss in weight, measured in milligrams per square centimeter, are set forth in Table III below. It will be seen that the alloys of the invention had a corrosion resistance comparable with that of the known alloy.

TABLE III

Alloy	Composition (weight percent)							Weight loss (mg./cm. ²)
	Ti	Al	Zr	B	C	N	Cr Ni	
A			1.0				50 Balance	480
13	3	1.5	0.3	0.003	0.04	0.015	50 do	437
14	4		0.3	0.003	0.04	0.015	50 do	389

The alloys in accordance with the invention may be employed for making articles and parts requiring high strength ductility and corrosion resistance, for example load bearing furnace parts, superheater tubes, straps and supports for heat exchangers, gas-turbine parts, for example turbine blades, rotors and the like, and particularly those which are exposed in use to the combustion products of low-grade hydrocarbon fuels, especially those containing vanadium, sodium and sulphur.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the scope and purview of the invention and appended claims.

We claim:

1. A process of producing a wrought corrosion-resistant nickel-chromium alloy product having high strength and ductility at elevated temperatures which comprises hot-working a two-phase nickel-chromium alloy containing, by weight, from 47 to 65% chromium, from 0 to 12% cobalt, from 0.02 to 0.1% carbon, from 0 to 0.01% boron, one or more of titanium, aluminium, molybdenum, tungsten, tantalum and niobium in amounts in the ranges from 1 to 6% titanium, from 0.5 to 5% aluminum, from 1 to 10% molybdenum, from 2 to 10% tungsten, from 2 to 10% tantalum and from 0.5 to 10% niobium, and such that,

$$3 \times (\text{percent Ti}) + 3 \times (\text{percent Al}) + 5 \times (\text{percent Mo}) + 2.5 \times (\text{percent W}) + 2.5 \times (\text{percent Ta}) + 5 \times (\text{percent Nb}) - 12 \geq 0$$

with the provisos that

(i) the sum of the aluminium and titanium contents does not exceed 6%;

(ii) the sum of the aluminum, titanium, niobium and tantalum contents does not exceed 15%; and
(iii) the sum of the tungsten and molybdenum contents does not exceed 10%

and one or more of zirconium, cerium, yttrium and hafnium in a total amount exceeding that required to combine with all the nitrogen present and sufficient to form a eutectic with the nickel, but not exceeding 4%, the balance, except for impurities including nitrogen in an amount not exceeding 0.1%, being nickel in an amount of at least 25%, to break down its cast structure and then solution-heating it at a temperature within the range of 50° C. below its solidus temperature for from ½ to 20 hours.

2. A process according to claim 1 in which the alloy is subsequently aged in the temperature range from 600 to 900° C. for from 4 to 20 hours.

3. A process according to claim 2 in which the alloy is heated at a temperature in the range from 1100 to 1150° C. for from ½ to 8 hours after the solution heating but before it is aged.

4. A process according to claim 1 applied to an alloy in which the chromium content is from 48 to 53%, the cobalt content does not exceed 2% and which contains one or more of titanium, aluminum, molybdenum, tungsten, tantalum and niobium in the ranges Ti from 2.5 to 4.0%, Al from 3.0 to 4.0%, Mo from 1.0 to 6.0%, W from 2.0 to 8.0%, Ta from 2.0 to 7.5% and Nb from 0.5 to 7.5%.

5. A process according to claim 4 in which the contents of zirconium, cerium and yttrium do not exceed 1% and the hafnium content does not exceed 1.5%.

6. A process according to claim 5 applied to an alloy containing both titanium and aluminum in the ranges 2.5 to 4.0% titanium and 3.0 to 4.0% aluminum.

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WAYLAND W. STALLARD, Primary Examiner

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