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CHROMIUM-NICKEL ALLOYS AND ARTICLES AND PARTS MADE THEREFROM

Philip James Ennis and Philip James Parry, Birmingham,
England, assignors to The International Nickel Com-
pany, Inc., New York, N.Y.

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9 Claims

ABSTRACT OF THE DISCLOSURE

Corrosion-resistant cast articles and parts made from chromium-nickel alloys containing one or more of the elements columbium, titanium and tantalum in carefully controlled amounts to obtain improved room-temperature ductility after prolonged service at high-temperatures and, in some cases, improved strength.

Chromium-nickel alloys containing approximately equal amounts of chromium and nickel are extensively used as furnace parts and similar articles because they are sufficiently strong and resistant to corrosion by fuel ash at elevated temperatures. In the as-cast condition they have moderately good tensile ductility as measured by their elongation to fracture in a tensile test. However on prolonged exposure to elevated temperatures in the range about 700 to about 900° C., the room-temperature ductility rapidly falls to very low values. The alloys indeed commonly become so brittle when, for example, a furnace containing parts made of them is cooled down for repairs that they are readily broken in the course of removal from the furnace. Thus, while the as-cast elongation of castings of 50% chromium-50% nickel alloy may be from about 6 to about 35%, heating at service temperatures (700 to 900° C.) causes it to fall to less than 1%.

Furthermore, the strength of nickel-50% chromium alloys, although adequate for some purposes, generally precludes their high temperature use in load-bearing applications, for example as support bars and support beams in residual fuel-oil burning superheaters, boilers and furnaces even though the high-temperature corrosion resistance of the alloys is most attractive for such uses. Generally speaking alloys of this type exhibit stress-rupture lives of less than about 40 hours at 17 hbars/700° C. and 6.2 hbars/900° C. Hitherto, cast and wrought 25% Cr/12% Ni and 25% Cr/20% Ni steels which have good strength have been used in such applications. However, the relatively limited corrosion resistance of these alloys necessitated their frequent replacement.

It is an object of the present invention to provide cast articles and parts characterised by improved room-temperature ductility after prolonged service at high temperatures.

It is a further object of this invention to provide alloys of the above type which are additionally characterised by a level of strength far in excess of that generally exhibited by alloys of this compositional type.

Other objects and advantages will become apparent from the following description.

Generally speaking, the present invention contemplates cast articles and parts having improved room-temperature ductility after prolonged exposure at elevated temperatures containing from about 40 to about 55% chromium, at least one metal from the group consisting of columbium, titanium and tantalum in an amount such that no appreciable amount of nitrogen remains uncombined and that some of the added element or elements is present uncombined in a total amount of at least about 0.2% but such that 0.5(percent Cb)+percent Ti+0.3(percent Ta) does not exceed about 1, the balance, apart from

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impurities including not more than about 0.3% nitrogen, being nickel.

By the term cast article or part is meant herein a shaped or investment casting suitable for use in the as-cast condition or on heat treatment.

At least about 40% chromium must be present in the alloys to impart excellent corrosion resistance to the alloys. However, amounts in excess of 55% lead to unacceptably low as-cast ductilities.

The present invention is based on the discovery that the presence of free nitrogen in the alloys from which the articles and parts are made causes a loss of room-temperature ductility after prolonged heating. Nitrogen is an impurity which is commonly introduced by the chromium, as commercial chromium usually contains from about 0.01 to about 0.1% nitrogen. In practice it is impossible to eliminate nitrogen from the alloys completely, although by vacuum melting the nitrogen content can be kept very low. In fact, if the alloys are melted under vacuum the nitrogen content will be in the approximate range 0.02 to 0.08%, and if they are melted in air it will be in the approximate range 0.06 to 0.2% as a general rule.

According to the invention we introduce enough of one or more of the nitride-forming elements columbium, titanium and tantalum into the molten alloy to ensure that no appreciable amount of nitrogen remains uncombined within the alloy and that there is at least 0.2% uncombined nitride-forming element in the alloy. It is preferred to add only one nitride-forming element, and then the amount of columbium introduced must be more than seven times the weight of the nitrogen present, the corresponding figures for tantalum and titanium being 13 and 3 respectively.

We have found that the room-temperature ductility after exposure to a temperature in the range of about 700 to about 900° C. for a period of days increases from only 1% elongation or thereabouts when the amount of nitride-forming element added is stoichiometrically equal to the nitrogen content to a maximum when the excess of the added element is about 0.4% in the case of columbium and titanium and about 0.5% in the case of tantalum. As the amount of any excess nitride-forming element increases above these values the room-temperature ductility decreases only slowly, so some excess can be tolerated with very little loss of ductility. However, the amount present uncombined must not be more than about 2% columbium, about 1% titanium or about 3.2% tantalum when only one of these elements is added. Since more than one may be added, the minimum may be expressed by the statement that percent Cb+percent Ti+percent Ta should, for improved ductility, be at least 0.2 and the maximum by the statement that 0.5 (percent Cb)+percent Ti+0.3 percent Ta) must not exceed about 1 (percent Cb) etc. being the percentage of the element that is present in the alloy uncombined.

It is not only too much of the added element that may cause the gain in ductility to be lost again. Too much nitrogen may have the same effect. The reason is that the embrittlement of the alloys in service is caused by precipitation of an alpha-chromium phase in the gamma-nickel matrix in a lamellar form. If the nitrogen is removed by forming a nitride with an added nitride-forming element, the precipitate is modified to a spheroidal form which does not reduce the ductility as severely as the lamellar precipitated. However, too much nitride, even in the spheroidal form, has a detrimental effect on the ductility, both in the as-cast condition and after service. Therefore the nitrogen content of the alloys must not exceed about 0.3%, and preferably does not exceed about 0.2%. Since, as explained above, vacuum-melted alloys

never contain as much as 0.2% nitrogen and air-melted alloys rarely contain more than 0.2%, the need to ensure that the nitrogen content does not exceed 0.3% does not cause much trouble in practice.

In addition the carbon content of the alloys should not exceed 0.1%, particularly so that the carbon does not sequester a major portion of the titanium, columbium or tantalum as the carbide and thus considerably reduce the uncombined level.

Although in making the alloys the nitrogen in the melt may be analysed and then the appropriate amount of nitride-forming element added, it is possible to produce satisfactory alloys without analysing for nitrogen during their production. In vacuum melting it is satisfactory to add from 0.3 to 1.5%, but preferably from 0.5 to 1%, columbium or from 0.8 to 3% tantalum or from 0.3 to 1% titanium. If the alloys are melted under air, the amount of columbium added may be from 0.6 to 2.2%, of tantalum from 1 to 4% and of titanium from 0.4 to 1.5%.

We have further found that the articles and parts are much improved in their room-temperature ductility after heating to 700-900° C. if before being put into service they are heated in the temperature range of about 1000 to 1250° C. for about ¼ to 4 hours.

The compositions and elongations (measured at room temperature on $5.65\sqrt{\text{Area}}$) of some alloys according to the invention and of some comparative alloys are given in Table I below. The alloys according to the invention were made by melting a charge of 50% chromium and 50% nickel in a high-frequency induction furnace either under vacuum or in air. The melts made under vacuum were thoroughly stirred before a nitride-forming element was introduced. In air-melting the charge of chromium and nickel was covered with a basic slag of 3:1 lime: cryolite mixture, and the melt was deoxidised with 0.15% aluminum and 0.03% magnesium, added as a nickel-magnesium alloy, prior to the addition of a nitride-forming element. The comparative alloys were made by similar procedures. In Table I "V" indicates vacuum melting and "A" air-melting. All the melts were cast as clusters of test-bars. These test-bars were used to determine the elongation of each alloy in (1) the as-cast state, (2) after the cast-bars had been heated for 65 hours at 700° C. and (3) after the bars had first been heated for one hour at 1100° C. and then for 65 hours at 700° C.

TABLE I

Alloy number	Composition, wt. percent			Excess nitride former or free nitrogen	Elongation (percent)		
	Cr	N	Addition		As cast	65 h./700° C.	1 h./1,100° C. plus 65 h./700° C.
1 (V)-----	50.1	0.02	0.7 Ti	0.64 Ti	29.3	5.4	9.4
2 (V)-----	48.2	0.04	0.5 Ti	0.38 Ti	33.1	8.4	11.5
3 (V)-----	49.9	0.08	1.0 Ti	0.76 Ti	24.7	2.2	9.2
4 (V)-----	49.7	0.04	0.5 Cb	0.2 Cb	36.0	5.8	21.9
5 (V)-----	50.5	0.02	1.0 Ta	0.74 Ta	21.0	2.5	18.9
6 (A)-----	50.0	0.065	1.0 Cb	0.55 Cb	28.4	n.d.	13.4
7 (A)-----	49.7	0.11	1.0 Cb	0.23 Cb	10.5	4.0	11.2
A (V)-----	50.2	0.04	-----	0.04 N	6.7	0.7	6.1
B (A)-----	50.0	0.13	-----	0.13 N	14.1	1.4	0.5
C (A)-----	50.0	0.4	-----	0.4 N	31.0	0.2	0.9
D (V)-----	50.0	0.04	0.2 Ti	0.08 Ti	32.1	0.4	0.7
E (V)-----	48.2	0.1	2.5 Ti	2.2 Ti	0.3	0.3	nil
F (A)-----	48.8	0.065	3.0 Cb	2.55 Cb	11.2	-----	3.9

NOTE.—n.d.=not determined.

Alloys A, B and C are typical of the prior art. As cast, the two air-melted alloys B and C have good ductility, but lose their nearly completely after heating to service temperature for 65 hours, and are very little affected by the heat treatment before being subjected to service heating. Although the nitrogen appears to have been combined in Alloy D, the amount of excess titanium was inadequate. Alloy E shows the effect of adding too much titanium, and Alloy F that of adding too much columbium. In contrast, the alloys according to the invention all had enough room-temperature ductility after the serv-

ice heating to prevent any likelihood of accidental fracture, and the improved ductility brought about by the heat treatment before the service heating is very clearly apparent.

It may be observed that the effect of an excess of the elements columbium, titanium and tantalum is not produced by another nitride-forming element, namely zirconium, which by forming a eutectic with the nickel when present in excess of the amount required to combine with the nitrogen embrittles the alloy at room temperature.

The invention further contemplates novel high strength chromium-nickel alloys containing from about 40 to about 55% chromium, columbium in an amount such that from about 0.1 to 2% remains uncombined, the balance, except for impurities including not more than about 0.3% nitrogen, being nickel.

The added columbium is preferably from about 1 to about 2% indicating an uncombined columbium level of about 0.2 to 1.3% based on the normally expected nitrogen content of about 0.1 to 0.2%. A particularly preferred alloy contains about 50% chromium and about 1.5% columbium, the balance being nickel and impurities.

In these novel alloys, some ductility can be sacrificed for some applications in the interests of high strength and the level of uncombined columbium may be as low as about 0.1%, but is preferably at least about 0.2%.

Examples of some novel alloys of this aspect of the invention and comparative alloys are given below. The alloys were made by melting individual charges of 50% chromium/50% nickel in air using a basic slag cover of 3:1 lime:cryolite mixture during melting. For the numbered alloys which are according to the invention, portions of the respective individual melts were thoroughly stirred before the various amount of columbium in the form of a Ni-70% Cb alloy were introduced. (Alternatively vacuum melting may be employed, in which case a slag cover is not required.) The melts were deoxidised with 0.15% aluminum and 0.03% magnesium, added as a nickel-magnesium alloy, prior to the addition of columbium. The alloys were cast at 1550° C. into investment moulds as tapered test bars of ½ to ¾ inch graduated diameter, which were then machined to test pieces. Table II shows the chromium, columbium and nitrogen contents of each alloy and the levels of uncombined columbium. The carbon content in each case was less than 0.02% and the balance nickel apart from other impurities.

TABLE II

Alloy number	Cr	N	Added Cb	Excess Cb
70 8-----	49.0	0.12	1.0	0.16
9-----	49.0	0.16	1.5	0.4
10-----	49.4	0.18	2.0	0.8
11-----	49.4	0.19	2.5	1.2
12-----	49.2	0.18	1.5	0.24
13-----	49.3	0.19	2.0	0.69
G-----	48.0	0.14	-----	-----
75 H-----	48.0	0.14	-----	-----

The stress-rupture properties of these alloys were measured under various stresses at different temperatures and the results are given in Table III.

TABLE III

Alloy	17 hbar/700° C.			21.5 hbar/700° C.		6.2 hbar/900° C.			2.7 hbar/1,000° C.	
	Life (hrs.)	Elongation (per cent)	M.C.R. (percent per hr.)	Life (hrs.)	Elongation (per cent)	Life (hrs.)	Elongation (per cent)	M.C.R. (percent per hr.)	Life (hrs.)	Elongation (per cent)
8	1,672	10.3	0.0003	371	7.1	45.5	7.7	0.001	267	5.0
9	1,653	5.5	0.0002			136	14.0	0.0003		
10	1,365	10.5	0.0004			195	23.0	0.0005		
11	947	5.6	0.0007			51	9.0			
12				520		107	5.9			
13				199	4.9	141	6.7			
G	38.6	7.3	0.002	10.5	18.7	32.5	8.6	0.002	31.5	5.5
H				8.8	6.0	14.5	8.4			

NOTE.—M.C.R.—Minimum Creep Rate.

The results of Table III clearly show the greatly improved stress-rupture lives and resistance to creep of the columbium-containing alloys 8 to 13 as compared with the columbium-free alloys G and H.

The novel alloys of this aspect of the invention generally possess excellent corrosion resistance, especially to environments where low grade fuel-oil is burned, together with the retention of adequate ductility after prolonged exposure at about 700 to about 900° C. and stress-rupture lives in excess of about 900 or 1000 hours at 17 hbars/700° C. and, in the case of the preferred alloys, in excess of about 100 hours at 6.2 hbars/900° C. They may thus be advantageously used in making cast articles and parts for use in a wide variety of high load-bearing high temperature applications demanding good corrosion resistance such as support bars and beams in superheaters, boilers and furnaces burning low grade fuel-oil; as furnace tubes in petrochemical plant process heaters; and as furnace grates in diverse plant including iron ore pelletising plant. The alloys of the invention may, of course, also be used for all conventional applications of cast nickel-50% chromium alloys, such as in corrosion-resistant high temperature applications involving relatively low stress-bearing conditions, particularly for furnace parts and similar articles subjected in use to residual fuel-oil ash environments.

Iron is an element sometimes present as an impurity in the chromium-nickel alloys in question. Thus, columbium could possibly be added in the form of ferro-columbium with the result that iron is also introduced, but only in such an amount as still to be regarded as an impurity. Other impurities present in the alloys are those commonly found in alloys of this type and include small amounts of manganese and silicon as well as residual deoxidants e.g. magnesium and aluminum.

A small amount of tantalum is commonly associated with columbium in the forms in which columbium is commercially available and up to one tenth of the columbium content of these is often tantalum. The high strength columbium-containing alloys of the invention may also contain such tantalum introduced into them with the columbium and when tantalum is present it is to be regarded as part of the columbium content. A larger portion of the columbium can also be replaced by tantalum on a weight for weight basis and references herein to the high strength alloys containing columbium are intended to cover such alloys having combined columbium and tantalum contents.

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 under-

stand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. Cast articles and parts made from a chromium-nickel alloy consisting essentially of about 40% to about 55% chromium, at least one metal from the group consisting of columbium, tantalum and titanium in an amount such that no appreciable amount of nitrogen remains uncombined and that some of the added element or elements is present uncombined in a total amount of at least about 0.2% but such that 0.5 (percent Cb)+percent Ti+0.3 (percent Ta) does not exceed about 1, the balance, apart from impurities including nitrogen in an amount not exceeding 0.3%, being nickel.

2. Cast articles and parts according to claim 1, made from a vacuum melted alloy to which one metal selected from the group consisting of about 0.3% to 1.5% columbium, about 0.8% to 3% tantalum and about 0.3% to 1% titanium is added.

3. Cast articles and parts according to claim 2 wherein from about 0.5% to about 1% columbium is added.

4. Cast articles and parts according to claim 1 made from an air-melted alloy containing not more than about 0.2% nitrogen and having added thereto one metal from the group consisting of from about 0.6% to 2.2% columbium, from about 1% to 4% tantalum and from about 0.4% to 1.5% titanium.

5. A high strength chromium-nickel alloy consisting essentially of about 40% to about 55% chromium, columbium in an amount such that from about 0.1% to about 2% remains uncombined, the balance, except for impurities including not more than about 0.3% nitrogen, being nickel.

6. An alloy according to claim 5 containing from about 1% to about 2% added columbium.

7. A high strength alloy consisting essentially of about 50% chromium, about 1.5% columbium, the balance, except for impurities including less than 0.2% nitrogen, being nickel.

8. Cast articles and parts according to claim 1, which have been heated at a temperature of about 1000 to about 1250° C. for about one quarter to four hours to improve the room temperature ductility thereof.

9. An alloy according to claim 5 wherein the amount of uncombined columbium is at least about 0.2%.

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RICHARD O. DEAN, Primary Examiner

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