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ALLOY STABILIZATION

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ABSTRACT OF THE DISCLOSURE

Sensitivity of certain nickel-chromium-base alloys to formation of deleterious sigma phase can be overcome by replacing nickel or iron in such alloys with about 0.5% to about 6% cobalt.

The present invention is concerned with nickel-chromium-base alloys and particularly with nickel-chromium-base alloys devoid of cobalt and particularly adapted to be employed at elevated temperatures under high stress and corrosive conditions.

It is known that alloys containing relatively large amounts of nickel and sufficient chromium to impart oxidation resistance to the alloy can be made to resist high temperatures by adding to the composition elements which cause precipitation of solid particles from the matrix of the alloy and elements which will stiffen the matrix and/or inhibit diffusion therein. Elements such as aluminum and titanium are very often employed to cause precipitant phases and elements such as molybdenum, tungsten, tantalum, columbium and the like are employed to strengthen the matrix. While it is possible to theorize that elements such as aluminum and titanium will react with nickel to form $Ni_3(AlTi)$ (i.e gamma prime phase) as a precipitate and that elements such as molybdenum and tungsten which will remain in the alloy matrix, in actual practice things do not appear to work out so neatly. Gamma prime phase will itself have the ability to dissolve elements other than nickel and aluminum and titanium, the amount and character of such elements being a function not only of the total composition of the alloy but also the function of the thermal conditions under which the alloy exists.

In nickel-base, chromium-containing high temperature alloys certain deleterious phases can form. One of these deleterious phases is known as sigma phase. Sigma phase occurs in the geometric form of plates and often is associated with unreliability of the alloy for extended service under high temperatures at high stress. All other things being equal, an alloy in which formation of sigma phase is inhibited is highly advantageous compared to an alloy in which sigma phase can form more freely.

Various forms of computations known as PHACOMP calculations have been employed to establish what is commonly termed a stability factor. Whatever their form, the computations arrive by one means or another at an assumed matrix composition for particular alloys. The matrix atomic fractions of the elements nickel, cobalt, chromium, tungsten, molybdenum, iron and perhaps others in the matrix are multiplied by various factors. The sum of said multiples is taken and the magnitude of this sum is equated with stability as to sigma formation shown by experience. One such stability equation applicable to iron-free alloys is as follows:

0.66 Ni matrix+1.71 Co matrix+4.66 (Cr+W+Mo) matrix+5.66 (Ta+Cb) matrix=stability factor

Using the foregoing equation, it has been assumed in the past that if the stability factor is less than about 2.50 the alloy will be reasonably stable against the formation of sigma phase.

It is to be noted that in the foregoing equation defining the stability factor, cobalt is treated in an essentially linear manner. In other words, according to the foregoing equation, cobalt contributes uniformly to instability at a rate, so to speak, of about 2.5 times the rate at which nickel contributes. The logical result one would expect from contemplation of the foregoing equation would be that if a marginally stable alloy devoid of cobalt exists, replacement of some nickel by cobalt in the matrix of said alloy would result in tending to convert said marginal instability to complete instability and the ready formation of deleterious sigma phase. It is the essence of the present invention and discovery applicable to nickel-chromium-base alloys which are essentially cobalt-free, that cobalt in small, critical amounts does not act in a linear manner and, contrary to the indication given by the foregoing equation, cobalt can act to inhibit formation of sigma phase.

It is an object of the present invention to provide alloys and objects made therefrom having increased stability against formation of sigma phase.

It is another object of the present invention to provide a process whereby alloys can be stabilized against formation of sigma phase.

A still further object is to provide a process of operating a device under thermal conditions which induce the formation of sigma phase.

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

Generally speaking, it has been discovered that the stability of nickel-chromium-base alloys having PHACOMP numbers (stability factors) in excess of about 2.0, marginally stable to the formation of sigma phase and containing no cobalt can be enhanced by including in the composition thereof an amount of cobalt within the range of about 0.5% to about 6% by weight. In order that those skilled in the art will correctly appreciate the present invention and the alloys to which the present invention pertains, it is to be understood that PHACOMP numbers (otherwise known as N_{V5} or stability factors) employed in this specification and claims are calculated as defined in the report on Air Force Contract No. 33 (615) 5126, Project No. 7351 conducted by TRW, Inc. under Task No. 735,105 for the Air Force Materials Laboratory at Wright Patterson Air Force Base and entitled "The Research on Micro Structural Instability of Nickel Base Alloys." This report is incorporated herein by reference.

In terms of chemistry, alloys to which the present invention pertains include alloys essentially free of cobalt and containing (in weight percent) about 0.02% to about 0.40% carbon, about 8% to about 22% chromium, up to about 9.0% molybdenum, up to about 7% tungsten, up to about 5% columbium, up to about 4% tantalum, up to about 20% iron, up to about 3% titanium, about 0.02% to about 6.5% aluminum, up to about 0.05% boron, up to about 0.2% zirconium with the balance being essentially nickel. Those skilled in the art will appreciate that alloys within the foregoing range of composition can be formulated so as to be stable or unstable with respect to sigma formation. It has been thought in the past that stable alloys will have a PHACOMP number below about 2.50. This is not necessarily true. Additions of cobalt in amounts of 0.5% to about 6% can provide stability against formation of sigma phase even when the alloy has a PHACOMP number as high as 2.67. In the absence of cobalt, at least one alloy having a PHACOMP number of 2.08, discussed at length hereinafter, is susceptible to sigma formation. Inclusion of only 1% of cobalt in this alloy, cures the instability so that when the alloy is tested, sigma phase will not form even when exposed to sigma phase inducing thermal conditions for at least 1500 hours.

The nominal chemical composition (in weight percent) and the PHACOMP number of a few representative commercial alloys to which the present invention is applicable is set forth in Table I.

TABLE I

Alloy	A	B	C	D
Element:				
C	0.12	0.05	0.15	0.04
Cr	12.5	12.0	15.5	18.6
Ni	(1)	(1)	(1)	(1)
Mo	4.2	4.5	5.0	3.1
Cb	2.0	2.0	----	5.0
Fe	----	----	4.5	18.5
Ti	0.8	0.6	2.5	0.9
Al	6.1	5.9	3.5	0.4
B	0.012	0.010	0.050	----
Zr	0.10	0.10	----	----
PHACOMP	2.68	----	2.050	2.295

[1] Balance.

Each of the alloys in Table I is a commercial alloy which is somewhat limited in its utility by virtue of its sensitivity to the formation of sigma phase under certain conditions of long term exposure to high temperatures. It has been found that inclusion of small amounts of cobalt in these alloys in place of equal percentages of nickel or iron will tend to stabilize the alloys against formation of sigma phase while at the same time the mechanical and engineering characteristics are virtually unaffected.

Table II contains the nominal chemical composition (weight in percent) of alloys of the present invention which alloys parallel compositions set forth in Table I.

TABLE II

	1	2	3	4	5	6	7
Element:							
C	0.12	0.12	0.12	0.05	0.15	0.04	0.04
Cr	12.5	12.5	12.5	12.0	15.5	18.6	18.6
Ni	(1)	(1)	(1)	(1)	(1)	(1)	(1)
Co	1	2	5	3	2	3	2
Mo	4.2	4.2	4.2	4.5	5.0	3.1	3.1
Cb	2.0	2.0	2.0	2.0	----	5.0	5.0
Fe	----	----	----	----	2.5	15.5	18.5
Ti	0.8	0.8	0.8	0.6	2.5	0.9	0.9
Al	6.1	6.1	6.1	5.9	3.5	0.4	0.4
B	0.012	0.012	0.012	0.010	0.050	----	----
Zr	0.10	0.10	0.10	0.10	----	----	----

[1] Balance.

The cobalt-containing alloys in Table II are much more resistant to the formation of sigma phase than are the cobalt-free alloys of Table I. In this connection it is to be understood that nominally cobalt-free alloys contain very small amounts of cobalt, for example up to 0.2% cobalt, as an impurity together with other impurities and incidental elements commonly occurring in nickel-chromium-base alloys.

In the work culminating in this specification, alloy samples were tested for mechanical and engineering characteristics with no significant differences being observed between cobalt-free alloys and alloys containing up to about 5% or 6% by weight of cobalt substituted for nickel or iron except for the susceptibility to formation of sigma phase. As to this latter characteristic, determined by holding unstressed specimens at 1500° F. and 1650° F. for times out to 3000 hours, the influence of small amounts,

i.e. 0.5% to about 5% of cobalt is dramatic. In terms of PHACOMP numbers cobalt in this range was effective in enlarging the range of sigma-free composition by up to 0.32 vacancy number (PHACOMP) unit. A cobalt-free alloy having a PHACOMP number of 2.23 exhibited the onset of sigma formation within 250 hours at 1500° F. When cobalt was substituted for nickel in this alloy in amounts of from 1% to 6% to give calculated PHACOMP numbers of 2.23 to 2.32, there was no evidence of sigma phase formation at 1500 hours at 1500° F.

While applicants do not intend to be bound by any theoretical explanation, it is believed that the beneficial and unexpected effects of cobalt discussed herein result from the fact that cobalt, in amounts below about 5% to 6% by weight, acts in a passive referee role as to the formation of sigma phase. It is theorized that in these small amounts, cobalt enters into gamma prime phase in the alloy and raises the solvus temperature thereof. This in effect stabilizes the gamma prime and inhibits the formation of undesirable compounds such as sigma phase and a body centered cubic phase known as "J" or "epsilon" phase. This action is directly in contrast to the action of iron in similar amounts which is known to lower the solvus temperature of gamma prime phase and thus hastens the precipitation of "J" phase and sigma phase.

The present invention is not to be confused with prior practice wherein it is known to include amounts of cobalt upwards of about 6% in nickel-chromium-base alloys. In amounts over about 5% to 6%, cobalt participates actively in the formation of sigma phase and the inhibitory effect of small amounts of cobalt is gradually lost. Such participation of cobalt in the larger amounts to the formation of sigma phase is directly predictable by the known PHACOMP calculations and is not part of the invention described and claimed herein.

Table III shows the composition a series of alloys which are for practical purposes identical except for the presence of various percentages of cobalt. Table III illustrates that even amounts of cobalt as low as 1% which barely change the calculated PHACOMP number are effective to change a sigma-prone alloy to a sigma-resistant alloy.

TABLE III

	PHACOMP Number	Sigma	Percent— Co	Cr	Al+Ti	W	Mo	Cb	Ni
Alloy E	2.23	Yes [1]	0	15	6.4	4.1	2.1	2.2	Balance
Example:									
8	2.24	No [2]	1.0	15	6.2	4.1	2.0	2.0	Do.
9	2.26	No [2]	2.0	15	6.4	4.1	2.0	2.1	Do.
10	2.27	No [2]	4.2	15	6.2	4.0	2.0	2.1	Do.
11	2.32	No [2]	6.1	15	6.3	4.0	2.0	2.1	Do.

[1] Sigma phase appears in less than 250 hours at 1,500° F.
[2] No sigma phase is evident after 3,000 hours at 1,500° F.

It is to be understood that all of the examples of the present invention and of the comparative alloys are made in the manner common to good practice in the metallurgical art, e.g. by vacuum melting and casting where oxidation sensitive elements are present, and are formed into specimens in the customary manner. Especially with regard to the alloys of the present invention comprising Examples 1 to 4 and 8 to 11, samples and objects made therefrom are customarily made by casting using state-of-the-art precision casting techniques. Precision cast objects such as turbine rotors, turbine blades and, in general, structures adapted to be employed in the hot stages of gas turbine engines in accordance with the present invention can be employed under sigma-phase-inducing conditions far longer than similar structures not in accordance with the present invention. For purposes of definition, it is to be considered that sigma-phase-inducing con-

ditions comprise essentially the temperature interval between about 1300° F. and 1750° F. However, it is to be understood that stresses and variations in temperature can modify such conditions substantially.

While the present invention has been described in conjunction with advantageous embodiments, those skilled in the art will recognize that modifications and variations may be resorted to without departing from the spirit and scope of the invention. Such modifications and variations are considered to be within the purview and scope of the invention.

We claim:

1. A process for producing alloys resistant to the formation of sigma-phase under sigma-phase inducing conditions of use comprising modifying the composition of marginally stable, cobalt-free alloys selected from the group consisting of Alloy A, Alloy B, Alloy C and Alloy D the nominal compositions in percent by weight of which are set forth in the following table:

TABLE

	Alloy			
Element	A	B	C	D
C	0.12	0.05	0.15	0.04
Cr	12.5	12.0	15.5	18.6
Ni	(1)	(1)	(1)	(1)
Mo	4.2	4.5	5.0	3.1
Cb	2.0	2.0	----	5.0
Fe	----	----	4.5	18.5
Ti	0.8	0.6	2.5	0.9
Al	6.1	5.9	3.5	0.4
B	0.012	0.010	0.015	----
Zr	0.10	0.10	----	----

[1] Balance.

to include therein, a replacement of an equal percent by weight of metal from the group consisting of nickel, iron and mixtures of nickel and iron, about 0.5% to about 6% by weight of cobalt based on total alloy content whereby the sigma-phase-free life of said alloys in use under sigma-phase inducing conditions is substantially extended.

2. A process as in claim **1** wherein cobalt is included in the alloys in an amount by weight of about 1% to about 5%.

3. A process as in claim **1** wherein about 0.5% to about 6% cobalt replaces an equal percent by weight of nickel in Alloy A.

4. A process as in claim **1** wherein about 0.5% to about 6% cobalt replaces an equal percent by weight of nickel in Alloy B.

5. A process for operating a device for extended periods of time under conditions wherein at least a part of said device is exposed to a thermal environment conducive to the formation of sigma-phase in nickel-chromium alloys marginally stable against the formation of sigma-phase comprising fabricating a component of said device exposed to said thermal environment of a modified alloy from the group consisting of Alloys A, B, C and D, the compositions of which alloys are set forth in percent by weight in the following table:

TABLE

	Alloy			
Element	A	B	C	D
C	0.12	0.05	0.15	0.04
Cr	12.5	12.0	15.5	18.6
Ni	(1)	(1)	(1)	(1)
Mo	4.2	4.5	5.0	3.1
Cb	2.0	2.0	----	5.0
Fe	----	----	4.5	18.5
Ti	0.8	0.6	2.5	0.9
Al	6.1	5.9	3.5	0.4
B	0.012	0.010	0.050	----
Zr	0.10	0.10	----	----

[1] Balance.

said alloy being modified such that 0.5% to about 6% of cobalt replaces an equal percent by weight of a metal from the group consisting of nickel, iron and mixtures of nickel and iron and operating said device with said fabricated component in place.

6. A process as in claim **5** wherein the Alloy A, B, C or D is modified to include therein about 1% to about 5% cobalt in place of an equivalent percent by weight of nickel.

References Cited

UNITED STATES PATENTS

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RICHARD O. DEAN, Primary Examiner

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,591,372 Dated July 6, 1971

Inventor(s) John Hockin et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 1, line 25, after "high" the words -- stress at high -- were left out.

Col. 2, line 55, "0.02%" should be -- 0.2% --.

Col. 5, in TABLE in Claim 1, under "Alloy C" column - between lines 30 and 31, "0.015" should be -- 0.050 --.

Col. 5, line 34, "a replacement" should be -- in replacement --.

Signed and sealed this 28th day of December 1971.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Acting Commissioner of Patents

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