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㋄ Applicant: Exxon Research and Engineering Company
P.O.Box 390 180 Park Avenue
Florham Park New Jersey 07932(US)

㋆ Inventor: Ayer, Raghaven
1670 Shippan Avenue
Stamford Connecticut 06902(US)

㋆ Inventor: Hayworth, Henry Charles
41 Silver Lake Drive
Summit New Jersey 07901(US)

㋆ Inventor: Humphries, Michael Joseph
67 Ironia-Mendham Road
Ironia New Jersey 07845(US)

㋇ Representative: Somers, Harold Arnold et al,
ESSO Engineering (Europe) Ltd. Patents & Licences Apex
Tower High Street
New Malden Surrey KT3 4DJ(GB)

�54 Alloys resistant to stress corrosion cracking.

�57 Disclosed are iron, nickel, and cobalt based austenitic alloys containing 12 - 50 wt.% Cr, from 0.001 - 0.2 wt.% C, 0 - 3 wt.% Mo, 0 - 3 wt.% Mn, 0 - 0.5 wt.% Si, 0 - 0.2 wt.% A1, 0 - 0.75 wt.% Zr, and at least one carbide-forming element whose carbide is more stable than chromium carbide, and which alloy, at equilibrium, generates a carbon concentration in solution which is insufficient to form chromium carbides at a temperature from about 425°C - 750°C. The preferred carbide-forming element is Hf and/or Ta.

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ALLOYS RESISTANT TO STRESS CORROSION CRACKING

FIELD OF THE INVENTION

The present invention relates to iron, nickel, and cobalt based alloys containing 12-50 wt.% Cr and 0.001 to 0.2 wt.% carbon, which alloys are substantially free of chromium carbides at equilibrium at temperatures from about 425°C - 750°C.

BACKGROUND OF THE INVENTION

There is a need, particularly in the petroleum and nuclear industries, for alloys which are resistant to sensitization caused by chromium carbide precipitation at elevated temperatures. Sensitization is the term commonly used to describe precipitation of chromium carbides at the grain boundaries of the alloy and the consequent depletion of chromium in the matrix adjacent to the grain boundaries. It is accepted in the art that the depletion of chromium from the matrix renders the alloy susceptible to intergranular corrosion and stress corrosion cracking.

These phenomena generally result when the the alloy is exposed subsequent to sensitization to an aqueous medium. In such environments, conventional alloys such as stainless steels often fail because of intergranular corrosion, stress corrosion cracking, or both, which are attributed to the prior precipitation of chromium carbides at the grain boundaries. Precipitation of chromium carbides at the grain boundaries is particularly troublesome in the temperature range of about 425°C to about 750°C. This temperature is a

common service temperature for many commercial applications. Chromium carbides may also form during fabrication of the alloys, particularly during welding. The precipitation of these chromium carbides generally occurs at the grain boundaries and is invariably associated with depletion of chromium at, and adjacent to, the grain boundaries. Below about 425°C, the kinetics of the process are unfavorable for the formation of chromium carbides, while above about 750°C, chromium from the grain interior diffuses to the grain boundary, thereby replenishing the grain boundary with chromium. The depletion of chromium accelerates crack propagation resulting in premature failure of the alloys.

Considerable effort has been spent in the metallurgical industry in attempts to develop alloys which are substantially free of chromium carbides during service. One such effort is directed at a means for producing alloys having a concentration of carbon below which chromium carbides will form. This concentration, generally below about 0.001 wt.%, is too low a concentration to be commercially feasible. Other efforts are directed at producing alloys containing elements, such a niobium and titanium, which tie-up the carbon in the form of niobium and titanium carbides. Such carbides, when formed, are generally not found at the grain boundaries as chromium carbides are. Although niobium and titanium carbides are more stable than chromium carbides, at equilibrium, in their presence, there is still enough carbon left in the matrix at equilibrium to cause precipitation of chromium carbides at the grain boundaries at temperatures from about 425°C to 750°C.

Neither one of these approaches has been successful for eliminating substantially all precipitation of chromium carbides. Consequently, there is still a need in the art for the development of alloys which contain substantially no chromium carbides during service and which are therefore resistant to intergranular corrosion and stress corrosion cracking.

SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided iron, nickel, and cobalt based austenitic alloys containing from about 12-50 wt.% Cr, from about 0.001 - 0.2 wt.% C, and at least one carbide forming element whose carbide is more stable than chromium carbide, and which alloy, at equilibrium, generates a carbon concentration in solution which is insufficient to form chromium carbides at a temperature from about 425°C - 750°C.

In preferred embodiments of the present invention, the alloys are comprised of:

12-25 wt.% Cr,
5-35 wt.% Ni,
0-3 wt.% Mo
0-0.5 wt.% Si
0.001- 0.2 wt.% C,
Hf and/or Ta in an amount from about
10(C+O+N) to 30(C+O+N) wherein the concentration of carbon(C), oxygen(O), and nitrogen(N), are expressed in wt.%,
the balance being Fe.

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In other preferred embodiments of the present invention, up to 3 wt.% Mn, up to 0.2 wt.% Al and up to 0.5% Si are present.

In still other preferred embodiments of the present invention, the alloys contain about 15-25 wt.% Cr, 70-80 wt.% Ni, 0.001 - 0.2 wt.% C, and Hf in an amount from about 10(C+O+N) to about 30(C+O+N), where C, O, and N are based on wt.%.

BRIEF DESCRIPTION OF THE FIGURES

The Figure hereof are photomicrographs showing the microstructure of alloys A, B, D, and E of the examples, after exposure at 1040°C for one hour followed by exposure at 590°C for 1000 hours. These photomicrographs illustrate the preferential attack at the grain boundaries by the oxalic acid etch as evidenced by voids, or holes, at the grain boundaries. It can be observed in these photomicrographs that the grain boundaries of alloy E are not attacked by the oxalic acid etch, this is because of the absence of chromium carbides and, hence, absence of depletion of chromium at the grain boundaries of alloy E.

DESCRIPTION OF THE INVENTION

Precipitation of chromium carbides is detrimental to the intergranular corrosion and stress corrosion cracking resistance of austenitic alloys because they deplete the grain boundaries, and the regions neighboring the grain boundaries, of chromium. By practice of the present invention, the formation of chromium carbides is avoided by the addition of one or more carbide forming elements whose carbide is more stable than chromium carbide and which alloy, at

equilibrium, has a carbon concentration, in the matrix, which is insufficient to form chromium carbides at a temperature from about 425°C to 750°C.

Preferred carbide forming elements suitable for use in the present invention are hafnium for iron, nickel, and cobalt based alloys, and tanatalum, for iron based alloys. Such carbide forming elements are present in an amount sufficient so that the con- centration of carbon in the matrix is too low to cause precipitation of chromium carbides. This amount, generally based on weight percent, is equal to or greater than, about 10(C+O+N) but less than or equal to about 30(C+O+N), preferably about 15(C+O+N). For economical reasons it may be desirable to use lower cost Hf-Zr alloys as opposed to the more expensive elemental Hf. Such Hf-Zr alloys are a by-product of the manufacturing process for producing Zr fuel rods in the nuclear industry and are available at a fraction of the cost of Hf. If Hf-Zr alloys are used in the practice of the present invention, they should be used such that no more than 0.75 wt.% Zr is present in the final alloy. The use of such carbide forming elements in these amounts substantially eliminates the precipitation of chromium carbides at the grain boundaries, thus resulting in a alloy having improved resistance to intergranular corrosion and stress corrosion cracking. Because the concentration of oxygen and nitrogen are usually much smaller with respect to carbon, the above criteria concerning the addition of hafnium and tantalum may be satisfied by considering the concentration of carbon alone. In cases where the concentrations of oxygen and nitrogen are unusually high, all three elements should be considered equally for satisfying the above criteria. When Hf and Ta are

used below about 10(C+O+N), the alloy, at equilibrium, contains sufficient amounts of carbon in the matrix to form chromium carbides. When Hf and Ta are used above about 30(C+O+N), intermetallic phases will form, which may degrade the physical and mechanical properties of the alloy.

The elements, and their concentrations, comprising the alloys of the present invention, are important because their combination results in a class of alloys having unexpectedly good resistance to intergranular corrosion and stress corrosion cracking.

Chromium is important in the alloys of the present invention because it increases the overall corrosion resistance of the alloy. It will be noted though that increasing amounts of chromium leads to the formation of sigma, or other similar intermetallic phases. The amount of chromium needed to provide corrosion resistance for the alloys of the present invention is at least about 12 wt.%, while a chromium content of up to about 50 wt.% may be needed in more severe corrosive environments and/or high temperatures.

Another preferred alloy is comprised of about 19 to 23 wt.% Cr, about 30 to 35 wt.% Ni, about 1.5 wt.% Mn, about 0.06 to 0.1 wt.% C, about 0.06 to 0.1 wt.% Al, up to about 0.5 wt.% Si, Hf in an amount of about 20(C+O+N), the balance being Fe. More preferred alloys of the present invention are comprised of about 17 to 19 wt.% Cr, about 9 to 12 wt.% Ni, about 1.5 to 2.5 wt.% Mn, up to about 0.5 wt.% Si, less than about 0.08 wt.% C, Hf in an amount of about 20(C+O+N), the balance being Fe.

The use of hafnium and/or tantalum in the iron based alloys and hafnium in the iron, nickel, and cobalt based alloys of the present invention results in the formation of stable hafnium and/or tantalum carbides. The formation of hafnium and tantalum carbides decreases the carbon concentration of the matrix, thereby leaving the concentration of carbon too low for the precipitation of chromium carbides. The use of other known carbide forming elements, such as niobium and titanium, in the alloys of the present invention, were surprisingly found not to have the same beneficial effect as hafnium and tantalum. That is, although niobium and titanium also deplete carbon from the matrix and result in the formation of stable niobium and titanium carbides, enough carbon still remains in the matrix, at equilibrium at a temperature of about 425°C to 750°C, to result in formation of chromium carbides. For purposes of the present invention, Hf is the preferred carbide forming element.

The alloys of the present invention may contain incidental impurities such as B, Sn, Pb, Zn, Bi, etc., each in an amount less than about 0.01 wt.%, as long as they do not render an adverse effect on the properties of the alloy.

The following examples serve to more fully describe the manner of practicing the above described invention as well as to set forth the best modes contemplated for carrying out various aspects of the invention. It is to be understood that these examples in no way serve to limit the true scope of this invention, but are presented for illustrative purposes.

Example 1

The experimental alloys used herein were prepared from substantially pure-element raw materials. The individual elements were weighed to constitute about 50 lbs and melted in a vacuum induction furnace. Once the major alloying elements were molten, the molten metal was poured into a 2-1/2 inch diameter cast iron mold. The solidified casting was stripped from the mold, homogenized at 1200°C, and hot rolled at 1000°C to produce 1/2 inch thick plates.

Table I below sets forth the alloy compositions used in this example.

TABLE I

Composition, wt.%

Alloy	Fe	Cr	Ni	Mn	C	Ti	Nb	Hf	Comments
A	Bal	18.3	9.9	2.2	.067	.27	---	---	Ti/C=4
B	Bal	18*	10*	2*	.07	---	0.6	---	.28 Ta
C	Bal	18.3	9.9	1.8	.073	.4	---	.28	Hf/C=3.8
D	Bal	17.3	10.2	2.3	.07	.46	---	.54	Hf/C=7.7
E	Bal	18.9	10.2	1.9	.073	.4	---	1.05	Hf/C=14.4

* nominal (not analyzed) compositions

Alloys A and B are commercially available alloy compositions with Alloy A containing Ti and Alloy B containing Nb and Ta. Alloy B is considered to be the best commercially available conventional alloy in the industry to resist polythionic acid stress corrosion cracking. Alloys C, D and E are alloys of the present invention. These alloys contain Hf/C ratios ranging from

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3.8 for alloy C, to 14.4 for alloy E. Although Alloys C, D, and E contain Ti, they all contain enough Hf, based on the amount of carbon, to prevent the formation of chromium carbides.

Example 2

Three coupons of each of the above alloys were solution treated at $1040^{\circ}C$ for 1 hr and water quenched. One coupon of each alloy was retained in the solution treated condition for microstructural observations. Another coupon of each alloy was exposed at $590^{\circ}C$ for a period of 100 hrs., and the third coupon of each alloy was exposed at $590^{\circ}C$ for 1000 hrs. The heat treated coupons were examined by scanning and transmission electron microscopy to determine the types of second phase particles which formed during aging. The results of these studies are shown in Table II below:

TABLE II

Relative Abundance of Second Phase Particles
of the Heat Treated Coupons*

Alloy	$1040^{\circ}C$/1 Hr	$1040^{\circ}C$/1 Hr +$590^{\circ}C$/100 Hrs	$1040^{\circ}C$/1 Hr +$590^{\circ}C$/1000 Hrs
A	TiC	TiC, $Cr_{23}C_6$	TiC, $Cr_{23}C_6$
B	(Nb,Ta)C	(Nb,Ta)C	(Nb,Ta)C, $Cr_{23}C_6$ Fe_2Nb
C	TiC, HfC	TiC, HfC, $Cr_{23}C_6$	TiC, HfC, $Cr_{23}C_6$
D	HfC, TiC	HfC, TiC	HfC, TiC, $Cr_{23}C_6$
E	HfC	HfC, Fe_2(Hf,Ti)	HfC, Fe_2(Hf,Ti)

* phases listed in decreasing order of abundance.

The data in Table II show that all of the
alloys contained primary carbides (Ti, Nb, Ta,
Hf-carbides) before aging, with the type and amount of
carbide varying from alloy to alloy. The commercial
alloys A and B contain TiC and (Nb,Ta)C, respectively,
while the alloys of the present invention contain TiC
and HfC. The type of carbide in the alloys of the
present invention depends on the Hf/C ratio. That is,
for alloys in which Hf/C <15, the primary carbide is a
mixture of TiC and HfC, while for Hf/C = 15, the
primary carbide is entirely HfC.

After aging for 100 hrs., the samples were
examined in a transmission election microscope and the
types of phases were characterized by x-ray
microanalysis and election diffraction analysis. The
results are shown in Table II. Commercial alloy A
and alloy C form chromium carbides while alloy B and
alloy D did not form any Cr carbides or any other
precipitates. Alloy E formed small amounts of $Fe_2(Hf,Ti)$
intermetallic precipitates both in the grains and at the
grain boundaries. This was caused by the presence of
titanium which is normally not required in the alloy.

After 1000 hrs. of aging, both the commercial
alloys (A and B) and the experimental alloys (C and D)
formed carbide precipitates. In the alloys that had
formed chromium carbides after 100 hrs., (alloys A and
C), the density of chromium carbides had increased after
1000 hrs. Alloy B and alloy D also formed chromium
carbides. The only alloy that did not form chromium
carbides was alloy E.

Figure 1 shows the microstructure of the alloys after 1000 hrs. of aging. In these micrographs, the formation of the chromium carbides are seen as holes at the grain boundaries. These holes are the result of preferential attack of the chromium depleted regions around the carbides by a 10% oxalic acid etch used to reveal the structure of the alloys. Alloys A, B, and D were etched for 15 seconds and alloy E for 45 seconds. Alloy E was etched for 45 seconds because after 15 seconds no sign of attack at the grain boundaries was observed. Even after etching for 45 seconds, Alloy E showed no sign of grain boundary attack. The absence of chromium carbides in alloy E is the result of Hf addition in sufficient quantities to tie up all or most of the carbon such that insufficient carbon is left to form detrimental chromium carbides during the aging treatment. The reduced carbon level at equilibrium at a temperature of 425°C to 750°C is below that level at which chromium carbide can form. The data show that precipitation of chromium carbide can be prevented by the addition of a sufficient quantity of a strongly carbide forming element which reduces the equilibrium concentration of dissolved carbon in the matrix to a level below that at which chromium carbide can form. It has been unexpectedly found that conventionally used carbide forming elements such as titanium and niobium are not capable of achieving this, while strongly carbide forming elements such as hafnium and tantalum can reduce the dissolved carbon to the necessary low levels. The data also show that no other primary carbide, such as TiC or NbC is capable of tying up all the carbon in the alloy.

1 pound (lb) = 453.6 g.

1 inch = 2.54 cm.

CLAIMS:

1. An austenitic iron, nickel, or cobalt based alloy comprised of about 12-50 wt.% Cr, 0 - 3 wt.% Mo, 0 - 3 wt.% Mn, 0 - 0.2 wt.% Al, 0 - 0.75 wt.% Zr, 0.001 - 0.2 wt.% C, and at least one carbide forming element whose carbide is more stable than chromium carbide and, which alloy at equilibrium, has a carbon concentration in solution which is insufficient to form chromium carbides at a temperature from about 425°C-750°C.

2. The alloy of claim 1 wherein the concentration of Cr is from about 15 to 25 wt.%.

3. The alloy of claim 1 or claim 2 wherein the said carbide-forming element is selected from hafnium or tantalum or a combination of Hf and Ta.

4. The alloy of claim 3 wherein the concentration of carbide-forming element selected from Hf and/or Ta is present in a concentration of from about 10 (C+O+N) to about 30 (C+O+N) wherein C, O and N are expressed in weight percent.

5. The alloy of claim 4 wherein the Hf and/or Ta is present in a concentration of about 15 (C+O+N) wherein C, O and N are expressed in weight percent.

6.   The alloy of any one of claims 3 to 5 wherein the Hf is provided as a Hf-Zr alloy such that the concentration of Zr in the final iron, nickel or cobalt-based alloy is no more than 0.75 wt.% Zr.

7.   The alloy of any one of claims 1 to 6 which is comprised of about 17 to 19 wt.% Cr, 9 to 12 wt.% Ni, 1.5 to 2.5 wt.% Mn, Hf in an amount such that Hf = about 20 (C+O+N), where C, O, and N are expressed in wt.%, and the balance is iron.
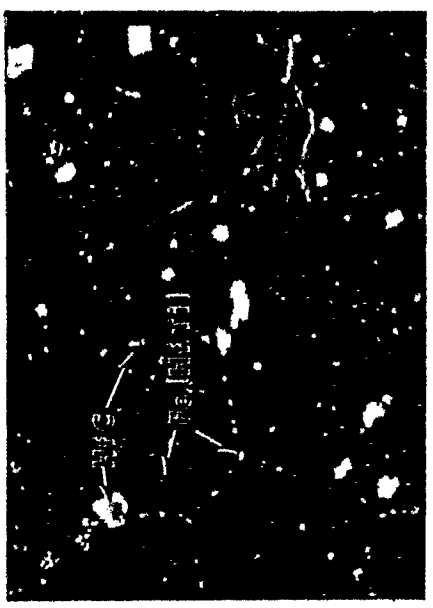
8.   The alloy of any one of claims 1 to 6 which is comprised of about 19 to 23 wt.% Cr, 30 to 35 wt.% Ni, 1.5 to 2.0 wt.% Mn, 0.05 to 0.1 wt.% Al, up to 0.5 wt.% Si, 0.05 to 0.1 wt.% C, Hf in an amount such that Hf = about 20 (C+O+N), where C, O, and N are expressed in wt.%, and the balance is iron.

9.   The alloy of any one of claims 1 to 6 which is comprised of 15 to 25 wt.% Cr, 70 to 80 wt.% Ni, 0.001 to 0.2 wt.% C, and Hf in an amount from about 10 (C+O+N) to 30 (C+O+N) where C, O, and N are expressed in wt.%.
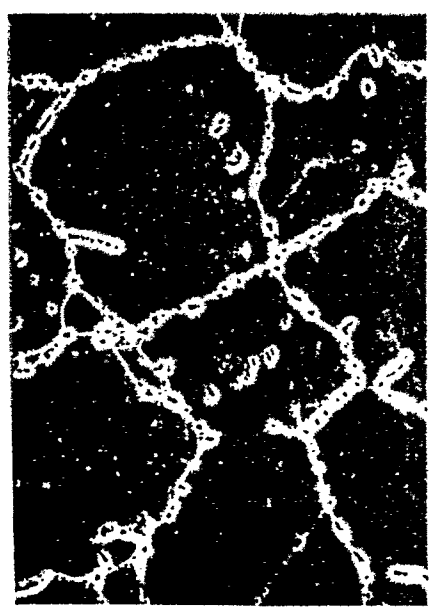
10.   An austenitic alloy which is resistant to stress corrosion cracking as in any one of claims 1 to 9 comprising no more than 0.08 weight percent carbon, the balance being iron.
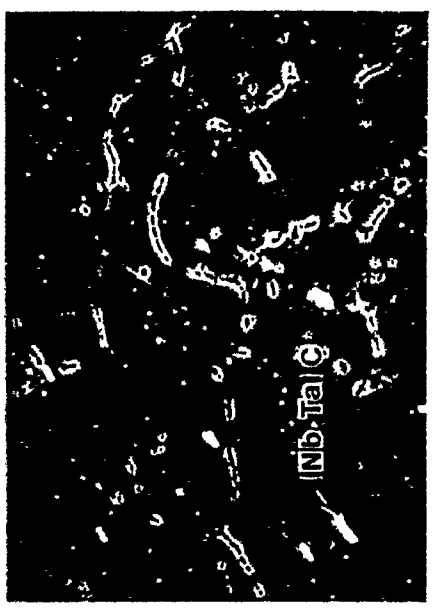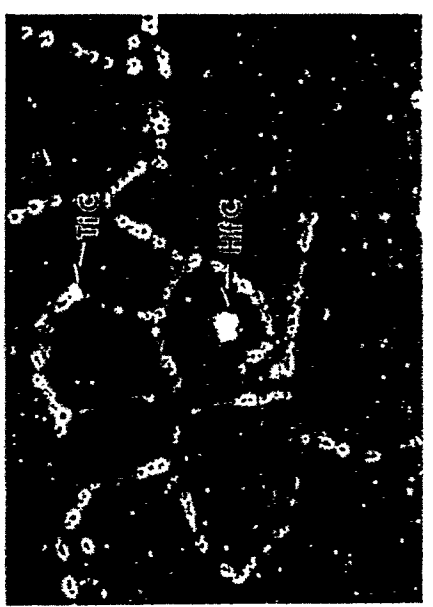
Alloy B

Alloy E

Alloy A

Alloy D

Figure 1