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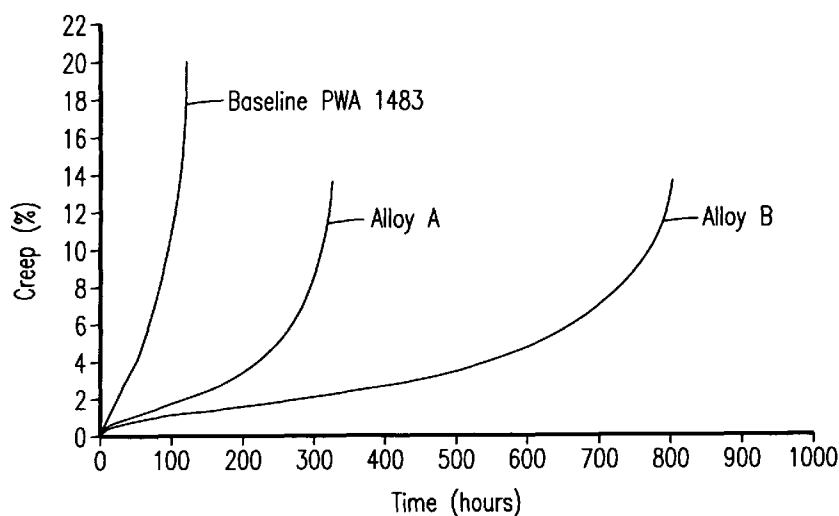


FIG. 1

(57) Abstract: Disclosed are novel nickel-base alloy compositions that may be cast as a single crystal or directionally solidified alloy consisting essentially of, by weight: 8-12% Cr, 10-14% Co, 0.3-0.9% Mo, 3-7% W, 2-8% Ta, 2.0-5.5% Al, 1.5-5.0% Ti, up to 2% Nb, less than 0.1% B, less than 0.1% Zr, 0.05-0.15% C, less than 0.5% Hf, 2-4% Re, 0.05-0.2% Si, up to 0.015% S, up to 0.1% La, up to 0.1% Y, up to 0.1% Ce, up to 0.1% Nd, up to 0.1% Dy, up to 0.1% Pr, up to 0.1% Gd, balance is Ni, and wherein (La+Y+Ce+Nd+Dy+Pr+Gd) is 0.001-0.1%. The compositions for the nickel-base superalloy have a balance between oxidation resistance, corrosion resistance, castability, and mechanical properties, such as creep resistance and thermo-mechanical fatigue resistance

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CORROSION RESISTANT ALLOY COMPOSITIONS WITH ENHANCED CASTABILITY AND MECHANICAL PROPERTIES

This application claims benefit of the 10 August 2007 filing date of United States Provisional Patent Application No. 60/955,092.

FIELD OF THE INVENTION

This invention relates in general to the field of nickel base superalloys possessing improved oxidation resistance, corrosion resistance, castability, and mechanical properties such as creep resistance and thermo-mechanical fatigue resistance. The present invention relates to alloys that may be cast as a single crystal or directionally solidified.

BACKGROUND OF THE INVENTION

Nickel base superalloys are alloys composed primarily of nickel with the addition of several other elements selected for their ability to survive an overall high temperature, high stress, and highly oxidative environment. Typically, this environment is that of a gas turbine engine.

The greatest difficulty encountered with the gas turbine environment is that the goals of creep resistance, thermo-mechanical fatigue resistance, and corrosion resistance are at odds with each other. Alloys with greater creep resistance typically sacrifice hot corrosion resistance and thermo-mechanical fatigue resistance. Alloys with greater hot corrosion resistance come at the expense of poor creep resistance and thermo-mechanical fatigue resistance.

BRIEF DESCRIPTION OF THE DRAWINGS

This invention is explained in the following description in view of the drawings that show:

Fig. 1 illustrates comparative creep testing of embodiments of the present invention (called Alloys A and B) and a prior art alloy PWA 1483.

Fig. 2 is a micrograph of Alloy A, after elevated temperature exposure to a thermally oxidized coal derived syngas test environment.

Fig. 3 is a micrograph of Alloy B, after elevated temperature exposure to a thermally oxidized coal derived syngas test environment.

Fig. 4 is a micrograph of the prior art alloy SieMet DS (PWA 1483 modified with grain boundary strengthening elements) after elevated temperature exposure to a thermally oxidized coal derived syngas test environment.

Fig. 5 is a micrograph of another prior art alloy CM247LC after elevated temperature exposure to a thermally oxidized coal derived syngas test environment.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides an alloy composition that may be cast as a single crystal alloy or may be directionally solidified, and that has better castability than the prior art alloy available from Cannon-Muskegon Corporation under the registered trademark CMSX-4, has better corrosion resistance than alloy CM247LC available from that same source, and has better mechanical properties than the prior art alloy available through United Technologies Corporation under the trademark PWA 1483. Typical weight percent compositions of these prior art alloys are shown in Table 1.

TABLE 1

	CMSX-4		PWA 1483		CM247LC	
	Min	Max	Min	Max	Min	Max
Co	9.3	10.0	8.5	9.5	9.0	9.5
Cr	6.4	6.6	11.6	12.7	8.0	8.5
Ti	0.9	1.1	3.9	4.25	0.6	0.9
Al	5.4	5.75	3.4	3.8	5.4	5.7
Ta	6.3	6.75	4.8	5.2	3.1	3.3
Mo	0.5	0.7	1.65	2.15	0.4	0.6
W	6.2	6.6	3.5	4.1	9.3	9.7
Hf	0.07	0.12	0	75ppm	1.0	1.6
Re	2.8	3.1	---	---	---	---
C	0	60ppm	0.05	0.09	0.07	0.08
B	0	25ppm	0	30ppm	.01	.02

Zr	0	75ppm	0	75ppm	.005	0.02
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The novel alloy compositions disclosed herein offer an improved set of properties that are particularly useful for application in Integrated Gasification Combined Cycle (IGCC) syngas fired gas turbines where relatively low quality fuels and high operating temperatures result in a highly corrosive environment.

Alloys of the present invention include Chromium (Cr) from 8-12 weight percent or about 10 weight percent to provide the compositions with a desired level of high temperature corrosion resistance.

Alloys of the present invention may include Aluminum (Al) at a concentration that is lower than is generally observed in highly oxidation resistant alloys, for example as low as 2 weight percent or in the range of 2.0-5.5 weight percent. Rare earth elements, Yttrium (Y), Silicon (Si), and Hafnium (Hf) are included to compensate for the reduction in Aluminum (Al) and to provide increased oxidation resistance.

The alloy compositions disclosed herein have intentional additions of rare earth elements Lanthanum (La), Yttrium (Y), Gadolinium (Gd), Praseodymium (Pr), Dysprosium (Dy), Neodymium (Nd), and Erbium (Er) in combined amounts of up to 0.1 weight percent. These rare earth additions provide improved oxidation resistance of the inventive alloys and enhance the compatibility of the alloy compositions with various coatings. The rare earth additions also aid in increasing the life of any overlying protective ceramic coating. The increase in coating life through the addition of rare earth elements is attributed to their ability to form sulfides and oxi-sulfides that reduce the residual Sulfur (S) content and prevent the diffusion of sulfur atoms to the alumina scale that is formed at the boundary between the coating and the substrate alloy.

Silicon (Si) is intentionally added to the present alloys to support the formation of a protective silicon dioxide surface oxide layer. The silicon dioxide provides enhanced oxidation resistance as the film is less susceptible to cracking compared with other protective oxide films. Excessive additions of

silicon are detrimental to the performance of the alloy; consequently, an addition of less than 0.15 weight percent or in the range of 0.05-0.2 weight percent is preferred.

The intentional addition of Hafnium (Hf) at levels similar to those of Silicon or less than 0.5 weight percent serves to further enhance the oxidation resistance.

An alloy composition consisting essentially of, by weight percent, 8-12% Cr, 10-14% Co, 0.3-0.9% Mo, 3-7% W, 2-8% Ta, 2.0-5.5% Al, 1.5-5.0 % Ti, up to 2% Nb, less than 0.1% B, less than 0.1% Zr, 0.05-0.15% C, less than 0.5% Hf, 2-4% Re, 0.05-0.2% Si, up to 0.015% S (without intentional sulfur addition), up to 0.1% La, up to 0.1% Y, up to 0.1% Ce, up to 0.1% Nd, up to 0.1% Dy, up to 0.1% Pr, up to 0.1% Gd, balance is Ni, and wherein $(La+Y+Ce+Nd+Dy+Pr+Gd)$ is 0.001-0.1%, provides for an overall range of alloys that exhibit creep resistance, thermo-mechanical fatigue resistance, corrosion resistance, and the ability to be cast as a single crystal or directionally solidified alloy. All compositions herein are specified in weight percent values unless specified otherwise.

The alloy composition from the above, but with the following ranges: 2-6% Ta, 2-5% Al, and 3-5% Ti, is selected to optimize its thermo-mechanical fatigue resistance.

The alloy composition from the above, but with the following ranges: 4-8% Ta, 3.5-5.5% Al, and 1.5-4.0% Ti, is selected to optimize its creep resistance.

The alloy composition from the above, but with the following ranges: 9.5-10.5% Cr, 11.5-12.5% Co, 0.45-0.75% Mo, 4.4-5.4% W, 3.4-4.4% Ta, 3.1-4.0% Al, 3.9-4.25% Ti, up to 0.5% Nb, less than 0.02% B, less than 0.02% Zr, 0.05-0.11% C, less than 0.25% Hf, 2.5-3.5% Re, 0.1-0.15% Si, up to 0.015% S (again with no intentional sulfur addition), up to 0.05% La, up to 0.05% Y, up to 0.05% Ce, up to 0.05% Nd, up to 0.05% Dy, up to 0.05% Pr, up to 0.05% Gd, balance is Ni, and wherein $(La+Y+Ce+Nd+Dy+Pr+Gd)$ is 0.01-0.05%, is selected for its thermo-mechanical fatigue resistance, ability to be cast as a single crystal alloy.

The alloy composition from the above, but with the following ranges: 9.5-10.5% Cr, 11.5-12.5% Co, 0.45-0.75% Mo, 4.4-5.4% W, 3.4-4.4% Ta, 3.1-4.0% Al, 3.9-4.25% Ti, up to 0.5% Nb, 0.005-0.015% B, up to 0.02% Zr, 0.05-0.11% C, less than 0.25% Hf, 2.5-3.5% Re, 0.1-0.15% Si, up to 0.015% S (again with no intentional sulfur addition), up to 0.05% La, up to 0.05% Y, up to 0.05% Ce, up to 0.05% Nd, up to 0.05% Dy, up to 0.05% Pr, up to 0.05% Gd, balance is Ni, and wherein (La+Y+Ce+Nd+Dy+Pr+Gd) is 0.01-0.05%, is selected for its thermo-mechanical fatigue resistance, ability to be cast as a directionally solidified alloy.

The alloy composition from the above, but with the following ranges: 9.5-10.5% Cr, 11.5-12.5% Co, 0.45-0.75% Mo, 4.4-5.4% W, 5.5-6.5% Ta, 4.2-4.8% Al, 2.0-2.8% Ti, up to 0.5% Nb, less than 0.02% B, less than 0.02% Zr, 0.05-0.11% C, less than 0.25% Hf, 2.5-3.5% Re, 0.1-0.15% Si, up to 0.015% S (again with no intentional sulfur addition), up to 0.05% La, up to 0.05% Y, up to 0.05% Ce, up to 0.05% Nd, up to 0.05% Dy, up to 0.05% Pr, up to 0.05% Gd, balance is Ni, and wherein (La+Y+Ce+Nd+Dy+Pr+Gd) is 0.01-0.05%, is selected for its creep resistance, ability to be cast as a single crystal alloy.

The alloy composition from the above, but with the following ranges: 9.5-10.5% Cr, 11.5-12.5% Co, 0.45-0.75% Mo, 4.4-5.4% W, 5.5-6.5% Ta, 4.2-4.8% Al, 2.0-2.8% Ti, up to 0.5% Nb, 0.005-0.015% B, less than 0.02% Zr, 0.05-0.11% C, less than 0.25% Hf, 2.5-3.5% Re, 0.1-0.15% Si, up to 0.015% S (again with no intentional sulfur addition), up to 0.05% La, up to 0.05% Y, up to 0.05% Ce, up to 0.05% Nd, up to 0.05% Dy, up to 0.05% Pr, up to 0.05% Gd, balance is Ni, and wherein (La+Y+Ce+Nd+Dy+Pr+Gd) is 0.01-0.05%, is selected for its creep resistance, ability to be cast as a directionally solidified alloy.

The alloy composition from the above, but with the following ranges: 10.0% Cr, 12.0% Co, 0.6% Mo, 4.9% W, 3.9% Ta, 3.5% Al, 3.9% Ti, less than 0.01% B, less than 0.01% Zr, 0.07% C, less than 0.1% Hf, 3.0% Re, less than 0.12% Si, up to 0.015 % S (again with no intentional sulfur addition), up to 0.02% La, up to 0.02% Y, up to 0.02% Ce, up to 0.02% Nd, up to 0.02% Dy, up to 0.02% Pr, up to 0.02% Gd, balance is Ni, and wherein

(La+Y+Ce+Nd+Dy+Pr+Gd) is between 150 and 400 ppm, is selected for its thermo-mechanical fatigue resistance, ability to be cast as a single crystal alloy.

The alloy composition from the above, but with the following ranges: 10.0% Cr, 12.0% Co, 0.6% Mo, 4.9% W, 3.9% Ta, 3.5% Al, 3.9% Ti, 0.01% B, 0.0075% Zr, 0.09% C, 0.1% Hf, 3.0% Re, less than 0.12% Si, up to 0.015 % S (again with no intentional sulfur addition), up to 0.02% La, up to 0.02% Y, up to 0.02% Ce, up to 0.02% Nd, up to 0.02% Dy, up to 0.02% Pr, up to 0.02% Gd, balance is Ni, and wherein (La+Y+Ce+Nd+Dy+Pr+Gd) is between 150 and 400 ppm, is selected for its thermo-mechanical fatigue resistance, ability to be cast as a directionally solidified alloy.

The alloy composition from the above, but with the following ranges: 10.0% Cr, 12.0% Co, 0.6% Mo, 4.9% W, 6.0% Ta, 4.5% Al, 2.4% Ti, less than 0.01% B, less than 0.01% Zr, 0.07% C, less than 0.1% Hf, 3.0% Re, less than 0.12% Si, up to 0.015 % S (again with no intentional sulfur addition), up to 0.02% La, up to 0.02% Y, up to 0.02% Ce, up to 0.02% Nd, up to 0.02% Dy, up to 0.02% Pr, up to 0.02% Gd, balance is Ni, and wherein (La+Y+Ce+Nd+Dy+Pr+Gd) is between 150 and 400 ppm (0.015%-0.04%), is selected for its creep resistance, ability to be cast as a single crystal alloy.

The alloy composition from the above, but with the following ranges: 10.0% Cr, 12.0% Co, 0.6% Mo, 4.9% W, 6.0% Ta, 4.5% Al, 2.4% Ti, 0.01% B, 0.0075% Zr, 0.09% C, 0.1% Hf, 3.0% Re, less than 0.12% Si, up to 0.015% S (again with no intentional sulfur addition), up to 0.02% La, up to 0.02% Y, up to 0.02% Ce, up to 0.02% Nd, up to 0.02% Dy, up to 0.02% Pr, up to 0.02% Gd, balance is Ni, and wherein (La+Y+Ce+Nd+Dy+Pr+Gd) is between 150 and 400 ppm (0.015%-0.04%), is selected for its creep resistance, ability to be cast as a directionally solidified alloy.

The compositions of this invention may be cast with processes known in the art.

Fig. 1 is a comparison of the creep properties of two embodiments of the present invention with those of prior art PWA 1483. The test was conducted at a temperature of 850°C. Alloy A has increased refractory metal content and the addition of 3 weight percent Rhenium (Re), as shown in Table

2. Alloy A is an example of an embodiment of the alloy composition that is designed to be cast as a single crystal and have improved thermo-mechanical fatigue resistance at the expense of some creep resistance. Alloy B is an example of an embodiment of the alloy composition that is designed to be cast as a single crystal and have improved creep resistance at the expense of some thermo-mechanical fatigue resistance.

Table 2

Exemplary Compositions (Weight percent).

Alloy ID	Ni	Cr	Co	Mo	W	Re	Ta	Al	Ti	C	Rare Earth
Alloy A	Bal.	10	12	0.6	4.9	3	3.9	3.5	3.9	0.07	0.03
Alloy B	Bal.	10	12	0.6	4.9	3	6	4.5	2.4	0.07	0.03
PWA 1483	Bal.	12.2	9	1.9	3.8	---	5	3.6	4.2	0.07	---
CMSX-4	Bal.	6.5	9.6	0.6	6.4	3	6.5	5.6	1	<0.006	---

Figs. 2-5 are Scanning Electron Microscope (SEM) slides that show various alloys after exposure to the same thermally oxidized coal derived syngas environment at about 1,000°C. Both of the novel alloys (Figs 2-3) have survived the environment and Alloy B (Fig. 3) shows particularly good condition with little evidence of corrosive attack. The Siemet DS (PWA 1483 modified with grain boundary strengthening elements) shows sub-surface penetration as seen in Fig. 4 and the protective oxide has spalled on the CM247LC as seen in Fig. 5.

While various embodiments of the present invention have been shown and described herein, it will be obvious that such embodiments are provided by way of example only. Numerous variations, changes and substitutions may be made without departing from the invention herein. Accordingly, it is intended that the invention be limited only by the spirit and scope of the appended claims.

CLAIMS

The invention claimed is:

1. A nickel base alloy composition consisting essentially of, by weight percent, 8-12% Cr, 10-14% Co, 0.3-0.9% Mo, 3-7% W, 2-8% Ta, 2.0-5.5% Al, 1.5-5.0 % Ti, up to 2% Nb, less than 0.1% B, less than 0.1% Zr, 0.05-0.15% C, less than 0.5% Hf, 2-4% Re, 0.05-0.2% Si, up to 0.015% S, up to 0.1% La, up to 0.1% Y, up to 0.1% Ce, up to 0.1% Nd, up to 0.1% Dy, up to 0.1% Pr, up to 0.1% Gd, balance is Ni, and wherein (La+Y+Ce+Nd+Dy+Pr+Gd) is 0.001-0.1%.

2. The composition of claim 1 selected for its thermo-mechanical fatigue resistance and comprising 2-6% Ta, 2-5% Al, and 3-5% Ti.

3. The composition of claim 1 selected for its creep resistance and comprising 4-8% Ta, 3.5-5.5% Al, and 1.5-4.0 Ti.

4. The composition of claim 1 selected for its thermo-mechanical fatigue resistance, ability to be cast as a single crystal alloy and comprising 9.5-10.5% Cr, 11.5-12.5% Co, 0.45-0.75% Mo, 4.4-5.4% W, 3.4-4.4% Ta, 3.1-4.0% Al, 3.9-4.25% Ti, up to 0.5% Nb, less than 0.02% B, less than 0.02% Zr, 0.05-0.11% C, less than 0.25% Hf, 2.5-3.5% Re, 0.1-0.15% Si, up to 0.015% S, up to 0.05% La, up to 0.05% Y, up to 0.05% Ce, up to 0.05% Nd, up to 0.05% Dy, up to 0.05% Pr, up to 0.05% Gd, balance is Ni, and wherein (La+Y+Ce+Nd+Dy+Pr+Gd) is 0.01-0.05%.

5. The composition of claim 1 selected for its thermo-mechanical fatigue resistance, ability to be cast as a directionally solidified alloy and comprising 9.5-10.5% Cr, 11.5-12.5% Co, 0.45-0.75% Mo, 4.4-5.4% W, 3.4-4.4% Ta, 3.1-4.0% Al, 3.9-4.25% Ti, up to 0.5% Nb, 0.005-0.015% B, up to 0.02% Zr, 0.05-0.11% C, less than 0.25% Hf, 2.5-3.5% Re, 0.1-0.15% Si, up to 0.015% S, up to 0.05% La, up to 0.05% Y, up to 0.05% Ce, up to 0.05% Nd, up to 0.05% Dy, up to 0.05% Pr, up to 0.05% Gd, balance is Ni, and wherein (La+Y+Ce+Nd+Dy+Pr+Gd) is 0.01-0.05%.

6. The composition of claim 1 selected for its creep resistance, ability to be cast as a single crystal alloy and comprising 9.5-10.5% Cr, 11.5-12.5% Co, 0.45-0.75% Mo, 4.4-5.4% W, 5.5-6.5% Ta, 4.2-4.8% Al, 2.0-2.8% Ti, up to 0.5% Nb, less than 0.02% B, less than 0.02% Zr, 0.05-0.11% C, less than 0.25% Hf, 2.5-3.5% Re, 0.1-0.15% Si, up to 0.015% S, up to 0.05% La, up to 0.05% Y, up to 0.05% Ce, up to 0.05% Nd, up to 0.05% Dy, up to 0.05% Pr, up to 0.05% Gd, balance is Ni, and wherein (La+Y+Ce+Nd+Dy+Pr+Gd) is 0.01-0.05%.

7. The composition of claim 1 selected for its creep resistance, ability to be cast as a directionally solidified alloy and comprising 9.5-10.5% Cr, 11.5-12.5% Co, 0.45-0.75% Mo, 4.4-5.4% W, 5.5-6.5% Ta, 4.2-4.8% Al, 2.0-2.8% Ti, up to 0.5% Nb, 0.005-0.015% B, less than 0.02% Zr, 0.05-0.11% C, less than 0.25% Hf, 2.5-3.5% Re, 0.1-0.15% Si, up to 0.015% S, up to 0.05% La, up to 0.05% Y, up to 0.05% Ce, up to 0.05% Nd, up to 0.05% Dy, up to 0.05% Pr, up to 0.05% Gd, balance is Ni, and wherein (La+Y+Ce+Nd+Dy+Pr+Gd) is 0.01-0.05%.

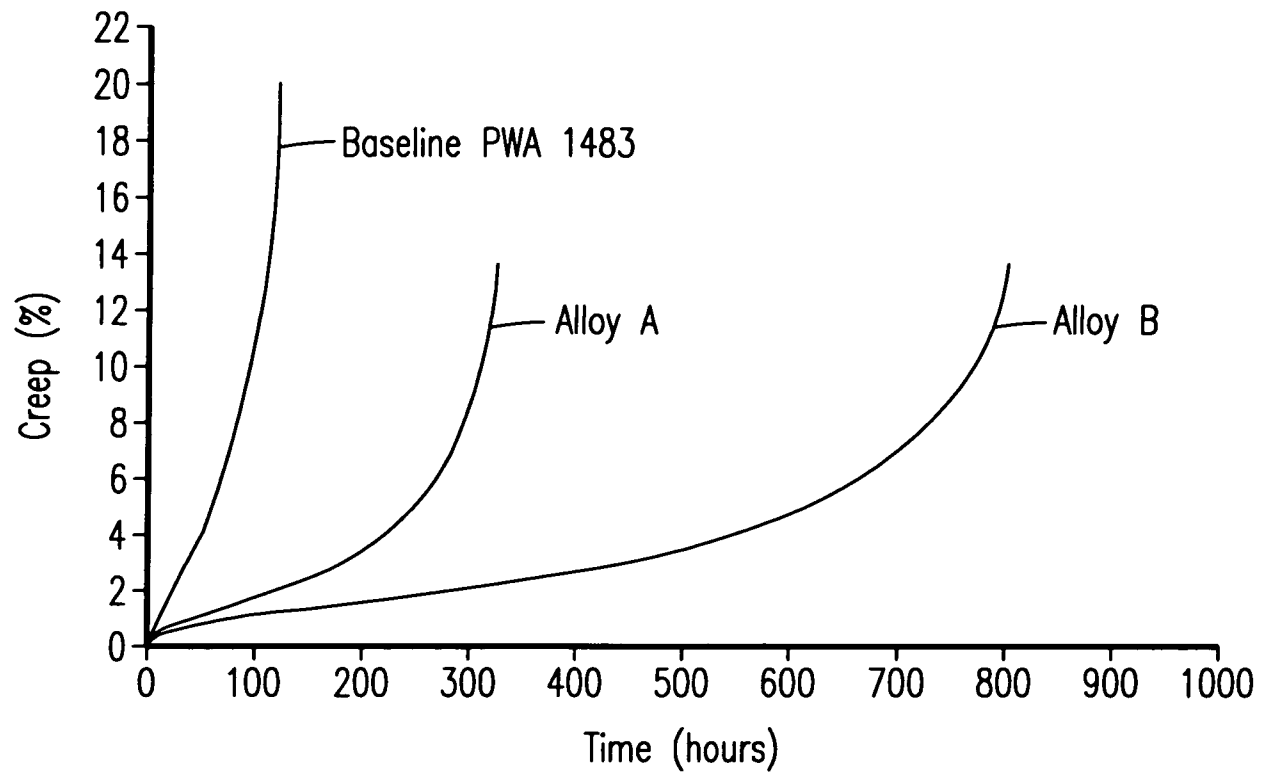
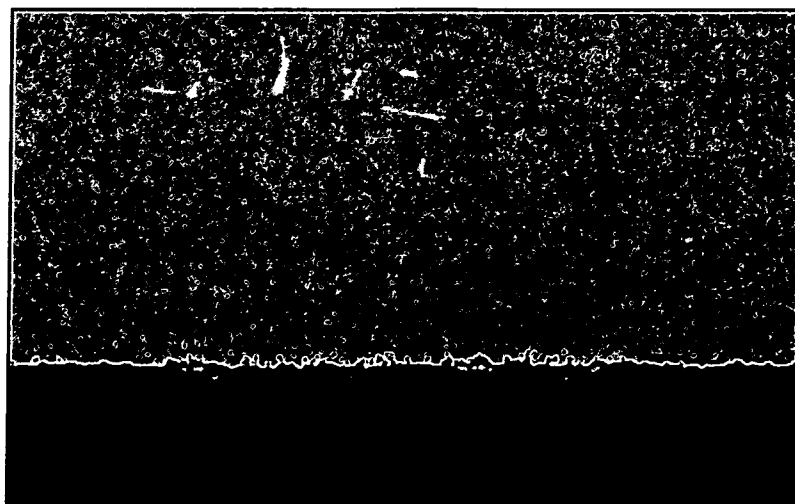
8. The composition of claim 1 selected for its thermo-mechanical fatigue resistance, ability to be cast as a single crystal alloy and comprising 10.0% Cr, 12.0% Co, 0.6% Mo, 4.9% W, 3.9% Ta, 3.5% Al, 3.9% Ti, less than 0.01% B, less than 0.01% Zr, 0.07% C, less than 0.1% Hf, 3.0% Re, less than 0.12% Si, up to 0.015 % S, up to 0.02% La, up to 0.02% Y, up to 0.02% Ce, up to 0.02% Nd, up to 0.02% Dy, up to 0.02% Pr, up to 0.02% Gd, balance is Ni, and wherein (La+Y+Ce+Nd+Dy+Pr+Gd) is 0.03%.

9. The composition of claim 1 selected for its thermo-mechanical fatigue resistance, ability to be cast as a directionally solidified alloy and comprising 10.0% Cr, 12.0% Co, 0.6% Mo, 4.9% W, 3.9% Ta, 3.5% Al, 3.9% Ti, 0.01% B, 0.0075% Zr, 0.09% C, 0.1% Hf, 3.0% Re, less than 0.12% Si, up to 0.015 % S, up to 0.02% La, up to 0.02% Y, up to 0.02% Ce, up to 0.02% Nd, up to 0.02% Dy, up to 0.02% Pr, up to 0.02% Gd, balance is Ni, and wherein (La+Y+Ce+Nd+Dy+Pr+Gd) is 0.03%.

10. The composition of claim 1 selected for its creep resistance, ability to be cast as a single crystal alloy and comprising 10.0% Cr, 12.0% Co, 0.6% Mo, 4.9% W, 6.0% Ta, 4.5% Al, 2.4% Ti, less than 0.01% B, less than 0.01% Zr, 0.07% C, less than 0.1% Hf, 3.0% Re, less than 0.12% Si, up to 0.015 % S, up to 0.02% La, up to 0.02% Y, up to 0.02% Ce, up to 0.02% Nd, up to 0.02% Dy, up to 0.02% Pr, up to 0.02% Gd, balance is Ni, and wherein (La+Y+Ce+Nd+Dy+Pr+Gd) is 0.03%.

11. The composition of claim 1 selected for its creep resistance, ability to be cast as a directionally solidified alloy and comprising 10.0% Cr, 12.0% Co, 0.6% Mo, 4.9% W, 6.0% Ta, 4.5% Al, 2.4% Ti, 0.01% B, 0.0075% Zr, 0.09% C, 0.1% Hf, 3.0% Re, less than 0.12% Si, up to 0.015% S, up to 0.02% La, up to 0.02% Y, up to 0.02% Ce, up to 0.02% Nd, up to 0.02% Dy, up to 0.02% Pr, up to 0.02% Gd, balance is Ni, and wherein (La+Y+Ce+Nd+Dy+Pr+Gd) is 0.03%.

1/2

*FIG. 1**FIG. 2*

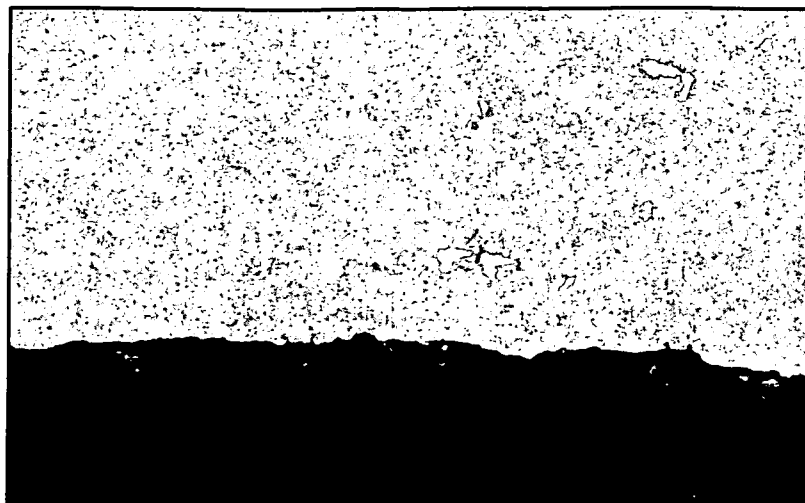


FIG. 3

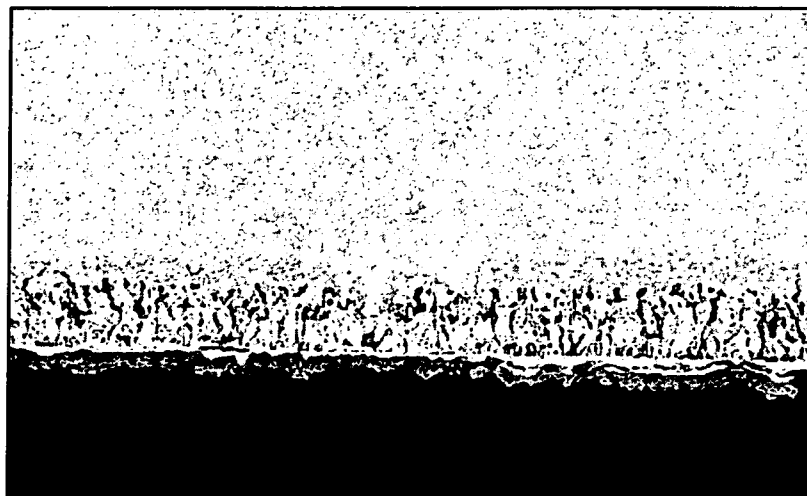


FIG. 4

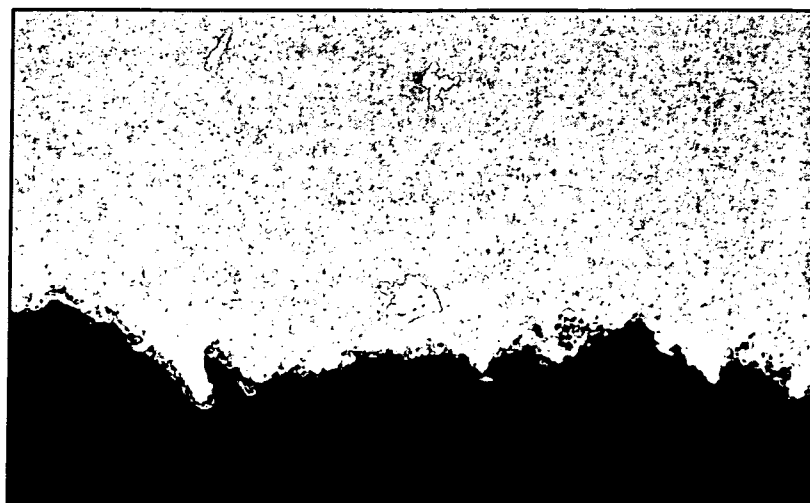


FIG. 5