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NICKEL BASE ALLOY

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This invention relates to nickel base alloys, and more particularly, to a solid solution type nickel base alloy of improved oxidation resistance and fabricability.

Presently available wrought nickel base alloys can be divided into two general classes: Ni-Cr-Al-Ti and Ni-Cr-Fe-Mo-W. The first class of alloys are "precipitation strengthened" by the formation of Ni_3 (Al, Ti) and depend on their aluminum and chromium content for oxidation resistance. Although the Ni-Cr-Al-Ti alloys are strong below 1600° F., their mechanical properties at higher temperatures become comparable to alloys of the Ni-Cr-Fe type which are "solution-strengthened" by Mo and/or W. In addition, the solution-strengthened Ni-Cr-Fe type alloys can contain larger amounts of chromium and thus are more oxidation resistant, especially at high temperatures.

A principal object of the present invention is to improve the oxidation resistance of the Ni-Cr-Fe-Mo-W type alloys.

Improved compositions of this type are critical to the construction of improved propulsion systems for aircraft as well as for high temperature processing equipment. In such systems and equipment, the alloys are generally utilized in those components exposed to the highest temperatures, for example, as inlet guide vanes and combustor sections in jet engines, doors and fittings on furnaces, as well as catalytic trays or reaction vessels for certain chemical processes.

Because of the high chromium content of the solution-strengthened type alloys and the presence of silicon, alloys of such compositions exhibit relatively good oxidation resistance for a nickel base alloy. However, still greater oxidation resistance is required for application such as in advanced gas turbine apparatus. Because of the embrittlement which would result from the increase of the chromium level, and the unacceptable low strength, low melting point and embrittlement which would be associated with any further increases in the silicon content, it has not been possible to improve the existing degree of oxidation resistance of solution strengthened type nickel base alloys within the present limits of the alloy constituents.

The above and other objects and advantages of the present invention will be more clearly understood from the following description and examples which are not meant as limitations on the scope of the present invention.

Briefly, one form of the present invention involves an improvement in a nickel base alloy of the solution strengthened type consisting essentially of the elements, Cr, Mo, Fe with the balance nickel and incidental impurities in which has been included from 0.05 to less than 0.3 weight percent lanthanum. In a preferred form, the alloy of the present invention consists essentially of, by weight, 20–23% Cr, 8–10% Mo, 17–20% Fe, up to 2.5% Co, up to 0.15% C, up to 2% W, 0.05 to less than 0.3% La with the balance Ni and incidental impurities.

In another form, the present invention contemplates the provision of the above alloy forms to which the La has been added during melting as one of the materials Ni_5La, $LaFe_5$, $LaCo_5$, $LaAl_2$, $LaSi_2$, LaC_2 and $LaCu_6$, preferably Ni_5La in the specific form of the present invention.

Although the element lanthanum along with cerium and other rare earth elements have been added to nickel base alloys to improve mechanical properties such as rupture strength at high temperatures or to improve electrical resistance characteristics, prior reports did not recognize the different kinds of effects which can be achieved through the inclusion of lanthanum in a solution strengthened type nickel base alloy which does not include the elements titanium and aluminum. It has been recognized, unexpectedly, that with regard to oxidation resistance, there is a different kind of oxide product which results from the oxidation of a nickel base alloy precipitation hardened through Al and Ti and a solution strengthened type nickel base alloy to each of which has been added the element lanthanum or cerium. The addition particularly of lanthanum to the solution strengthened type Ni-Cr-Fe alloys increases the rate of incorporation of chromium in the alloy into the scale. Through this thermodynamic effect, the amount of chromium in the surface oxide is increased to the point that a very protective, tightly adherent scale of almost pure Cr_2O_3 results. In effect, the alloy oxidizes as if it possessed a much higher chromium content than could be tolerated by limits of strength and fabricability. However, the extent to which this thermodynamic effect can be used is limited based on fabricability.

In order to more fully understand this effect, two alloys which are typical of the two classes of nickel base alloys discussed were modified by additions of both Ce and La. The following Table I gives the composition of these two alloys in the unmodified form. Alloy A is typical of the precipitation hardened type including the elements Ti and Al whereas Alloy B is typical of the solution strengthened type not including Al and Ti.

TABLE I.—Ni BASE ALLOY WITH INCIDENTAL IMPURITIES

[Percent by weight]

	Alloy A	Alloy B
Cr	18–20	20.5–23.
Mo	9–10.5	8–10.
Ti	3–3.3	
Al	1.4–1.6	
Co	10–12	2.5 max.
Fe	5. max.	17–20.
C	.12 max.	.15 max.
W		2 max.
B	.01 max.	
Si	.5 max.	1 max.
Mn	.1 max.	1 max.

Examples of Alloys A and B along with their modifications including La and Ce were exposed at 1800° F. and the resultant weight-gain was determined. These data are given in the following Table II and along with the condition or type of surface oxide coating which resulted from the oxidation test.

TABLE II.—OXIDATION TESTS AT 1800° F.

Alloy	Weight gain (mg./cm.²)		Surface Oxide Coating Condition
	24 hrs.	100 hrs.	
Alloy A	1.79	3.45	Spalled.
Alloy A+0.1 Ce	1.51	3.86	Do.
Alloy A+0.1 La	1.56	5.17	Very adherent.
Alloy B	0.82	1.72	Spalled.
Alloy B+.5 Ce	0.60	0.84	Very adherent.
Alloy B+.5 La	0.40	0.68	Do.

Table II shows the different kind of effect resulting from the addition of Ce and La to the two classes of nickel base alloys discussed. In addition, it is to be noted that the addition of Ce to Alloy A results in a spalled coating whereas the addition of La to Alloy A results in a very adherent type of coating. This shows that a different type of mechanism exists with regard to the reaction of these two rare earth elements on precipitation hardening nickel base alloys. On the other hand, the addition of Ce and La to Alloy B results in a very adherent coating. The oxidation resistance of La additions, however, are unexpectedly greater than those resulting from the addition of Ce.

Although the oxidation resistance of Alloy B was generally improved by additions up to 0.5 weight percent La, the fabricability of the alloy was different for varying amounts of La. For example, Alloy B was modified with additions of 0.05, 0.07, 0.15 and 0.3 weight percent additions of La. It was found that Alloy B including 0.3 weight percent addition of La was not fabricable whereas the other modifications were even more fabricable than the unmodified alloy. These modifications within the range of 0.05 to less than 0.3 weight percent lanthanum were cold rolled at a reduction of about 25% per pass whereas Alloy B itself and Alloy B modified with 0.3 weight percent La could not be readily cold rolled. Thus the improvement in fabricability which might have been generally concluded from prior references is not generally applicable throughout the range of additions of La to nickel base alloys.

In order to more fully study the mechanical properties of the alloy of the present invention, two 15 pound heats were vacuum melted and reduced to 0.060 inch sheet without difficulty. During initial melting trials it was found that preparation of these alloys through the addition of elemental lanthanum does not result in the retention of any appreciable lanthanum. Lanthanum (M.P. 1688° F., density 0.224 lb./in.^{3}) is a highly reactive metal lighter than nickel (M.P. 2647° F., density 0.322 lb./in.^{3}) and with a much lower melting point.

However, it was found that the high melting point and comparable density of Ni_5La (M.P. 2410° F., density 0.302 lb./in.^{3}) allows the controlled and economical alloying of lanthanum with nickel base alloys. Other lanthanum materials having similar properties and which can be used according to the tolerance of the alloy composition being melted to add La to the alloy are $LaFe_5$, $LaCo_5$, $LaAl_2$, $LaSi_2$, LaC_2 and $LaCu_6$. During the melting of the alloy of the present invention, 0.15 weight percent La was added as Ni_5La. The resulting composition was, by weight, 22.1% Cr, 18.2% Fe, 9.9% Mo, 1.2% W, 0.8% Si, 0.15% C, 0.067% La with the balance essentially nickel and impurities. This indicates a 50% La recovery. The rest of the vacuum melting procedure was that used in standard practice; namely, pumping down to produce a vaccum, melting the base or base and major addition (e.g.: Ni or Ni and Cr); carbon deoxidation if necessary; addition of minor alloying elements; homogenization; then addition of La material at least 5–10 minutes before pouring.

A comparison of the oxidation resistance between this particular form of the present invention and Alloy B are shown in the following Table II.

TABLE III.—400 HR. OXIDATION COMPARISON

Temp., ° F.	Internal Oxidation Depth (mils/side)	
	Present Invention	Alloy B
1,600	0.18	0.40
1,800	0.96	1.50
2,000	1.60	3.05
2,200	4.10	7.60

The following mechanical properties are those of the above identified specific form of the alloy of the present invention.

TABLE IV.—MECHANICAL PROPERTIES

TENSILE

[Solutioned 15 min. at 2175° F.+aged 48 hrs. at 1400° F.]

Temp. (° F.)	UTS (K s.i.)	0.2% YS (K s.i.)	Percent El (in./in).
Room	138	108	10.2
1,400	66	58	46.5
1,600	35	29	40.4
1,800	13		63.5

STRESS RUPTURE

Temp. (° F.)	Stress (K s.i.)	Life (hrs.)	Percent El (in./in.)
1,650	7.5	130	47.4
1,800	3.5	115	54.7
1,900	2.0	72	97.4

In Table IV "UTS" means "ultimate tensile strength"; "O.2% YS" means "'0.2% Yield Strength"; "% El" means "% Elongation" based on a specimen having a gage length of 1 inch; and "K s.i." means "thousands of pounds per square inch."

Thus the addition of the element lanthanum within the range of 0.05 to less than 0.3 weight percent and preferably by the new method of adding La as Ni_5La, results in a different kind of oxidation improving mechanism and different effect on fabricability within the solution strengthened type of nickel base alloys and between precipitation strengthened nickel base alloys and solution strengthened nickel base alloys.

Although the present invention has been described in connection with specific examples, it will be understood by those skilled in the art the variations and modifications of which the present invention is capable. For example, it will be understood that the addition of La may carry some Ce because of their occurrence in nature and the production practicality of making less costly types of additions. However since the presence of Ce will reduce the amount of the preferred La addition which can be added without incurring deleterious effects on fabricability, the presence of Ce and other rare earths in such commercial alloy additions as Mischmetal is deleterious to the maximum properties of the alloy.

What is claimed is:

1. A nickel base alloy of improved oxidation resistances and good fabricability consisting essentially of, by weight: 20–23% Cr; 8–10% Mo; 17–20% Fe; 0.05 to less than 0.3% La; up to 2.5% Co; up to 0.15% C; up to 2% W; with the balance Ni and incidental impurities.

2. A nickel base alloy of improved oxidation resistances and good fabricability consisting essentially of, by weight: 22% Cr; 10% Mo; 18% Fe; 0.07% La; up to about 1% W; up to about 1% Si; up to about 0.15% C; with the balance Ni and incidental impurities.

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