

- [54] **HEAT-RESISTANT AND CORROSION-RESISTANT HIGH CHROMIUM-NICKEL ALLOY**
- [75] Inventors: **Kazumi Shimotori; Hirokazu Tokoro**, both of Kawasaki; **Shinichi Nakamura; Katsuhiko Kawakita**, both of Yokohama, all of Japan
- [73] Assignee: **Tokyo Shibaura Electric Co., Ltd.**, Kawasaki-Shi, Japan
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- [58] Field of Search **75/171, 170, 134 F; 148/32, 32.5**

[56] **References Cited**
UNITED STATES PATENTS

2,570,193	10/1951	Bieber et al.	75/171
2,809,139	10/1957	Bloom et al.	75/171
3,015,558	1/1962	Grant et al.	75/171

Primary Examiner—Richard O. Dean
Attorney, Agent, or Firm—Oblon, Fisher, Spivak, McClelland & Maier

[57] **ABSTRACT**

A heat-resistant and corrosion-resistant high chromium-nickel alloy, consisting of 32 to 40 percent by weight chromium, 2 to 9 percent by weight tantalum, 2 to 5 percent by weight molybdenum, 0.5 to 3 percent by weight (aluminum + titanium), 0.05 to 0.5 percent by weight carbon, 0.025 to 0.35 percent by weight boron, with the remainder being substantially nickel and incidental impurities is provided.

This alloy is not only characterized by excellent heat-resistant properties and excellent corrosion-resistance, but is also characterized by very great mechanical strength properties at elevated temperatures, and has good high temperature workability so that it can be formed by hot forging techniques. Hence, this alloy is suitable for the construction of parts which require great mechanical strength properties at elevated temperatures, such as gas turbine blades which operate under low grade residual fuel oil combustion.

1 Claim, No Drawings

HEAT-RESISTANT AND CORROSION-RESISTANT HIGH CHROMIUM-NICKEL ALLOY

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a heat-resistant and corrosion-resistant high chromium-nickel alloy.

2. Description of the Prior Art

Heretofore, industry has relied on nickel base super alloys, such as those strengthened by γ' (Gamma prime)-Ni₃, (Al, Ti) phase, and cobalt base super alloys, for applications requiring good heat-resistant properties.

An increasing demand has been developing, however, for alloy materials which not only have excellent high temperature mechanical properties, but which also possesses excellent corrosion resistance at elevated temperatures. Such an alloy would find wide application in the chemical processing industry and as structural material in the construction of thermal engines.

Heretofore, attempts were made to improve the anti-oxidative properties of conventional super alloys by the incorporation of increased amounts of chromium. The chromium content, however, is limited by the fact that added quantities of chromium to conventional alloys will adversely affect the high temperature mechanical properties.

In general, the maximum amount of chromium contained in the alloy was about 28 percent by weight, and usually no more than 20 percent by weight. While these additional quantities of chromium did have some beneficial effect in enhancing anti-oxidative properties, it was at best a compromise between enhanced anti-oxidative properties and reduced high temperature mechanical strength.

A need exists, therefore, for a high chromium-nickel alloy which is characterized by excellent heat resistance, excellent corrosion resistance and strong mechanical strength at elevated temperature.

SUMMARY OF THE INVENTION

Accordingly, it is one object of this invention to provide a high chromium-nickel alloy, which possesses excellent heat-resistance, excellent corrosion-resistance and good high temperature mechanical strength properties, and has good high temperature workability, so that it can be hot forged.

Another object of this invention is to provide a structural material which is satisfactory for application in the construction of parts which will be subjected to high temperature and high stress service, such as gas turbine blades for turbines using low grade residual fuel oils.

These and other objects have now herein been attained by providing a high chromium-nickel alloy consisting of 32 to 40 percent by weight of chromium, 2 to 9 percent by weight tantalum, 2 to 5 percent by weight molybdenum, 0.5 to 3 percent by weight (aluminum + titanium), 0.05 to 0.5 percent by weight carbon, 0.025 to 0.35 percent by weight boron, with the remainder being substantially nickel and incidental impurities. In one embodiment, the alloy of this invention may be a mixture of manganese, silicon, calcium, magnesium, rare earth elements and scavenger such as Misch metal.

DETAILED DESCRIPTION OF THE INVENTION

The effect of each element contained in the alloy of this invention is as follows.

Chromium, (aluminum + titanium) and boron provide good high temperature corrosion-resistance. If the chromium content exceeds the upper limit of 40 percent, an α phase may appear in large quantities in solidification of the alloy. If the chromium content is less than 32 weight percent, satisfactory corrosion-resistance will not be obtained.

Chromium, tantalum, molybdenum and (aluminum + titanium) improve the high temperature mechanical strength. In particular, tantalum has an outstanding effect on the high temperature mechanical strength.

The use of tantalum enables significant increases in high temperature mechanical strength while the use of chromium enables good corrosion-resistance. If the alloy contains greater than 9 weight per cent tantalum, there will be little increase in high temperature mechanical strength.

The addition of 5 weight per cent molybdenum can render the alloy brittle because of the formation of a Sigma (σ) phase over long periods of heating. Also, it renders the alloy more corrosive to high temperature oxidation.

(Aluminum + titanium) are the most effective additions to improve mechanical strength. The effectiveness of each of aluminum and titanium on the mechanical strength and corrosion-resistance is nearly equal. However, if amounts of greater than 3 weight percent are used, the alloy can become brittle and the long time stress rupture strength will diminish due to the appearance of an α phase.

Carbon will decrease hardness of the alloy and increase elongation and is essential for long time stability of creep strength. More than 0.5 weight percent carbon, however, is undesirable because it will reduce the corrosion resistance of the alloy.

Comparatively, the boron content of the alloy of this invention is greater than used in conventional alloys. If the boron content falls to below 0.025 weight percent, however, its effectiveness is reduced. On the contrary, if the boron content exceeds 0.35 weight percent, the alloy will become brittle.

The alloy of this invention, therefore, is characterized by excellent high temperature corrosion-resistance and excellent high temperature mechanical strength.

At high temperatures, the alloy of the invention will form a Gamma (γ) phase matrix. Accordingly, it is desirable to heat treat the alloy to stabilize the structure, at a temperature adjacent to the use temperature to form the Gamma (γ) phase.

Having now generally described the invention, a further understanding can be obtained by reference to certain specific examples which are provided herein for purposes of illustration only and are not intended to be limiting unless otherwise specified.

EXAMPLE 1

In Table I, "A" refers to the present invention and "B" refers to the prior art.

Each mixture of the component in the composition as shown in Table I was weighed into an alumina crucible and was melted by use of high frequency heating. The molten mass of alloy obtained was cast into a metal mold to form the shape of a rod. After solution-treating

at a temperature of 1,220°C. for 4 hours, the rod was cooled in air. The test pieces were cut from the sound portion of the rod by X-ray analysis. These pieces were prepared by aging to effect stabilization of the structure at a temperature of 900°C. for 2 hours. Thereafter, the test pieces were tested for ultimate tensile strength at elevated temperatures and creep rupture (or stress rupture). The results of these tests are shown in Table II. It was found that the optimum additions of Ta, Nb, (Al + Ti), C and B provided remarkable increases in the high temperature mechanical strength.

ple was weighed into an alumina crucible and was melted by high frequency heating. The molten mass of alloy obtained was cast into a metal mold to form the shape of a rod. After solution-treating at a temperature of 1,220°C. for 4 hours in order to form the f.c.c. Gamma (γ) single phase structure, the rod was permitted to cool in air. The test pieces were cut from the sound portion of the bar (or rod) by X-ray analysis, and were aged to stabilize the structure, at a temperature of 900°C. for 2 hours. Thereafter, the test pieces were subjected to a corrosion test with a synthetic ash at a

TABLE I

Sample No.	Compositions of Samples Composition (% by weight)							Ni
	Cr	Al	Ti	Mo	Ta	C	B	
A-131	36	0.5	1	4	5	0.2	0.2	Balance
A-76	32	1	1	4	5	0.2	0.2	do.
A-77	40	1	1	4	5	0.2	0.2	do.
A-36	36	1	1	4	2	0.2	0.2	do.
A-72	36	1	1	4	8	0.2	0.2	do.
B-75	36	1	1	0	5	0.2	0.2	do.
A-32	36	1	1	5	5	0.2	0.2	do.
B-73	36	0	0	4	5	0.2	0.2	do.
A-127	36	0	0.5	4	5	0.2	0.2	do.
A-135	36	1.5	1.5	4	5	0.2	0.2	do.
B-39	36	1	1	4	5	0	0	do.
A-78	36	1	1	4	5	0.05	0.2	do.
A-79	36	1	1	4	5	0.5	0.2	do.
A-92	36	1	1	4	5	0.2	0.025	do.
A-54	36	1	1	4	5	0.2	0.35	do.
B-90	36	1	1	4	5	0.2	0.5	do.
B-38	36	1	1	4	1	0	0	do.

TABLE II

Sample No.	Results of Tests			
	800°C. 20 kg/mm ² creep		Tensile test at 800°C. in the pull rot velocity of 25 mm/min.	
	Rupture time (hr.)	Elongation (%)	Tensile strength (kg/mm ²)	Elongation (%)
A-131	85.0	10.7	68.0	10.0
A-76	32.7	4.8	66.2	8.2
A-77	72.6	1.9	70.9	4.1
A-36	34.5	2.6	65.3	13.4
A-72	68.1	2.5	68.1	15
B-75	20.5	3.6	58.0	0
A-32	82.4	3.8	76.4	1.2
B-73	5.4	23.1	24.7	32.1
A-127	30.5	21.2	48.1	12.7
A-135	46.3	5.7	89.1	2.2
B-39	65.0	0	71.3	3.5
A-78	64.1	4.3	68.1	8.1
A-79	78.3	9.2	60.1	5.0
A-92	62.1	4.5	56.0	11.0
A-54	61.3	3.6	60.3	2.6
B-90	18.3	0	69.3	3.0
B-38	14.9	2.3	57.6	4.3

Moreover, it was found that the additions of C and B provided remarkable increases in the character of long time creep strength.

TABLE III

Sample No.	Results of Creep Tests	
	Rupture time (hr.) 800°C. 15 kg/mm ² creep	
A-131	987.1	
B-39	315.9	
B-38	134.7	

EXAMPLE 2

In this example, the effects of some elements on corrosion-resistant properties at high temperatures were studied. Namely, each sample was prepared by adding various elements to 36% Cr—Ni alloy base. Each sam-

ple was weighed into an alumina crucible and was melted by high frequency heating. The molten mass of alloy obtained was cast into a metal mold to form the shape of a rod. After solution-treating at a temperature of 1,220°C. for 4 hours in order to form the f.c.c. Gamma (γ) single phase structure, the rod was permitted to cool in air. The test pieces were cut from the sound portion of the bar (or rod) by X-ray analysis, and were aged to stabilize the structure, at a temperature of 900°C. for 2 hours. Thereafter, the test pieces were subjected to a corrosion test with a synthetic ash at a

temperature of 1,100°C. The corrosive weight loss after heating for 30 hours is shown in Table IV. As shown in that Table, the sample of this invention showed greater corrosion resistance than U-500 (a conventional Ni base alloy). The relation between the amount of additional elements and the corrosive weight loss of alloy is shown industrially by the empirical formula:

$$\Delta W = -155 + 3.0 \text{ Cr}\% + 5.0 (\text{Al}\% + \text{Ti}\%) + 1.5 \text{ Co}\% + 75\text{B}\% + 25.5\text{C}\% - 1.6 (\text{Mo}\% + \frac{1}{2}\text{W}\%) - 0.5 \text{ Ta}\% - 4.0 \text{ Nb}\% \text{ at } 1,100^\circ\text{C.}$$

Where ΔW (mg/cm²/hr.) is the corrosive weight loss per unit surface area per unit hour at 1,100°C.

Chromium imparts corrosion-resistance to these alloys of this invention, and saves 90 mg/cm² of corrosive weight loss per unit weight percent. Also, (aluminum + titanium) and boron effectively improve the corrosion-resistance.

TABLE IV

Sample No.	Results of corrosion test with a synthetic ash* Corrosion loss (mg/cm ²) after applying a synthetic ash* onto the surface of the samples and maintaining at 1,100°C. for 30 hours
A-131	940
S-816 (control)	4,584
U-500 (control)	2,770

*synthetic ash (20% by weight Na₂SO₄+ 80% by weight V₂O₅).

Where S-816 (control): 0.38 weight % C, 20 weight % Cr, 20 weight % Ni, 4 weight % Mo, 4 weight % W, 4 weight % Nb, 4 weight % Fe, remainder Co.

U-500 (control): 0.08 weight % C, 18 weight % Cr, 19 weight % Co, 4 weight % Mo, 2.9 weight % Al, 0.006 weight % B, 0.05 weight % Zr, remainder Ni.

From the results as above mentioned, it was found that Ta, Mo, (Al + Ti), C and B were substantially effective in achieving a high Cr—Ni alloy having the desired properties as enumerated in the objects.

In general, Nb can be substituted for Ta, Zr can be substituted for B and W can be substituted for Mo. These substitutions, however, are not as effective as the preferred components. Namely, Nb and Zr are significantly inferior to Ta or B in corrosion-resistance. Moreover, the effect of W on the tendency to promote Sigma (σ) phase is different from that of Mo. Never-

theless, if desired, up to 10 to 20 percent by weight of the Ta, B or Mo may be substituted by the elements Nb, Zr and W as above mentioned, and the similar characteristics will still be obtained. Cobalt, in amounts of less than a few percent, may be substituted for nickel.

It is necessary to avoid the addition of iron (Fe) to the alloy. If more than 2 to 3 percent by weight iron (Fe) is added to the alloy, the alloy will be severely hardened and will be more brittle in mechanical properties.

Having now fully described the invention, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made thereto without departing from the spirit or scope of the invention. Accordingly,

What is claimed as new and intended to be covered by letters patent is:

1. A heat-resistant and corrosion-resistant high chromium-nickel alloy consisting essentially of 36 to 40 percent by weight chromium, 5 to 9 percent by weight tantalum, 2 to 5 percent by weight molybdenum, 0.5 to 3 percent by weight (aluminum + titanium), 0.05 to 0.5 percent by weight carbon, 0.025 to 0.35 percent by weight boron, and the remainder being substantially nickel and incidental impurities.

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