United States Patent

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[54] **MAGNETIC ALLOY**
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[56]   **References Cited**
          UNITED STATES PATENTS

2,829,048	4/1958	Cochardt et al.	148/158 X
2,981,620	4/1961	Brown et al...................	148/32.5 X
3,331,715	7/1967	Bulino et al...................	148/158 X
3,415,643	12/1968	Freche et al.	148/3 X

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ABSTRACT: A cobalt base alloy is described having highly desirable mechanical and magnetic properties which alloy is suited for use at temperatures of up to 750° C. The cobalt base alloy contains nickel, iron, aluminum, tantalum, zirconium and boron, and optionally may contain titanium, niobium and beryllium.

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MAGNETIC ALLOY

This is a continuation-in-part of application Ser. No. 584,368 filed Oct. 5, 1966 now abandoned.

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of section 305 of the National Aeronautics and Space Act of 1958, public law 85-568 (72 STAT. 435; 42 U.S.C. 2457).

This invention is directed to a cobalt-base alloy and to members made from the alloy which, after appropriate heat treatment, exhibit highly desirable magnetic and mechanical characteristics.

In the hostile, near-vacuum environment of space, where the heat generated by the components of spacecraft and space stations, is difficult to dissipate, such components will be expected to function at elevated temperatures in excess of 600° C. In particular, the rotors for electric motors and generators aboard a spacecraft or space station would be required to function even though the component or ambient temperature reached such high levels.

The majority of creep resistant alloys which have been developed for applications at temperatures in excess of 600° C. are nonmagnetic, even though such alloys are generally either iron-nickel- or cobalt-base. The ferritic creep resistant alloys, which do possess ferromagnetic properties, have a temperature ceiling for operation of about 500° C. Even after relatively short service at temperatures above 500° C. these ferritic alloys suffer a great loss in their mechanical strength. The most recent advances in the art indicate that the temperature ceiling for operation of ferritic alloys can be increased to some extent, but that the maximum operating temperature for even these newest alloys will apparently not exceed 600° C.

In U.S. Pat. No. 2,829,048, issued Apr. 1, 1958, there is disclosed a cobalt-base high damping alloy which is characterized by substantial creep resistance at temperatures up to 650° C. and is particularly suitable for use in members such as turbine blades. This prior art alloy comprises essentially, by weight, from 65 percent to 88 percent cobalt, 1 percent to 2 percent titanium, from 0.1 percent to 1.5 percent aluminum, the total of aluminum and titanium being at least 1.5 percent, carbon below 0.1 percent and preferably not exceeding 0.05 percent, and the balance, at least 8 percent, and preferably between 16 percent and 25 percent, being nickel with incidental impurities not exceeding 1 percent. This alloy is ferromagnetic to a substantial degree at temperatures up to 650° C.

It is the object of this invention to provide alloy members having high creep resistance combined with ferromagnetic properties at temperatures up to 750° C.

It is another object of this invention to provide a precipitation hardened cobalt-base alloy member containing predetermined amounts of nickel, iron, aluminum, tantalum, zirconium and optionally boron, the alloy exhibiting high creep resistance and good ferromagnetic properties at temperatures up to 750° C.

It is a further object of this invention to provide a precipitation hardened cobalt-base alloy member containing predetermined amounts of nickel, iron, aluminum, tantalum with one or both of the elements titanium and niobium, zirconium and optionally boron, the alloy having high creep resistance and good ferromagnetic properties at temperatures in excess of 600° C.

Other objects of the invention will, in part, be obvious and, in part, will appear hereinafter.

The alloy composition disclosed provides a high creep resistance and good ferromagnetic properties including high permeability at relatively high ambient temperatures. This alloy is cobalt-base with a face centered cubic lattice, which is precipitation hardened by a γ' (gammaprime) phase of the type Ni_3Al. The nickel atoms in this phase are in part replaced by cobalt atoms and the aluminum atoms are replaced in part by tantalum atoms, or by a suitable combination of tantalum and titanium, tantalum and niobium, or tantalum with both titanium and niobium.

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More particularly, the invention is directed to a precipitation hardenable cobalt-base alloy characterized by good creep resistance and ferromagnetic properties at temperatures up to 750° C., the alloy comprising 10 percent to 20 percent by weight of nickel, 5 percent to 10 percent by weight of iron, 1.2 percent to 2 percent by weight of aluminum, 3 percent to 6 percent by weight of tantalum, the total of aluminum and tantalum not exceeding 7 atom percent, and the ratio of aluminum to tantalum as expressed in atom percent being between 1:1 and 2:1, from 0.1 percent to 0.3 percent by weight of zirconium, from optional to 0.002 percent by weight of boron and the balance cobalt except for small amounts of incidental impurities. The above-described alloy may also contain an effective amount of beryllium up to 0.2 percent by weight as a strengthener.

A preferred alloy composition comprises from 12 percent to 16 percent by weight of nickel, 5 percent to 6 percent by weight of iron, 1.2 percent to 1.5 percent by weight of aluminum, 5 percent to 6 percent by weight of tantalum, from 0.1 percent to 0.3 percent by weight of zirconium, from 0.0005 percent to 0.002 percent by weight of boron and the balance cobalt except for small amounts of incidental impurities.

As indicated above, the total amount of the hardening elements tantalum and aluminum is limited in the alloys of the invention to 7 atom percent of the alloy. Titanium and niobium may be used in conjunction with tantalum and aluminum up to a maximum of 2 percent by weight of each with beneficial result, however, the total amount of these four elements in the alloy should not exceed 7 atom percent with the atom ratio of aluminum to the sum of the other elements being between 1:1 and 2:1. In any case, tantalum is present in the alloys of this invention in an amount of from 2.5 percent to 4 percent by weight when used with titanium and/or niobium.

One aspect of the invention involves the improvement obtained by the substitution of tantalum in whole or in part for the titanium employed in alloys of this type which rely for their improved properties upon precipitation of the γ' phase. As has been indicated, the tantalum replaces at least some of the aluminum in the γ' precipitate. By this addition of tantalum an improvement of strength is achieved in the alloy comparable in magnitude to that obtained with a titanium addition, without, however, as great a sacrifice in magnetic properties.

Another aspect of the invention involves measures to avoid or suppress the occurrence of any discontinuous or cellular grain boundary precipitate. A cellular precipitate can be developed in precipitation hardened cobalt-base alloys and has a remarkable effect in increasing the damping capacity of these alloys. Methods for obtaining such cellular precipitates in cobalt-base alloys, and the improved damping capacity thereby achieved, has been pointed out in copending U.S. Pat. No. 3,331,715 which issued July 18, 1967 in the names of Bulina and Brown.

In addition to its beneficial effect upon damping properties, a cellular precipitate also has the effect of improving the short time tensile properties. However, the long time creep properties are adversely affected by such precipitate, and this is seriously detrimental in the contemplated applications of this alloy. Though a small amount of such cellular precipitate for example, less than 3 percent, by volume can be tolerated in the alloy, the development of a greater volume of discontinuous precipitate at the grain boundary during the aging procedure or during service must be avoided.

For the above reason, the total amount of additions which tend to promote the formation of the cellular precipitate must be carefully controlled. Since aluminum and tantalum play a large role in the formation and in the promotion of the cellular precipitate structure, it has been found that the total amount (by atom percent) of aluminum plus tantalum, or aluminum plus tantalum, titanium and niobium when these latter elements are present, should not exceed 7 percent, and the ratio of aluminum atoms to tantalum (or tantalum plus titanium and/or niobium) atoms should be approximately 2:1, but not

TABLE I

[Properties of Co base alloys]

Alloy	Composition, wt. percent	Aged 1 hr. at 750° C., measured at 600° C.			Measured at room temp.			
					Aged 1 hr. at 700° C.		Aged 100 hr. at 700° C.	
		Magn. Mom., c.g.s.	y.s., K.s.i.	H$_c$, oe.	VHN	H$_c$, oe.	VHN	H$_c$, oe.
1-B-V-1	Co-5, Fe-0.27, Zr-14.6, Ni-1.44, Al-1.66, Ti-5.20, Ta	91	102	2.2	320	3.0	388	26
1-B-V-4	Co-5, Fe-0.26, Zr-14.8, Ni-1.25, Al-5.19, Ta	106	93	1.4	296	2.8	343	10.6
1-B-V-5	Co-5, Fe-0.27, Zr-9.85, Ni-1.60, Al-5.3, Ta	105	89	1.3	282	2.7	320	9.3
1-B-V-6	Co-5, Fe0.24, Zr-15.0, Ni-1.19, Al-1.66, Ti-3.1, Ta	100	92	1.5	293	2.9	338	14.2
1-B-S-2	Co-5.2, Fe-15.2, Ni-4.98, Ta-1.36, Al-0.12, Zr-0.065, Be-0.002, B	102	88		303	2.9	336	18.7
1-B-S-1	Co-5.8, Fe-15.3, Ni-4.98, Ta-1.28, Al-0.21, Zr-0.002, B	104	88	0.722	308	3.5	331	14.7
Alloy N	Co-0.3, Fe-0.2, Zr-0.3, Si-0.3, Mg-23.4, Ni-0.4, Al-1.7, Ti	100*	85*	6.31*	200	5.5	302	17.0

*Commercial heat treatment.

Alloy N is a commercial damping alloy.

less than 1:1. Since small amounts of zirconium tend to suppress the formation of cellular precipitate, the presence of up to 0.5 percent and preferably about 0.1 percent to about 0.3 percent zirconium is highly desirable. Boron may optionally be present in an amount of up to about 0.002 percent and is effective for suppressing the formation of cellular precipitate. When boron is present the combined zirconium and boron should not exceed about 0.5 percent.

Since cellular precipitate is the product of prolonged aging in cobalt-base alloys, short time aging of 1 to 5 hours at temperatures between 700° C. and 800° C. is preferred to produce precipitation hardening. A two-stage aging treatment may also be employed; the first stage being the above outlined short time aging, and the second stage being an aging treatment at temperatures below 700° C. for several hours. The two-stage aging treatment provides a means for obtaining higher short time tensile strength while avoiding development of cellular precipitate.

Still another novel aspect of the invention relates to the suppression of the cobalt-rich hexagonal ε (epsilon) phase during cooling of the alloy to room temperature. The existence of such an ε phase in the matrix increases the coercive force of the alloy member to a substantial degree, and therefore would decrease the permeability at room temperature. To accomplish the suppression of this undesirable ε phase at least 5 percent by weight of iron is added.

The alloys of the invention can be produced by melting the ingredients by nonconsumable arc melting or in a vacuum induction furnace. For example, following the nonconsumable arc melting procedure employing a tungsten electrode, the alloy was cast into ingots under an argon atmosphere at a pressure of 200 Torr. The ingots were hot rolled at 1,100° C. and then cold rolled to sheets.

In the vacuum induction melting procedure the alloy ingredients were melted and cast into 15 pound ingots using an MgO crucible in a vacuum induction furnace operating at 10 kilocycles per second. In this last instance the basic alloy components iron, nickel, and cobalt were melted in the crucible under a vacuum of 2×10^{14} Torr. The alloying elements were then added as master alloys under argon at a pressure of 280 Torr. The molten alloy composition was cast at the same low pressure of argon in an iron mold which yielded a rod-shaped ingot 5 cm. in diameter. In each case this ingot was remelted by using it as a consumable electrode in a vacuum arc furnace at a vacuum of 1×10^{14} Torr. An ingot of about 7.5 cm. diameter was obtained. After removing the surface layer of the ingot, the ingot was hot forged at 1,150° C. to a bar of 25×50 mm. cross section. From each of these bars a piece was cut off, hot rolled at 1,050° C. and then cold rolled to sheet.

The final heat treatment of the cold rolled sheet consists of a homogenization anneal of 1,000° C. or higher in a preheated furnace with argon or helium atmospheres, followed by moderately rapid cooling (20° to 30° C. per minute). Aging treatments to produce precipitation hardening are carried out in a bath of alkali and alkaline chlorides between 600° C. and 800° C.

Magnetic saturation measurements were taken on small samples (2.5 millimeters in diameter and length). These samples are placed in the gap of a magnet with a field gradient of 1,000 oersteds per centimeter and a mean field of 11,500 oersteds. The measured values are determined with an accuracy of 1 percent, as magnetic moment per gram (σ) in c.g.s. units, which can be converted into magnetic saturation B_s expressed in gauss by $B_s = 4\pi \times \delta \times \sigma$. The density δ is approximately 8.8 grams per cubic centimeter. The values of magnetic moment given below, when multiplied by 110, represent the saturation in gauss with a possible error of 5 percent.

The coercive force was measured on specimens 35 mm. long, 8 mm. wide and 1.5 mm. thick with an accuracy of 2 percent by a precision type magnetic field probe and a magnetizing coil. In the following table of the composition, certain physical and magnetic properties of the alloys of the invention are set forth along with similar data for a damping alloy of the prior art.

The compositions listed in the first column of the above table were obtained by chemical analysis of the ingot. It will be noted that the first four alloys are free of deliberate additions of boron while alloys 1-B-S-2 and 1-B-S-1 have specific boron additions. The next three columns contain properties measured at 600° C., as magnetic moment/g. yield stress at 2 percent offset on flat samples and the coercive force. The last four columns contain the values of hardness and coercive force measured at room temperature during isochronal aging at 700° C. for 1 hour and 100 hours respectively. These values are compared to the commercial damping alloy. It is clear that both the boron containing and boron-free alloys demonstrate a substantial improvement in yield strength, magnetic saturation and coercive force. The listed alloys of the invention do not have detectable discontinuous cellular precipitate, while the commercial damping alloy has such cellular precipitates to the extent of about 15 percent of the observed cross sectional area.

Additional DC and AC magnetic properties were determined for ring-shaped specimens of alloy 1BS1 and are compared with the properties of a commercial damping alloy in table II below.

TABLE II

[Magnetic properties of alloys at elevated temperatures—Ring specimens: $D_0 = 75$ mm., $D_i = 62.5$, 0.625 mm. thick]

	DC Properties			
Alloy	Test temp., ° C.	B $_{(100\ oe.)}$, kg.	B $_{(250\ oe.)}$, kg.	H$_c$ $_{(200\ oe.)}$, oe.
1BS1	650	10.3	11.3	0.722
Alloy N	595	10.3	11.3	20.88

	AC Properties			
Alloy	Test temp., ° C.	B$_{tip}$, kg.	Frequency (cycl/sec.)	P$_{c/lb}$.	P$_{n/lb}$.
1BS1	650	6	400	7.74	8.66
Alloy N	595	6	400	41.3	77

The test temperature in the above table is somewhat higher for the alloy of this invention than for the commercial alloy;

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i.e., the test conditions for IBSl alloy are more rigorous than for Alloy N. Despite this, the DC induction is identical for the two materials and the coercive force is better for the alloy of the invention by a factor of almost 30. As far the AC properties, the core losses are nearly 6 times greater for the commercial alloy and the exciting volt amperes per pound is more than 8 times higher for the commercial alloy than for alloy IBSl.

In the manufacture of this alloy the procedures followed should be similar to those employed in producing super alloys. In order to obtain the magnetic properties as specified, segregations and inhomogeneities are avoided or eliminated during the processing. Vacuum arc melting of the alloy with chill casting is a preferred ingot making process, with long soaking periods at temperatures around 1,200° C. or higher applied before of after hot rolling.

Annealing of the alloy at the final gauge should be done at temperatures in excess of 1,050° C. for a reasonable time with air cooling. The most suitable aging temperatures are between 700° and 800° C. as indicated above.

The alloys of this invention are primarily intended for use in the rotor and stator structures of electrodynamic machines such as motors and generators. While it is common for such structures to be assembled from a plurality of laminations, and the alloys of the invention may be used in this form; it is also contemplated that part or all of the rotor of stator structures may be formed from a solid mass of the alloy of the invention; for example, a forging.

There has thus been provided an alloy composition and processing procedure suitable for making alloy members which retain magnetic properties and good creep resistance at temperatures up to 750° C.

I claim as my invention:

1. A precipitation hardening cobalt base alloy characterized by good creep resistance and ferromagnetic properties at temperatures up to 750° C., consisting essentially of from 10 percent to 20 percent by weight of nickel, from 5 percent to 10 percent by weight of iron, from 1.2 percent to 2 percent by weight of aluminum and from 2.5 percent to 6 percent by weight of tantalum, the sum of aluminum plus tantalum not exceeding 7 atom percent of the alloy, and the ratio of aluminum to tantalum expressed in atomic percent being within the range between 1:1 and 2:1, up to about 0.5 percent by

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weight of zirconium, optional to 0.002 percent by weight of boron and the balance essentially cobalt except for small amounts of incidental impurities.

2. The alloy of claim 1 containing an effective amount of beryllium of up to 0.2 percent by weight.

3. The alloy of claim 1 wherein the tantalum is present within the range between 2.5 percent and 4 percent by weight and at least one metal selected from the group consisting of titanium, niobium and mixtures thereof, said titanium when present not exceeding 2 percent by weight and said niobium when present not exceeding 2 percent by weight, the sum of aluminum plus tantalum plus titanium plus niobium not exceeding 7 atom percent of the alloy, with the ratio of aluminum atoms to tantalum plus titanium plus niobium atoms being within the range between 1:1 and 2:1.

4. The alloy of claim 3 containing an effective amount of beryllium of up to 0.2 percent by weight.

5. A precipitation hardenable cobalt base alloy consisting essentially of from 12 percent to 16 percent by weight of nickel, from 5 percent to 6 percent by weight of iron, from 1.2 percent to 1.5 percent by weight of aluminum, from 5 percent to 6 percent by weight of tantalum, from 0.1 percent to 0.3 percent by weight of zirconium, from 0.0005 percent to 0.002 percent by weight of boron and the balance essentially cobalt except for incidental impurities.

6. The alloy of claim 5 containing an effective amount of beryllium of up to 0.2 percent by weight.

7. A dynamoelectric machine rotor or stator formed of an alloy having the composition of claim 1.

8. The alloy of claim 5 in which there is present at least one metal selected from the group consisting of titanium, niobium and mixtures thereof in which the sum of the aluminum plus tantalum plus titanium plus niobium does not exceed 7 atomic percent and in which the ratio of aluminum atoms to tantalum plus titanium plus niobium atoms is within the range between 1:1 and 2:1.

9. The alloy of claim 8 containing an effective amount of beryllium of up to 0.2 percent weight.

10. The alloy having the composition of claim 1 in which the alloying components are selected to produce a microstructure in the precipitation hardened condition characterized by having less than 3 percent by volume of cellular precipitate.

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