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REFRACTORY ALLOY

Gilbert Cavalier, Saint-Germain-en-Laye, France, assignor to Institut de Recherches de la Siderurgie, Saint-Germain-en-Laye, France

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The present application is a continuation-in-part of my copending application, Ser. No. 319,469, filed Oct. 28, 1963, and entitled "Refractory Alloy," now abandoned.

The present invention relates to an alloy and, more particularly, to a non-ferrous alloy which at relatively high temperatures will resist oxidation and possess a high creep strength.

It is an object of the present invention to provide an alloy which at temperatures of at least 1400° C., and even higher, possesses sufficient creep strength and resistance to oxidation so as to be suitable for use in the construction of heating elements for electrical furnaces, or for castings which will resist the action of oxidizing agents and maintain their strength at elevated temperatures. Alloys according to the present invention give excellent results even when used at temperatures above 1500° C.

It is a further object of the present invention to provide an alloy which in addition to the above-described qualities also possesses a sufficiently low electric resistivity so that it can be used in the manufacture of induction heating elements.

The majority of alloys available up to now for the above-indicated purposes are of such quality that, for instance, induction heating elements made thereof cannot be used at temperatures exceeding 1350° C. and thus, the alloy of the present invention because of its high creep strength and resistance to oxidation even at temperatures of 1400° C. or higher is particularly suitable for the manufacture thereof of heating elements for electromagnetic induction heating devices.

Other objects and advantages of the present invention will become apparent from a further reading of the description and of the appended claims.

With the above and other objects in view, the present invention contemplates a highly temperature resistant alloy, the alloy consisting essentially of 21% to 35% aluminum, 0% to 4% copper, 0% to 4% of at least one metal selected from the group consisting of tungsten, molybdenum, vanadium and chromium, the balance being at least one metal selected from the group consisting of nickel and cobalt, wherein in the absence of copper said at least one metal selected from the group consisting of tungsten, molybdenum, vanadium and chromium is present in an amount of at least 0.2%, and in the absence of said at least one metal selected from the group consisting of tungsten, molybdenum, vanadium and chromium said copper is present in an amount of at least 0.2%.

Surprisingly it has been found that the heat resistance of alloys according to the present invention significantly exceeds the heat resistance of alloys conventionally used for similar purposes. The alloys according to the present invention include the following ranges of composition wherein, as throughout this specification, all percentage figures are percent by weight: 21 to 35 percent of aluminium, 0.2 to 4 percent of copper and the remainder principally at least one of the metals nickel and cobalt. Preferably and especially for the most effective alloys, the composition should be kept within the ranges 21.8 to 32.8 percent aluminium, 0.2 to 4 percent copper and the remainder at least one of nickel and cobalt.

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It has been discovered also that an equally good performance may be obtained by employing in combination with the aluminium and one or both of nickel and cobalt, one or more of Mo, W, V and Cr in amounts of 0.2 to 4 percent. Excellent results are also obtainable when employing 21 to 35 percent aluminium and 0.1 to 4 percent copper along with 0.1 to 4 percent of one or more of the metals Mo, W, V and Cr.

Thus, broadly, the present invention is concerned with a refractory, non-ferrous alloy which comprises at least three metals, namely aluminum with or without Cu and at least one metal each of the two groups described above.

According to one preferred embodiment, the alloy of the present invention is composed of aluminum, nickel and copper and contains between 21.8% and 32.8% of aluminum; between 67% and 78% of nickel; and between 0.2% and 4% of copper.

According to another preferred embodiment, the alloy of the present invention is composed of aluminum, cobalt and copper and contains aluminum in an amount of between 21.8% and 32.8%; cobalt in an amount of between 67% and 78%; and copper in an amount of between 0.2% and 4%.

Another preferred alloy according to the present invention is composed of a mixture in any proportion of the aluminum nickel copper alloy and the aluminum cobalt copper alloy described above.

Mention has been made above that the greater portion of the alloy is principally one or more of nickel and cobalt. This is noted specifically because, while desiring the purest raw materials in the production of these high-temperature alloys there is some limited permissibility of impurities and remainders of deoxidizing additions such as Fe, Mg, Si, Mn, etc. In general the total of such elements should not exceed one percent.

The alloy of the present invention may contain inclusions of oxides of its constituents, particularly of mixed oxides, for instance of Al_2O_3 and NiO, or Al_2O_3 and CoO. These oxides may develop or be developed during the course of melting and alloying or subsequently by exposure to an oxidizing atmosphere at elevated temperature. Specifically, good results have been obtained with a total oxide content of up to 1000 p.p.m. in the form of such mixed oxides.

The copper in all of the above-described compositions may be completely or partially replaced by one or more of the metals molybdenum, tungsten, vanadium and chromium within the indicated proportions. Thus, according to another preferred embodiment of the present invention, the alloy contains in addition to aluminium and nickel or cobalt, copper and at least one of the metals molybdenum, tungsten, vanadium and chromium.

The alloys of the present invention may be advantageously produced by a method according to which first the aluminium and copper are melted together and thereafter the remaining constituents of the alloy are successively introduced while simultaneously the temperature of the molten metal is raised. The operation is advantageously effected in an oxidizing atmosphere. If there are more than one remaining constituent to be introduced, then these remaining constituents preferably are introduced in such sequence that the melting point of the molten metal mixture is prorgessively raised by the introduction of the remaining constituents.

It will be understood that the alloy according to the present invention may be considered a derivative of stoichiometric alloys of aluminium with nickel and/or cobalt. However, it is known that such alloys, consisting essentially of two constituents, due to their high brittleness are not suitable for industrial use at high temperatures.

By introducing, in accordance with the present invention, at least a third or also a fourth or more constituents, i.e., by forming for instance a ternary or quaternary alloy of the qualitative and quantitative composition described above, an alloy is obtained which possesses the resistance to oxidation which is shown by the above-mentioned binary, stoichiometric alloy, but very importantly overcoming the brittleness of this stoichiomertic alloy. Furthermore, by the inclusion of oxides of such constituents, the creep strength of the alloy is improved.

The alloy of the present invention is preferably prepared by first melting the most fusible constituents of the alloy together and thereafter, in a second melting stage, to add the other constituents, particularly cobalt and/or nickel, at a higher temperature, during which second stage the metal is homogenized by stirring. The process of the present invention is efficiently performed by heating the alloy constituents by induction. As the alloy is produced in the presence of an oxidizing atmosphere, such as air, oxides of aluminum and nickel and/or cobalt, mainly mixed oxides of the type Al_1O_3–NiO or

$$Al_2O_3\text{–}CoO$$

will be formed and remain in the alloy.

No care will be exerted to eliminate such oxides as they are not detrimental to the good qualities of the alloy and give it excellent mechanical properties at high temperature.

Within the broad range of maximum and minimum percentages of the individual constituents of the alloy of the present invention, alloys will be obtained suitable for use at a maximum working temperature of at least 1400° C., while alloys within the percentage limits of the preferred ranges will be suitable for industrial use at temperatures of 1500° C. and even higher.

The following examples are given as illustrative only, without limiting the invention to the specific details of the examples.

Example 1

In an induction heated crucible in contact with the surrounding air, a liquid alloy is produced composed of 30% Al, 69% Ni, 1% Cu and 900 p.p.m. of oxides of these metals. With the help of a quartz tube of 4 mm. diameter which is subjected to a progressive partial vacuum, several samples are lifted from the metal bath in the form of small bars.

The thus-formed small bar is heated to 1535° C. and thereafter, while this temperature is maintained, an electric current of 315 amperes and 1.56 volts is passed through the bar for a period of 169 hours during which no recognizable change takes place in the bar. Particularly the weight of the bar does not change in an appreciable manner which proves that the metal is not oxidized except possibly to an extremely low degree. The resistivity of the alloy at 1535° C. was determined to be 49.5×10^{-6} ohm-centimeter.

Example 2

An alloy of the composition Al 29%, Co 70%, Cu 1%, and containing 800 p.p.m. of oxides of these metals is produced in a heated crucible in contact with the surrounding air. In the manner described in Example 1, small sample bars are withdrawn from the molten metal.

The sample bars are then heated at 1620° C. and at that temperature an electric current of 315 amperes is passed through the bars for an entire week. Thereafter, no noticeable change is found in the composition of the bars. Particularly their weights have not changed in an appreciable manner.

Similar experiments were carried out with an alloy of the prior art composition Ni 82%, Al 17%, Cu 1%. This alloy cannot even be used in the manner described in the above examples because it starts to melt partially upon reaching this temperature of 1400° C.

The alloy composition of the present invention is entirely novel and can be used at temperatures which are more than 50° C. higher than those at which the conventional alloys lose their usefulness. The difference of more than 50° C. is very important and one cannot ignore that the calories made available for heat transfer at high temperatures are extremely valuable. It will be understood that the alloy of the present invention is of great interest to the industry in connection with electric resistance heating arrangement.

Without attempting to limit the present invention to any specific theory, it might be assumed that upon solidification of the alloy a conglomerate of crystals is formed, whereby the strength of adherence of the crystals to each other and thus the cohesion of the alloy will be greatly influenced by small amounts of material interposed between adjacent crystals.

In the case of binary alloys of aluminum and nickel or aluminum and cobalt, this interposed material will consist of small amounts of oxides of the alloy forming metals. These oxides have very little power of adhesion and, consequently, there will be little cohesion between the crystals of the binary alloy.

These crystals will consist of for instance Al-Ni formed of a solid solution which may contain an excess of either nickel or aluminum, depending on whether the nickel content is higher or lower than 68%. Similarly, Al-Co crystals are formed of the solid solution whereby, depending on whether the cobalt is present in an amount of more or less than 64%, an excess of nickel or cobalt will remain.

If, in accordance with the present invention, copper and/or one or more of the metals molybdenum, tungsten, vanadium or chromium are incorporated in the alloy, then these additional metals will be located at the interfaces between the Al-Ni or Al-Co crystals. Since the power of adhesion of these additional metals in contact with the binary crystals is much higher than that of the oxides, the presence of these additional metals will greatly increase the cohesion of the crystals and thus of the alloy.

In other words, the adhesive forces of the material at the interfaces of the crystals seem to be of decisive importance for the cohesion and thus the mechanical characteristics in the alloy. These forces of the oxides are small while, in contrast thereto, the metals which are added to the binary alloy in accordance with the present invention, namely copper and/or at least one metal selected from the group consisting of tungsten, molybdenum, vanadium and chromium greatly increase the cohesive forces between the interfaces of the binary crystals.

Example 3

An alloy of the composition Al 29.5%, Ni 70%, Cr 0.5% and containing 850 p.p.m. of oxides of these metals is produced in an induction heated crucible in contact with the surrounding air. In the manner described in Example 1, with the help of a quartz tube of 3.5 mm. inner diameter, several samples are lifted from the metal bath in the form of small bars.

The sample bars are then heated at 1480° C. and at that temperature, an electric current of 270 amperes and 1.54 volts is passed through the bars for a period of 56 hours. The resistivity of the alloy calculated at 1480° C. equals 56.8×10^{-6} ohm-centimeter. No change in the condition of the alloy bar could be found after the above described 56 hours passage of electric current therethrough.

Example 4

An alloy of the composition: Al 30.8%, Co 68%, Mo 0.4%, Cu 0.8%, and containing 600 p.p.m. of oxides of these metals is produced in contact with the surrounding air. With the help of a quartz tube having an inner diameter of 3.5 mm. and in the manner described in Example 1 small sample bars are withdrawn from the molten metal.

The sample bars are then heated to 1570° C. and at that temperature an electric current of 330 amperes and 1.68 volts is passed through the sample bars. The resistivity of the alloy at 1570° C. is 52×10^{-6} ohm-centimeter.

Example 5

An alloy of the composition: Al 30%, Ni 69%, Cu 1% and about 60 p.p.m. of oxides of these metals is produced in a protective argon atmosphere in order to keep the oxide content as low as practically possible.

In the manner described in Example 4, small sample bars are withdrawn from the molten alloy, and the sample bars are then heated for 48 hours at a temperature of 1520° C., during which period no recognizable changes take place in the thus heated bars.

Without further analysis, the foregoing will so fully reveal the gist of the present invention that others can by applying current knowledge readily adapt it for various applications without omitting features that, from the standpoint of prior art, fairly constitute essential characteristics of the generic or specific aspects of this invention and, therefore, such adaptations should and are intended to be comprehended within the meaning and range of equivalence of the following claims.

What is claimed as new and desired to be secured by Letters Patent is:

1. A high temperature resistant alloy, said alloy consisting of 21% to 35% aluminum, an amount not exceeding 4% of a substance selected from the group consisting of copper and at least one metal selected from the group consisting of tungsten, molybdenum, vanadium and chromium, the balance being at least one metal selected from the group consisting of nickel and cobalt, wherein

(a) in the absence of copper, at least one metal selected from the group consisting of tungsten, molybdenum, vanadium and chromium is present in an amount of at least .2%,

(b) in the absence of nickel and of metals selected from the group consisting of tungsten, molybdenum, vanadium and chromium, said copper is present in an amount of at least .2%,

(c) in the presence of nickel, at least one of said metals selected from the group consisting of tungsten, molybdenum, vanadium and chromium is present in an amount of at least .2%, and

(d) in the simultaneous presence of copper and at least one metal selected from the group consisting of tungsten, molybdenum, vanadium and chromium, said copper and at least one metal selected from the group consisting of tungsten, molybdenum, vanadium and chromium are each present in an amount of at least .2%.

2. A highly temperature resistant alloy as defined in claim 1, and consisting essentially of 29% aluminum, 70% cobalt and 1% copper.

3. An alloy as defined in claim 2, and including between 800 and 1000 parts per million of oxides of the metals of said alloy.

4. An alloy as defined in claim 1, and including up to about 1000 parts per million of oxides of the metals of said alloy.

5. A highly temperature resistant alloy according to claim 1, being free of nickel and including 21.8% to 32.8% aluminum and 67% to 78% cobalt.

6. A high temperature resistant alloy, said alloy consisting of 21% to 35% aluminum, between 0.2% and 4% copper, the balance being cobalt.

7. A high temperature resistant alloy, said alloy consisting of 21% to 35% aluminum, between 0.2% and 4% of at least one metal selected from the group consisting of tungsten, molybdenum, vanadium and chromium, the balance being nickel.

8. A high temperature resistant alloy, said alloy consisting of 21% to 35% aluminum, between 0.2% and 4% of at least one metal selected from the group consisting of tungsten, molybdenum, vanadium and chromium, the balance being cobalt.

9. A high temperature resistant alloy, said alloy consisting of 21% to 35% aluminum, at least 0.2% of copper, at least 0.2% of a metal selected from the group consisting of tungsten, molybdenum, vanadium and chromium, the combined amount of said copper and said at least one metal not exceeding 4%, the balance being nickel.

10. A high temperature resistant alloy, said alloy consisting of 21% to 35% aluminum, at least 0.2% of copper, at least 0.2% of a metal selected from the group consisting of tungsten, molybdenum, vanadium and chromium, the combined amount of said copper and said at least one metal not exceeding 4%, the balance being cobalt.

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DAVID L. RECK, *Primary Examiner.*

R. O. DEAN, *Assistant Examiner.*