Oct. 9, 1956 W. BETTERIDGE ET AL 2,766,155

PRODUCTION OF HIGH TEMPERATURE ARTICLES AND ALLOYS THEREFOR

Filed Dec. 2, 1952

2 Sheets-Sheet 1

Fig. 1.

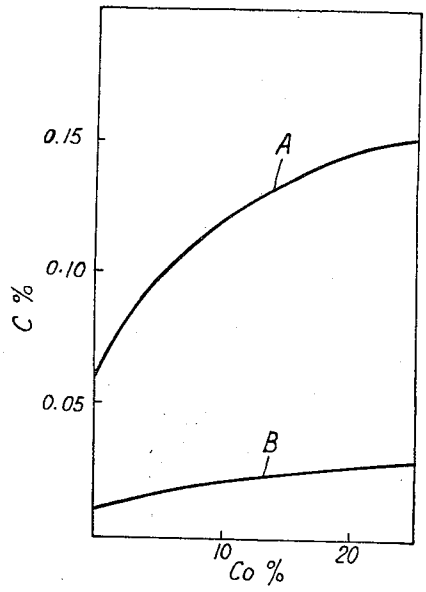
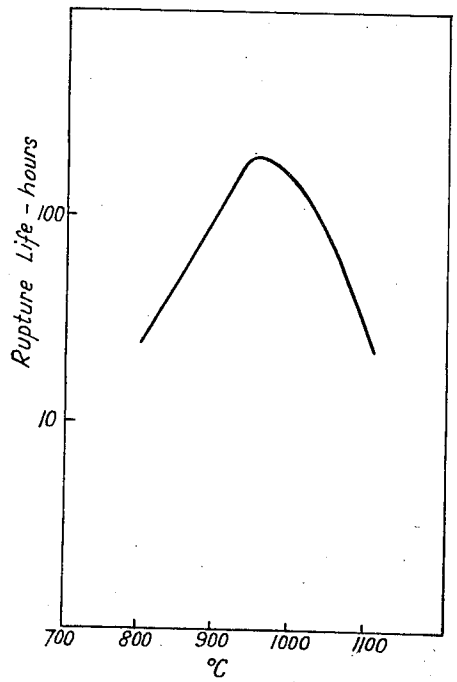


Fig. 2.



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Fig. 3.

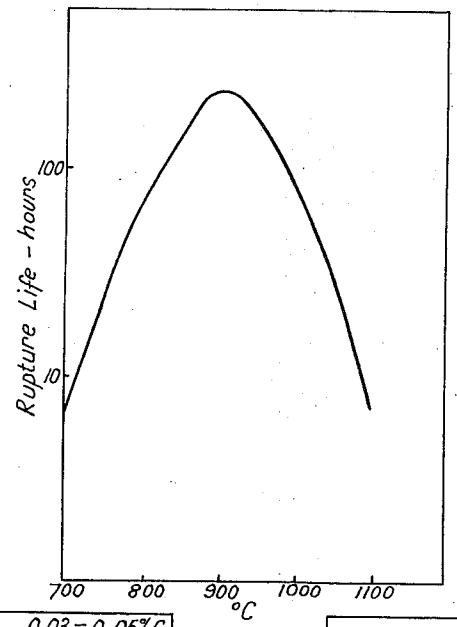


Fig. 4.

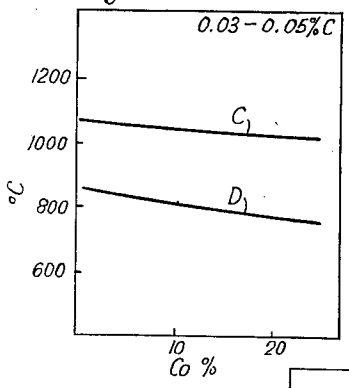


Fig. 5.

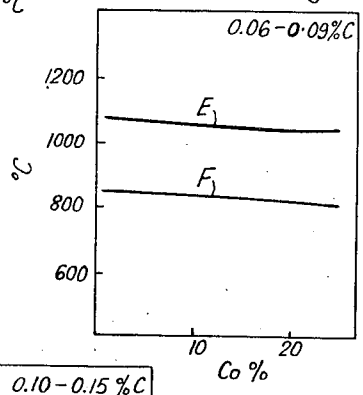
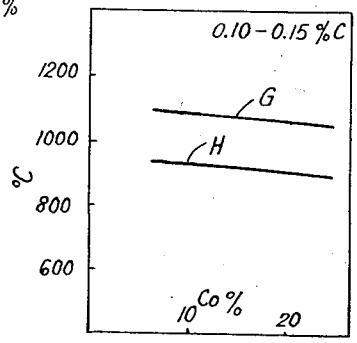


Fig. 6.



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PRODUCTION OF HIGH TEMPERATURE ARTICLES AND ALLOYS THEREFOR

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6 Claims. (Cl. 148—21.9)

The present invention relates to heat-resistant nickel alloys and the heat treatment thereof, and, more particularly, to a special heat treatment for selected carbon-containing, age-hardenable, nickel-chromium alloys suitable for use under high loads at elevated temperatures.

In recent years, many alloys have been proposed for use at elevated temperatures, particularly heat-resistant and corrosion-resistant, nickel-base alloys of the age-hardenable type. In employing these alloys in high-temperature applications involving high stresses, it is usually necessary to heat treat the alloys in order to obtain the required combination of high-temperature physical properties and also in order to ensure satisfactory performance at elevated temperatures. Alloys from which articles and parts, which are subjected to prolonged stress at high temperatures, i. e., those in the order of 600° C. and upwards, are made must possess not only resistance to corrosion at high temperature but also resistance to creep. The alloys most successfully used for this purpose are nickel-chromium alloys which contain a precipitable phase consisting of nickel, titanium and aluminium and having the apparent composition $Ni_3(TiAl)$, i. e., the Ni_3Al phase with partial substitution of titanium for aluminium. This constituent enters into solid solution at a high temperature and when the alloy is heated at a lower temperature is precipitated in a form which effects hardening of the alloys and improves the creep properties. A heat treatment commonly employed comprised subjecting age-hardenable, nickel-chromium alloys to a high-temperature solution treatment which was usually followed by an ageing or precipitation hardening treatment at a lower temperature. While this type of heat treatment usually improved the strength properties of such age-hardenable alloys, it was found that the properties of these heat-treated alloys would vary somewhat at elevated temperatures and could not always be obtained consistently. Although many attempts were made to provide heat treatments to overcome the foregoing difficulty and to provide heat-treated alloys having optimum combination of high-temperature properties, none, as far as we are aware, was entirely satisfactory when carried into practice commercially on an industrial scale.

It has now been discovered that an improved combination of high-temperature properties, including long fracture life, can be consistently obtained by employing a special heat treatment on special carbon-containing, age-hardenable nickel-chromium alloys and age-hardenable nickel-chromium-cobalt alloys.

It is an object of the present invention to provide a heat treatment which consistently imparts to carbon-containing nickel alloys improved and optimum strength properties at elevated temperatures.

Another object of the invention is to provide a heat treatment for special heat-resistant, age-hardenable, carbon-containing nickel alloys, said heat treatment imparting enhanced strength properties at elevated temperatures,

particularly improved fracture life, improved resistance to creep, low creep rate, etc.

It is a further object of the invention to provide improved heat-treated nickel alloys having improved combination of properties at elevated temperatures.

Other objects and advantages will become apparent from the following description.

The alloys with which the invention is concerned may be broadly defined as those which contain from 10 to 25% chromium, 1.8 to 4.0% titanium, 0.5 to 4.0% aluminium, up to 25% cobalt and up to 10% iron. These alloys always contain some carbon. The present invention is based on the discovery that improved resistance to creep under substantial stress, e. g., 17 long tons per square inch at 750° C., or greater certainty in the development of the best creep-resisting properties under severe conditions of stress and temperature such as lead to failure in a few hundred hours, can be produced by certain heat treatments applied to alloys which themselves are characterised by critical carbon contents.

We have discovered that the carbon content should depend upon the cobalt content, increasing with the cobalt content.

In the accompanying drawings,

Figure 1 is a graph showing the way in which the carbon content varies with and is determined by the cobalt content;

Figures 2 and 3 are graphs showing the variation of the life (on a logarithmic scale) with the temperature employed in one step of the heat treatment; and

Figures 4 to 6 are graphs in each of which temperature is plotted against cobalt content, to demonstrate how the temperature in the said step may vary with different cobalt contents and corresponding carbon contents in the preferred alloys.

Referring first to Figure 1, we choose an alloy such that the carbon content is within the range defined by the intersection of the ordinate corresponding to the cobalt content with the lines A and B. It will be seen that in a cobalt-free alloy the carbon content must be from 0.02 to 0.06% and when the cobalt content is 25% the carbon content must be from 0.03 to 0.15%.

The heat treatment to which the alloys are subjected according to the invention consists in first heating the alloy at a temperature of from 1150 to 1250° C., the duration of the heating being from 2 to 12 hours at 1150° C. and from ½ to 4 hours at 1250° C., with intermediate periods at intermediate temperatures. Next the temperature is reduced to a maximum of 1100° C. and held within the range of 1100 to 800° C. for at least 2 hours. At the end of this step the alloy is cooled to room temperature or other convenient low temperature, and then held at a temperature which leads to substantial hardening, this temperature normally being within the range 650 to 850° C. but being in any case lower than the temperature of the second step and the alloy being held there for from 1 to 24 hours.

The temperature at which the second step of the heat treatment takes place depends upon the composition of the alloy, and particularly on the carbon content. We have found that for any given alloy the time before rupture when the alloy is tested under severe conditions of stress and temperature increases to a maximum as the temperature at which the second step of the heat treatment is carried out increases, and then decreases rapidly as this temperature is further increased. Thus we find that for any given alloy there is a critical temperature, well above the normal age-hardening temperature, at which the longest life is produced.

The nature of the temperature range, and the way in which it varies with the carbon and cobalt contents, will

be better understood by means of examples and by reference to Figures 2 and 3.

Example 1

The alloy from which the results shown in Figure 2 were obtained contained 0.06% C, 2.33% Ti, 0.99% Al, 19.10% Cr and 0.42% Fe, the balance being substantially all nickel. This alloy, after treatment for 3 hours at 1250° C., was cooled directly to 950° C. held there for 24 hours, water-quenched and aged for 16 hours at 700° C. As shown in Figure 2, the alloy then had a life to rupture of 198 hours under a stress of 17 long tons per square inch at 750° C. When the second step of the heat treatment was carried on at 900° C. instead of 950° C., the life was only 100 hours, and when this step was carried on at 1000° C. the life was only 120 hours. On the other hand, when the second step was carried on at 1090° C. the life was about 40 hours and when it was carried on at 850° C. the life was only 50 hours. In this case, it will be seen, the temperature range giving substantial life is from about 855 to about 1060° C., though to get the best life the second heating step should be carried on in the narrower range of 925 to 1050° C.

Next the results obtained with another cobalt-free alloy will be given.

Example 2

The alloy in this case contained 0.043% C, 2.36% Ti, 1.13% Al, 19.1% Cr and 0.27% Fe, the balance being substantially all nickel. It thus differed from the alloy of Example 1 principally in its lower carbon content. When treated and tested as in Example 1 with various temperatures in the second step of heat-treatment, the life to rupture was found to be 221 hours when this temperature was 1025° C., 140 hours at 1050° C. and only 53 hours at 1075° C.; when the temperature was 950° C. the life was 185 hours, at 850° C. it was 136 hours, at 825° C. it was 90 hours and at 800° C. it was only 40 hours. In the case of this alloy, therefore, the second heating step should be carried out in the temperature range of about 820 to about 1060° C.

The temperature to be used in the second step of the heat treatment depends also on constituents of the alloy other than the carbon. Thus it is materially affected by the cobalt content. When the cobalt content is as high as 20%, the temperature range for the second step should be somewhat lower.

This reduction in the temperature used in the second step with a high cobalt content is illustrated by the following examples.

Example 3

The alloy contained 0.044% C, 2.33% Ti, 1.25% Al, 20.2% Cr, 19.6% Co, with the balance substantially all nickel. The carbon content, which is the most important figure other than the cobalt content, was, it will be seen, substantially the same as in Example 2. The same heat-treatment was applied with varying temperatures in the second step, but this alloy was tested under more severe conditions, i. e., a stress of 19 long tons per square inch at 750° C. When the temperature in the second step was 950° C. the life was 600 hours. On reducing the temperature in the second step to 875° C. the life was 420 hours, to 850° C. the life was 280 hours and to 825° C. the life was 190 hours. On increasing the temperature in the second step to 1025° C. the life fell to 300 hours and when it was 1050° C. the life was only 140 hours. In the case of this alloy, therefore, the range of temperatures in which the second heating step should be carried out is from about 850 to about 1025° C. and it is desirable to work as closely as possible to 950° C.

Example 4

This example, which is illustrated by Figure 3, relates to an alloy containing 20.34% chromium, 19.85% cobalt, 2.44% titanium, 1.13% aluminium, 0.03% carbon and the balance substantially all nickel, which was tested at 19 long tons per square inch and 750° C. With this alloy, when the temperature in the second step was 750° C., the life to rupture was 7 hours; the life rose to a maximum of 232 hours at 910° C. In this case the temperature range giving substantial life is from about 775 to 1030° C. and preferably is from 810 to 1010° C.

Figures 4 to 6 show how the ranges of temperature of the second step of the heat treatment of the preferred alloys described vary with the cobalt and carbon contents, Figure 4 relating to alloys containing 0.03 to 0.05% carbon, Figure 5 to alloys containing 0.06 to 0.09% carbon and Figure 6 to alloys containing 0.10 to 0.15% carbon. In Figure 4 the temperature must be within the range defined by the intersection of the ordinate corresponding to the cobalt content with the lines C and D. For instance with 0.04% carbon and 10% cobalt, reference to Figure 4 shows that the temperature range is from 800 to 1040° C. Likewise in Figure 5 the part of the ordinate intersected by the lines E and F, and in Figure 6 the part intersected by the lines G and H, shows the range.

We prefer to transfer the alloys straight from the furnace in which the solution heating takes place to another in which the second heating step takes place, and to make this second heating step substantially isothermal. However, slow cooling through the permissible temperature range of the second heating step may also produce satisfactory results.

After the second step of the heat treatment it is usually most convenient to let the alloy cool to room temperature and subsequently to re-heat it to the ageing temperature, but if desired the alloy can again be transferred direct to a furnace in which the ageing takes place, or be kept in the furnace in which the second step has taken place, the temperature of that furnace being reduced to the ageing temperature.

The alloys are not restricted in composition to the elements named above. As usual, there may be other elements, e. g. silicon up to 1% and copper up to 2%. Moreover, the alloys may be modified by the addition of molybdenum and tungsten up to 10% each, niobium, tantalum or vanadium or any combination of these in a total amount up to 5%, zirconium up to 0.3% and boron up to 0.05%. In every case the balance of the alloy is nickel, except for impurities and residual deoxidants, e. g. manganese, calcium and magnesium.

While reference has been made throughout to the treatment of the alloys, it is to be understood that in general they are heat treated after being fabricated into articles or parts (e. g., turbine blades) or into bar, strip, forgings or stampings from which such parts can be machined.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. A method of improving the resistance to creep of an alloy consisting essentially of from 10 to 25% chromium, 1.8 to 4.0% titanium, 0.5 to 4% aluminium, up to 25% cobalt, up to 10% iron, carbon in an amount within the range defined by the intersection of the ordinate corresponding to the cobalt content with the lines A and B shown in Figure 1 of the accompanying drawings, and the balance nickel, except for impurities and residual deoxidants, which comprises first heating the alloy at a temperature of from 1150 to 1250° C. with the duration of this heating step being from 2 to 12 hours at 1150° C. and from ½ to 4 hours at 1250° C. and with intermediate periods at intermediate temperatures subsequently heating the alloy for at least two

hours at a temperature which does not exceed about 1100° C. and is not less than about 800° C. and which is correlated to the carbon and cobalt contents in accordance with Figs. 4, 5 and 6 of the accompanying drawing, and thereafter holding the alloy for from 1 to 24 hours at a temperature which is within the range 650 to 850° C. but is in any case lower than the temperatures of the preceding heating steps, whereby a heat-treated alloy is obtained characterised by having improved fracture life at elevated temperatures.

2. A method of improving the resistance to creep of an alloy consisting essentially of from 18 to 20% chromium, 2.0 to 2.4% titanium, 1.0 to 1.4% aluminum, up to 25% cobalt, up to 2% iron, carbon in an amount within the range defined by the intersection of the ordinate corresponding to the cobalt content with the lines A and B shown in Figure 1 of the accompanying drawings, and the balance nickel, except for impurities and residual deoxidants, which comprises first heating the alloy at a temperature of from 1150 to 1250° C. with the duration of this heating step being from 2 to 12 hours when the temperature is at 1150° C. and being from ½ to 4 hours when the temperature is at 1250° C. and with the duration of this heating step being for intermediate periods at intermediate temperatures, subsequently heating the alloy for at least two hours at a temperature which does not exceed about 1100° C. and is not less than about 800° C. and which is correlated to the carbon and cobalt contents in accordance with Figs. 4, 5 and 6 of the accompanying drawing, and thereafter holding the alloy for from 1 to 24 hours at a temperature which is within the range 650 to 850° C. but is in any case lower than the temperature of the second step, whereby a heat-treated alloy is obtained characterised by having improved fracture life at elevated temperatures.

3. A method according to claim 2, applied to an alloy with a carbon content of from 0.03 to 0.05%, in which the temperature in the second step of the heat treatment is correlated to the carbon and cobalt contents in accordance with Figure 4 of the accompanying drawings.

4. A method according to claim 2, applied to an alloy with a carbon content of from 0.06 to 0.09%, in which the temperature in the second step of the heat treatment is correlated to the carbon and cobalt contents in accordance with Figure 5 of the accompanying drawings.

5. A method according to claim 2, applied to an alloy with a carbon content of from 0.10 to 0.15%, in which the temperature in the second step of the heat treatment is correlated to the carbon and cobalt contents in accordance with Figure 6 of the accompanying drawings.

6. The method of improving the resistance to creep of a columbium-free alloy at high temperatures according to claim 1 in which the columbium-free alloy being heat treated to impart enhanced fracture life at high temperatures contains at least one additional constituent from the group consisting of silicon up to 1%, copper up to 2%, molybdenum up to 10% tungsten up to 10%, zirconium up to 0.3%, and boron up to 0.05%.

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