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EROSION RESISTANT DISPERSION HARDENED METALS

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ABSTRACT OF THE DISCLOSURE

Dispersion hardened metals based on nickel or cobalt containing a small proportion of nickel and chromium are modified to improve high temperature erosion resistance by the inclusion of a large proportion of iron.

The present invention relates to formed dispersion hardened nickel or cobalt alloys which contain chromium for improved oxidation resistance.

The need for metal alloys capable of withstanding the elevated temperatures and other conditions which are now encountered in industry, turbine blades, vanes and burner cans for jet engines being outstanding examples, is well known. The ordinary alloys of nickel and cobalt are inadequate and superalloys were developed and adopted by industry to a considerable extent. However, the elevated temperature resistance of even these uniquely superior alloys is still limited and, in an effort to provide resistance to even higher temperatures, dispersion hardened nickel and cobalt alloys have been tried. These possess a significantly improved capacity to maintain their strength at high temperature, but other high temperature properties (especially erosion resistance) are not comparable with those of typical superalloys and this invention attempts to improve the capacity of the dispersion hardened alloys to resist the tendency of high velocity high temperature oxidizing gases as are encountered in a jet engine to erode the metal surfaces, an action which can lead to a catastrophic failure of the eroded part.

The invention is directed to metal structures which are prepared by powder metallurgy procedures in which the powder is consolidated under pressure, sintered, extruded, then formed as desired and then recrystallized. More particularly, the powder which is consolidated comprises nickel or cobalt, from 8 to 35% of chromium and a minor proportion of finely divided particles of a refractory metal oxide having a free energy of formation at 1000° C. greater than 100 kilocalories per gram atom of oxygen which is incorporated in the powder in a manner which permits these particles to become pervasively dispersed in the metal to dispersion harden the same. When the predominant metal is cobalt instead of nickel, at least 10% by weight of nickel should be present in order that the metal which is formed will have a crystal lattice structure predominantly constituted by a face-centered cubic crystal lattice structure. This structure is maintained over the entire temperature range of from room temperature to 2400° F.

In accordance with the invention, it has been found that while small amounts of many metals may be incorporated in the dispersion hardened metals under consideration, most of these degrade the erosion resistance making a poor situation even worse. In contrast, when large amounts of iron are incorporated in the dispersion hardened metals under consideration the erosion resistance of the dispersion hardened metal is vastly improved and can even be made significantly superior to that provided by the lower temperature resistant superalloy.

Relatively small amounts of manganese up to about 1% by weight may also be present and help to enhance erosion resistance, but the effect of the manganese is minimal at the higher proportions of iron which are preferred in the invention. Large amounts of manganese tend to embrittle the alloy and are preferably avoided. Most other additives are detrimental and should be avoided for best results. Thus, other metals are desirably held to a maximum of 3% by weight, preferably to a maximum of 1% by weight so that, by difference, the nickel, chromium, cobalt and iron will constitute at least 97% and preferably at least 99% of the metal of the alloy.

At least 3% by weight of iron should be present, though it takes about 5% of iron to improve the typical dispersion hardened metal to where it is a match for a typical superalloy and 8% or more to provide any significant superiority. Up to about 25% can be present, but not more than 22% iron is preferred.

The above percentages are based on the total weight of the alloy.

While the proportion of finely divided particles of metal oxide is of secondary significance in the present invention, it is usually convenient to utilize from 0.5 to 6% by volume of refractory metal oxide particles having an average particle size less than about 200 millimicrons. Preferred proportions are from 1–4% by volume. While numerous illustrations of appropriate refractory metal oxides are well known in the art, thoria is particularly preferred.

The erosion resistance of a formed metal piece is of especial importance with respect to turbine airfoil shapes such as blades and vanes and, here, a common test which is used to determine whether the metal possesses satisfactory erosion resistance is as follows.

The erosion rig consists of a converging nozzle burner that produces a flame from the combustion of JP–4 or JP–5 jet engine fuel. The velocity of the hot gases is approximately 1,000 ft./sec. These hot bases provide the temperature and erosion characteristics that simulate a gas turbine engine. A number of erosion bar specimens are held in a spindle and rotated at 1750 r.p.m. in the burner flame. The specific weight and shape of the erosion bars is of secondary significance so long as these factors are constant from test to test.

In some tests salt is injected into the hot gases. The salt, in combination with sulfur in the fuel, accelerates the rate of attack. The test without salt or sulfur additives is called oxidation-erosion while, with additives, it is sulfidation-erosion.

The test specimens are weighed before and after the test and the erosion is conveniently reported in milligrams per hour per square centimeter of exposed test specimen. In the tests which have been conducted, the test specimen was approximately 3" long with a 2" piece exposed to the test and the specimen weighed 60–65 grams with 30.5 square centimeters of surface being exposed. The cross-section of the exposed piece corresponds to that portion of a circle which is cut by a 30° wedge passing through the circle and having its apex ½" from the center of the circle. The narrow end of the wedge is then severed 0.2" forward of the center of the circle in order to provide a cross-section which broadly simulates an air foil.

As will be evident, the weight loss as a function of time will vary depending upon the physical and chemical characteristics of the piece under test and it is convenient to compare the weight loss of the test specimen with the weight loss which is normally experienced by a superalloy. It is on this basis that it has been concluded that large proportions of iron are uniquely capable of providing the erosion resistance which is needed without impairing other important properties of the alloy.

In preferred practice of the invention, the dispersion hardened metal is processed by powder metallurgy, the

powder being pressed and then sintered at elevated temperature and extruded to form an extruded piece having a density of substantially 100% of the theoretical density and then swaged at elevated temperature. Most preferably, the worked product is then annealed at a temperature of from 65–98% of the said melting point to recrystallize the same temperature being measured in degrees Kelvin based on the melting point of the metal unmodified with the refractory oxide. The finished product before or after annealing can be machined or forged to any desired shape.

In this way there is formed a turbine component which possesses great strength at elevated temperature and which is capable of resisting erosion forces as well as or better than conventional superalloys.

The invention is illustrated in the example which follows:

EXAMPLE

A powder having the composition Ni–20 Cr–15 Fe–2 ThO_2 is prepared by coprecipitating a nitrate salt solution containing $Cr(NO_3)_3$, $Fe(NO_3)_3$, $Ni(NO_3)_2$ and $Th(NO_3)_4$ in the proportions determined by the composition noted above. The coprecipitation may be carried out by the simultaneous addition to a heel of water of the nitrate salt solution and an ammonium hydroxide-ammonium carbonate solution. The precipitate is filtered and washed, and the filter cake is dried and calcined in an air circulating oven at 450° C. The dried powder is mixed with 11% water and briquetted. The briquettes are placed in a tray in a reduction furnace and hydrogen is passed through the furnace with the temperature thereof raised 100° per hour so that reduction is substantially complete when a temperature of 400° C. is reached. Heating is continued to a maximum of about 750° C. Passage of hydrogen is continued until the effluent gas has a dew point of —50° C.

After the briquettes are reduced, they are crushed and pulverized to a particle size of about —50 mesh. This powder is then hydrostatically compacted at 60,000 p.s.i. with 3 pounds of the above powder being compacted to a nominal 2" diameter billet. The compacted billet is machined without lubricants to approximately a 2" diameter x 5" long billet which is canned in a cylindrical mild steel can (⅛" wall thickness). Mild steel end plates (⅛" thick) fitted with ¼" O.D. x .022" wall stainless steel tubing are welded in place to seal the can (except for the entrance and exit tubing lines in the end plates).

The canned billet is sintered in flowing dry hydrogen, holding the billet temperature successively at 400, 600, 850, and 1750° F. to achieve an exit gas dew point ≦—70° F. Following the final dry hydrogen sinter, the billet is cooled from 1750° F. to room temperature under flowing argon. After cooling the assembly is evacuated, and the gas tubes are sealed by fusion welding.

The sealed billet is placed in a 1750° F. furnace in air. When a billet temperature of 1750° F. is attained, the assembly is extruded through a ¾" diameter die to produce an extruded bar section. The resulting mild steel jacketed-nickel-chrome-iron-thoria bar is essentially 100% dense.

The extruded bar is sandblasted and cropped to a 2 foot length of ¾" diameter bar. The bar is hot swaged at 1800° F. to ⅜"' diameter in a series of reductions of approximately 12½% each. The swaged bar is machined to remove all steel can and surface contamination resulting from the hot processing steps and the product is then annealed at 2400° F., for 1 hour. The product is then machined to form a test specimen as previously described and tested in the manner indicated to reveal markedly superior erosion resistance.

A repeat of the foregoing example, but utilizing a 50% replacement of nickel with cobalt (the cobalt being supplied in the form of cobalt nitrate), provides comparable results in that the presence of the iron markedly increases the erosion resistance of the dispersion modified alloy.

The invention is defined in the claims which follow.

We claim:

1. A dispersion-hardened metal having a density of substantially 100% of the theoretical density and characterized by improved erosion resistance and comprising nickel, or cobalt in admixture with at least 10% by weight of nickel, to provide a face-centered cubic crystal lattice structure, and from 8 to 35% by weight of chromium, said metal having pervasively dispersed therein a minor proportion of finely divided particles of a refractory metal oxide having a free energy of formation at 1000° C. greater than about 100 kilocalories per gram atom of oxygen, said metal further comprising from 3 to 25% by weight of iron, said nickel, chromium, cobalt and iron constituting at least 97% of the metal.

2. A dispersion-hardened metal as recited in claim **1** in which said refractory metal oxide is dispersed in an amount of from 0.1 to 6% by volume and has an average particle size less than about 200 millimicrons.

3. A dispersion-hardened metal as recited in claim **1** in which said refractory metal oxide is thoria.

4. A dispersion-hardened metal as recited in claim **1** in which said iron is present in an amount of from 8 to 22%.

5. A dispersion-hardened metal as recited in claim **4** in which said nickel, chromium, cobalt and iron constitutes at least 99% of the metal.

6. A dispersion-hardened metal as recited in claim **1** in which said dispersion-hardened metal is formed to desired shape and then annealed to recrystallize the same.

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