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3,494,807

## DISPERSION HARDENED COBALT ALLOY SHEET AND PRODUCTION THEREOF

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8 Claims

### ABSTRACT OF THE DISCLOSURE

Dispersion-hardened metal sheet based on cobalt containing from 8–35% of chromium and at least about 10% of nickel to provide a face-centered cubic crystal lattice structure is consolidated to plate form and then rolled predominantly in one direction at a temperature of about from 800° F. to 100° F. below the recrystallization temperature of the sheet to reduce the thickness of the sheet at least 50%. The rolled sheet is then reheated to substantially totally recrystallize the metal therein to provide a product having excellent elevated temperature strength and oxidation resistance and which possesses acceptable room temperature ductility.

The present application is a continuation-in-part of our prior copending application S.N. 475,869, filed July 29, 1965, now Patent No. 3,388,010.

This invention relates to processes for producing dispersion-hardened metals in the form of sheet having acceptable ductility at room temperature and excellent elevated temperature strength and oxidation resistance, and to the products so produced. More particularly the invention is directed to such processes wherein a powder comprising cobalt and 8 to 35%, preferably from 10 to 30% of chromium by weight, and a minor proportion of nickel to be defined hereinafter, said metals having pervasively dispersed therein particles of a refractory metal oxide having a free energy of formation at 1000° C. greater than 100 kilocalories per gram atom of oxygen, said particles having an average size less than about 80 millimicrons and being present in the proportion of 0.1 to 6% by volume based on the total volume of the dispersion-hardened metals is consolidated to plate form at a temperature below about 2400° F., the novel processes comprising the steps of (1) rolling said plate predominantly in one direction at a temperature of about from 800° F., preferably 1100° F. to 100° F. below its recrystallization temperature, said rolling being sufficient to effect at least a 50% reduction in the thickness of the plate, and (2) thereafter heating said rolled product to a temperature and for a time sufficient to substantially totally recrystallize the metal therein. The invention is further particularly directed to dispersion-hardened cobalt-nickel-chromium sheet which can be produced by the novel processes, said sheet comprising cobalt, nickel and about from 8 to 35% by weight of chromium, said metal having pervasively dispersed therein about from 0.1 to 6% by volume of 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 and an average particle size less than about 200 millimicrons, preferably less than 100 millimicrons, said product being in the form of sheet characterized by acceptable room temperature ductility and excellent high temperature strength and oxidation resistance and preferably by having an enlarged grain structure characterized by the presence of a substan-

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tial proportion of grains having a grain size on the ASTM grain size chart of 3 or larger and a laminar shape in the plane of the sheet.

In preferred processes of the invention the alloy is produced from powders consisting essentially of cobalt, about 10% to about 25% of nickel, and about 15 to 25% of chromium, and the dispersed refractory oxide is thoria in the amount of 1 to 4%, preferably about 2% by volume, and having a particle size in the powder less than about 40 millimicrons, preferably about 10 to 40 millimicrons. In one preferred aspect of the novel processes the consolidated plate is rolled, predominantly (at least 75%) in one direction and at a temperature of about from 800° F., preferably 1100° F. to 100° F. below its recrystallization temperature, to effect at least a 50% reduction in thickness, the rolled product is formed to a desired shape and thereafter the formed product is heated to a temperature and for a time sufficient to substantially totally recrystallize the metal. The particle size of the thoria may increase during rolling and recrystallization and may grow to a size of up to 200 millimicrons, but preferably, the final particle size is less than about 100 millimicrons.

Now according to the present invention, it has been found that if a consolidated metal plate, containing a dispersed refractory oxide such as thoria, is rolled into sheet under controlled temperature conditions, and the sheet is thereafter heated at a temperature high enough to effect recrystallization of the metal therein, the sheet products obtained have the desired room temperature ductility as well as the necessary elevated temperature strength and oxidation resistance. Furthermore, the room and elevated temperature yield and ultimate tensile strengths and room temperature ductility of the novel sheet products of this invention remain substantially unchanged after exposure in air to temperatures of 2400° F. for 100 hours.

In the products of the invention, the thoria or other refractory oxide is pervasively dispersed in the metal product. By this is meant that the thoria or other oxide is present in the grains as well as at the grain boundaries and is not so agglomerated as to cause large areas of aggregates of the refractory metal oxide to be present in any particular part of the product.

Referring more particularly to the alloy compositions which are employed in accordance with the invention, the invention relates to cobalt base alloys which, though they may contain nickel will contain a major proportion of cobalt based on the total quantity of cobalt and nickel in order that the high temperature properties of the cobalt will predominate. These cobalt alloys are modified by the inclusion therein of chromium, there being at least about 8% by weight of chromium in the alloy in order to provide a minimum improvement in oxidation resistance. On the other hand, the chromium content cannot exceed 35% by weight, for in such instance, the alloy is not workable. It is to be particularly stressed that the chromium-modified cobalt alloys do not themselves respond to the present invention but to the contrary, there must be present in the alloy a sufficient proportion, normally about 10% by weight, of nickel, in order to change the crystal lattice structure of the alloy so that it is 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.

While the proportion of nickel may be increased above the minimum specified, it should not be increased to the point where the characteristics of nickel predominate and the preferred nickel concentration is from 15–25% by weight.

It should also be appreciated that other metals may also be present, without altering the basic contribution. From this standpoint, up to 22% by weight of molybde-

num, iron, tungsten, or any mixture thereof may be used and up to a total of 6% by weight may be present of manganese, vanadium, titanium, silicon, aluminum, magnesium, zirconium, columbium, yttrium and tantalum.

Broadly stated, in a process of the invention one starts with powders comprising cobalt, nickel and from 8 to 35% by weight of chromium, the metal having pervasively dispersed therein about from 0.1 to 6% by volume, preferably 1 to 4%, of a suitable refractory oxide having an average particle size less than about 80 millimicrons. The refractory oxide must have a free energy of formation at 1000° C. greater than 100 kilocalories per gram atom of oxygen, and preferably greater than 106 kilocalories. Such a powder containing, say cobalt, 20%, nickel, 18% chromium and 2 volume percent thoria, can be prepared, for instance, by co-precipitating the hydrous oxides of cobalt nickel and chromium together with colloidal thoria of suitable size, drying the co-precipitate, and reducing the cobalt nickel and chromium oxides to the corresponding metals with hydrogen and finely divided carbon at a temperature of from 850 to 950° C.

The oxide-modified metal powder is then compacted, sintered, and hot worked at a temperature below 2400° F. into a coherent, consolidated plate having substantially theoretical density. The hot work can be conducted by such methods as forging or extrusion. It will be understood that these processes can be carried out as closely connected steps of a single operation, as when one extrudes a compacted powder billet directly into the shape of a ribbon or sheet-bar.

The plate so obtained is rolled to sheet, predominantly in one direction and at a temperature of about from 800° F. to 100° F. below its recrystallization temperature.

Irrespective of the manner of preparing the consolidated body in the form of a material suitable for working to the final gauge sheet, the final rolling to the ultimate dimensions is also effected at a temperature in the range of about from 800° F., preferably 1100° F., to a maximum temperature which is 100° F. below the recrystallization temperature of the sheet at that state of processing. If extensive rolling is attempted at a temperature below about 800° F. cracking of the sheet may be encountered due to rapid work-hardening of the alloy and its reduced ductility and high hardness under these conditions. If, on the other hand, temperatures above about 100° below the recrystallization temperature are used, incipient recrystallization may occur in part or all of the sheet, and with this recrystallization a loss of ductility is encountered.

The final step of the process—namely, recrystallization, comprises heating the rolled sheet to a temperature above its recrystallization temperature and maintaining such temperature until substantially complete recrystallization has occurred. After recrystallization, the strengths at the elevated temperatures encountered in use are found to be improved. If desired, the recrystallized sheet can be given final finishing treatment, such as cold-rolling up to a 20% reduction in thickness to provide good gauge control and flatness.

It is desirable to keep the thoria particle size relatively small in the sheet product; the tendency is for the particle size to increase during the process.

The measurement of particle size of the dispersed refractory oxide such as thoria in these products can be made by several techniques, each of which offers different combinations of precision, validity, range and ease of operability. A B.E.T. specific surface area measurement can be made of the residues extracted from the metal sample by bromine-methanol solution and this surface area converted to average diameter by assuming the particles are spherical. This method has the advantage of employing relatively large samples, but the results can be clouded by, for example, high surface area phases which along with the thoria are insoluble in the Br-methanol extraction medium.

A second method employs the measurement of X-ray line breadth, which is a standard method for small particles of crystalline substances. Here the problem area for thoria particles is loss of precision at approximately below 15 mu and above 80 mu. This method is generally satisfactory for powder samples of Co-20 Ni-18 Cr-2 ThO<sub>2</sub>, but because of factors of preferred orientation, absorption characteristics, etc., the method is less satisfactory for consolidated samples (sheet) of the same alloy or samples containing small amounts of thoria or for samples whose dispersoids have weaker diffraction lines, such as Al<sub>2</sub>O<sub>3</sub>. The method is specific to the dispersoid phase and can be operated so that the results are not clouded by the presence of other phases.

Other methods relying on electron microscopy can also be employed for thoria size measurement. Particles of thoria down to 10 mu and even less, projecting above the polished surface of a metallographic sample, can be replicated, viewed, and measured on electron photomicrographs. Non-dispersoid particles can be distinguished from the dispersoid if their morphology is different. Similarly an extraction residue from a sample (used in the B.E.T. method) can be dispersed on a carbon substrate and the particle size determined by means of electron photomicrographs. Again, foreign phases (those which are not the dispersoid) can be avoided in the average size measurement only if their morphology is different. Transmission electron microscopy can also be used to measure dispersoid size, particularly in the case of thoria because of its high absorption characteristics, but this method tends to overlook or under emphasize the larger particles. The size measurements involving electron microscopy are often time consuming and in addition can be, although they may not necessarily be, biased because of the small volume of sample analyzed.

In samples of Co-20 Ni-18 Cr-2 ThO<sub>2</sub> of the present invention, X-ray line breadth and B.E.T. measurements have been employed for thoria size, and it has been found that the X-ray measurements yield a size number about 10 mu larger than B.E.T. method when the size is about 20 mu (B.E.T.). These samples contained less than 100 p.p.m. C, N, S, and less than 1000 p.p.m. O<sub>2</sub> as measured by vacuum fusion. Electron photomicrographs of replicas from such a sample reveal that virtually all (99%) of the dispersoid particles are below 80 mu, and the average size, although not precisely measured by particle-counting techniques, appears by that method to be consistent with the X-ray and B.E.T. measurement. Particle sizes referred to in this application are the B.E.T. values unless otherwise specified.

The novel metal products produced according to the processes of the invention have the following desirable properties:

(1) They are oxidation-resistant at high temperature. The cobalt-20% nickel-18% chromium-2 vol. percent thoria sheet, for example, can withstand hundreds of hours of cyclic oxidation exposure to temperatures of 2200° F. with a weight gain of less than 10 mg./cm.<sup>2</sup>. This performance is better than any commercially available superalloy.

(2) They exhibit high strength at high temperature. At 2000° F. a sheet of cobalt-20% nickel-18% chromium-2 vol. percent thoria can withstand a stress of 5,500 p.s.i. for more than 20 hours. Generally speaking, the sheet of this invention is at least twice as strong at 2000° F. as commercially available superalloy sheet. This high tensile strength is an important reason for utilizing cobalt.

It can be bent and formed at about room temperature into hardware requiring the oxidation resistance and strength developed by the dispersion-modified alloy compositions. Of course, the cobalt-base alloys are not as ductile as the nickel-base alloys and some ductility is sacrificed for the greater strength conferred by cobalt.

The grain sizes and shapes influence the above-men-

tioned and other mechanical properties of products of the invention in the manner herein described.

It will be noted that many of the characteristics of the novel products of this invention are developed after the rolling but before the final recrystallization step. In view of this fact, it is possible to take advantage of these characteristics in various metal-forming operations before the final annealing or recrystallization. For instance, applications requiring severe forming, bending, crimping and so on can be performed after heating the rolled material to temperatures approximating those used during rolling operations.

The products of this invention have high utility by reason of their above-mentioned properties. For instance, they are particularly well suited for use in making turbine engine parts for operation at very high temperatures and in oxidizing atmospheres typical of the combustion gas compositions generated by burning hydrocarbon fuels.

The invention will be better understood by reference to the following illustrative example.

#### EXAMPLE

A Co-20% Ni-18% Cr-2%  $\text{ToO}_2$  powder is prepared by coprecipitating  $\text{CoCO}_3$ - $\text{NiCO}_3$ - $\text{Cr}(\text{OH})_3$ - $\text{ThO}_2$ , filtering, washing, and drying at 300° C. One hundred parts of this powder are blended with 12 parts of carbon, the blend heated in hydrogen at 400° C. to reduce the cobalt and nickel oxides, and then at 925° C. in  $\text{H}_2$ - $\text{CH}_4$  mixture to reduce the  $\text{Cr}_2\text{O}_3$ . Excess carbon is removed by heating in hydrogen at 875° C. The particle size of the thorium in the powder is about 16 millimicrons.

The powder is hydrostatically compacted at 60,000 p.s.i., and the compacted billet is machined without lubricants to approximately 2" in diameter x 4" long and canned in a cylindrical mild carbon steel can ( $\frac{1}{8}$ " wall thickness). Mild carbon steel end plates ( $\frac{1}{8}$ " thick) fitted with  $\frac{1}{4}$ " O.D. x .022" wall stainless steel tubing are welded in place to seal the can (excepting 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 of about -60° 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 2000° F. furnace in air. When a billet temperature of 2000° F. is attained, the assembly is extruded to a nominal 0.5" x 1.0" sheet bar section. The resulting mild steel jacketed cobalt-nickel-chrome-thorium sheet bar is essentially 100% dense.

The sheet bar is converted to sheet by rolling transverse to the extrusion direction to effect a total reduction of 85% at a decreasing temperature starting from 2000° F. and decreasing to 1300° F. The sheet is pickled in  $\text{HNO}_3$  to remove the carbon steel can and then recrystallized by heat treating at a temperature of 2400° F. for one hour. The resultant sheet product has a tensile strength at 2000° F. greater than 18,000 p.s.i. and a stress rupture life of greater than 20 hours at 2000° F. at a stress of 6,500 p.s.i.

The invention is defined in the claims which follow. We claim:

1. In a process for producing a dispersion-hardened metal sheet having room temperature ductility and excellent elevated temperature strength and oxidation resistance in which powder comprising cobalt, from 8 to 35% chromium by weight and at least about 10% by weight of nickel to provide a face-centered cubic crystal lattice structure, said metal having pervasively dispersed therein particles of a refractory metal oxide having a free energy of formation at 1000° C. greater than 100 kilocalories per gram atom of oxygen, said particles in said powder having an average size less than about 80 millimicrons and being present in the proportion of 0.1 to 6% by volume

based on the total volume of metals, is consolidated to plate form at a temperature below about 2400° F., the steps comprising (1) rolling said plate predominantly in one direction at a temperature of about from 800° F. to 100° F. below its recrystallization temperature, said rolling being sufficient to effect at least a 50% reduction in the thickness of the plate, and (2) thereafter heating said rolled product to a temperature and for a time sufficient to substantially totally recrystallize the metal therein.

2. A process as recited in claim 1 in which said cobalt is present in major proportion based on the total quantity of cobalt and nickel.

3. A process as recited in claim 1 in which said metal oxide is thorium.

4. A process as recited in claim 1 in which said powder includes up to 22% by weight of molybdenum, iron, tungsten or mixture thereof and up to a total of 6% by weight of manganese, vanadium, titanium, silicon, aluminum, magnesium, zirconium, columbium, yttrium and tantalum.

5. In a process for producing a dispersion-hardened metal sheet having room temperature ductility and excellent elevated temperature strength and oxidation resistance in which powder consisting essentially of cobalt, from 10 to 30% chromium by weight and from 15-25% by weight of nickel to provide a face-centered cubic crystal lattice structure, up to 22% by weight of molybdenum, iron, tungsten, or mixture thereof, and up to a total of 6% by weight of manganese, vanadium, titanium, silicon, aluminum, magnesium, zirconium, columbium, yttrium and tantalum, said metal having pervasively dispersed therein particles of a refractory metal oxide having a free energy of formation at 1000° C. greater than 100 kilocalories per gram atom of oxygen, said particles in said powder having an average size less than about 80 millimicrons and being present in the proportion of 1% to 4% by volume based on the total volume of metals, is consolidated to plate form at a temperature below about 2400° F., the steps comprising (1) rolling said plate predominantly in one direction at a temperature of about from 1100° F. to 100° F. below its recrystallization temperature, said rolling being sufficient to effect at least a 75% reduction in the thickness of the plate, and (2) thereafter heating said rolled product to a temperature and for a time sufficient to substantially totally recrystallize the metal therein.

6. In a process for producing a dispersion-hardened metal sheet having room temperature ductility and excellent elevated temperature strength and oxidation resistance in which powder comprising cobalt, from 8 to 35% chromium by weight and at least about 10% by weight of nickel to provide a face-centered cubic crystal lattice structure, said metal having pervasively dispersed therein particles of a refractory metal oxide having a free energy of formation at 1000° C. greater than 100 kilocalories per gram atom of oxygen, said particles in said powder having an average size less than about 80 millimicrons and being present in the proportion of 0.1 to 6% by volume based on the total volume of metals, is consolidated to plate form at a temperature below about 2400° F., the steps comprising (1) rolling said plate predominantly in one direction at a temperature of about from 800° F. to 100° F. below its recrystallization temperature, said rolling being sufficient to effect at least a 50% reduction in the thickness of the plate, (2) forming the rolled product to a desired shape, and (3) thereafter heating said rolled product to a temperature and for a time sufficient to substantially totally recrystallize the metal therein.

7. A dispersion-hardened cobalt-chromium sheet comprising cobalt, from 8 to 35% by weight of chromium, and at least about 10% by weight of nickel to provide a face-centered cubic crystal lattice structure, the metal of said sheet having pervasively dispersed therein about from 0.1 to 6% by volume of particles of a refractory

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metal oxide having a free energy of formation at 1000° C. greater than about 100 kilocalories per gram atom of oxygen, said particles having an average particle size less than about 200 millimicrons, said product being in the form of sheet characterized by room temperature ductility and high temperature strength and oxidation resistance, and by having an enlarged grain structure characterized by the presence of a substantial proportion of grains having a grain size on the ASTM grain size chart of 3 or larger and a laminar shape in the plane of the sheet.

8. A dispersion-hardened cobalt-chromium sheet as recited in claim 7 in which said chromium is present in an amount of from 10-30%, said nickel is present in an

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amount of from 10-25% and said refractory oxide is thoria present in a proportion of 1 to 4% by volume.

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