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3,446,679

DISPERSION-STRENGTHENED NICKEL-CHROMIUM FOIL

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4 Claims

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This invention relates to improved, dispersion-strengthened nickel-chromium alloy foil and processes for producing it, and is more particularly directed to dispersion-hardened nickel-chromium foil comprising nickel and about 10 to 30% 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 80 millimicrons said foil being less than 0.010 inch thick and characterized by good room temperature ductility and high temperature strength, and by having both (a) elongated grains having a length-to-thickness ratio greater than about 2 and a grain thickness in the range of about from 15 to 200 microns and (b) equiaxed grains having an average thickness of about from 10 to 80 microns, said equiaxed grains having annealing twins, and is further particularly directed to processes for making such foil, said processes comprising (1) preparing a dispersion-hardened nickel-chromium sheet having a grain structure characterized by the presence of a substantial proportion of grains with a length-to-thickness ratio greater than about 2 and a grain thickness in the range of about from 15 to 200 microns, (2) annealing the sheet at a temperature in the range of 1800 to 2400° F. and thereafter (3) cold-rolling to a gauge reduction of from 10 to 90 percent and (4) continuing the sequence of annealing and thereafter rolling until the composition has a thickness less than 0.01 inch.

In preferred processes and products of the invention the alloy consists essentially of nickel and about 15 to 25%, preferably about 20%, of chromium and the dispersed refractory oxide is thoria in the proportion of 1 to 4%, preferably about 2%, by volume, and having a particle size less than about 40 millimicrons, preferably about 10 to 40 millimicrons. In one preferred aspect of the novel processes the sheet, as above described, is annealed to effect full recrystallization and thereafter is rolled, in a single direction and at ambient temperature, to effect at least a 10% reduction in thickness, and the process of annealing and thereafter rolling is repeated until the sheet is less than 0.01 inch in thickness.

It is already known that sheet products having excellent service characteristics at elevated temperatures can be produced by powder metallurgy techniques employing nickel dispersion-hardened by such refractory oxides as thoria. However, in the fabrication of dispersion-hardened nickel-chromium alloys into the form of foil by conventional hot- or cold-rolling methods the products often crack and break up during fabrication.

Now according to the present invention, it has been found that if a sheet product, containing a dispersed refractory oxide such as thoria, is rolled to foil under controlled conditions, the foil products obtained have the desired room temperature ductility as well as the necessary elevated temperature strength and oxidation resistance.

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.

For improved high temperature strength in dispersion-modified nickel-chromium alloys it is desirable to have a relatively coarse-grained structure, but for good room temperature ductility it is desirable to have a fine-grained structure—preferably a fine-grained, cubic-textured structure. For maximum high temperature strength a coarse-grain structure is preferred. To get an optimum balance of both high strength at high temperature and satisfactory ductility at room temperature the grain thickness in a product of this invention is controlled at above about 15 microns, preferably in the range of 15 to 200 microns, and still more preferably 20 to 60 microns.

To measure the grain size of products of the invention conventional metallographic techniques are used. Certain etchants will reveal the presence of twins to a greater extent than grain boundaries, whereas for other etchants the reverse is true. In the dispersion-hardened alloys the twins often do not extend completely across the grains. Twins can be recognized by geometry relationships they bear to each other and can thereby be distinguished from the overall grain structure.

Broadly stated, in a process of the invention one starts with a powder comprising nickel and from 10 to 30% by weight of chromium, the metal phase 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—nickel, 20% Cr and 2 volume percent thoria, can be prepared, for instance, by coprecipitating the hydrous oxides of nickel and chromium together together with colloidal thoria of suitable size, drying the co-precipitate, and reducing the 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 2200° 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. In the early stages of the rolling step, plate having a recrystallization temperature of 1600 to 1900° F. and above can advantageously be substantially reduced in thickness at a temperature of 1500 to 1800° F., the temperature in any event being low enough to avoid recrystallization. In this way substantial economies are achieved, because at these relatively high temperatures a number of passes through the rolling mill can be effected before it is necessary to reheat the work piece.

Irrespective of the manner of preparing the consolidated body in the form of a material suitable for working to the sheet, the 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 hard-

ness 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. An increase in strength is also encountered, and this merely adds to the problem of further rolling.

Having generated the desired dispersion-strengthened sheet product, it is next rolled to foil, by the alternate annealing rolling technique above described.

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

A Ni-20-CR-2-ThO₂ powder was prepared by coprecipitating NiCo₃-Cr(OH)₃-ThO₂, filtering, washing, and drying at 300° C. One hundred parts of this powder were blended with 12 parts of carbon, the blend heated in hydrogen at 400° C. to reduce the nickel oxide, and then at 925° C. in H₂-CH₄ mixture to reduce the Cr₂O₃. Excess carbon was removed by heating in hydrogen at 875° C. The particle size of the thoria in the powder was about 16 mμ.

The powder was hydrostatically compacted at 60,000 p.s.i., to a rectangular slab 3½" x 6" x 12", and canned in a mild steel can (⅛" wall thickness). Mild steel end plates (⅛" thick) fitted with ¼" O.D. x .022" wall stainless steel tubing were welded in place to seal the can (excepting for the entrance and exit tubing lines in the end plates).

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

The sealed billet was placed in a 1800° F. furnace in air. When a billet temperature of 1800° F. was attained, the assembly was forged to a slab 1½" x 8" x 14". The resulting mild steel jacketed-nickel-chrome-thoria sheet bar was essentially 100% dense.

The grain size of the as-forged sheet bar was approximately 0.5μ (nearly equi-axed). The Rockwell C hardness of the sheet bar was 38. Chemical analyses of the as-forged sheet bar indicated it to contain about 25 p.p.m. sulfur and 125 p.p.m. carbon. The ThO₂ particle diameter (by extraction and B.E.T. surface area) was 18 mμ.

The forged piece was decanned by machining to top and bottom surfaces, cropped to sound material on the ends, and then recanned in ½ inch thick top and bottom cover plates. The resulting assembly was heated to 1300° F. and rolled in a single direction to a sheet thickness of 0.075 inch, reheating every second pass to 0.5 inch and every pass from 0.5 inch to final gauge.

This sheet was converted to foil by a sequence of annealing at 2200° F. and thereafter rolling to 20% reduction steps. Final gauge of the foil was 0.0035 inch.

The final foil had a transverse ultimate tensile strength of 7100 p.s.i. at 2000° F. It could be bent flat on itself without cracking.

Metallurgical examination of the foil showed that about 40% of the structure consisted of grains about 40 microns long and about 10-20 microns thick. The remainder of the structure consisted of equiaxed grains about 10-30 microns in diameter. The equiaxed grains showed twins.

I claim:

1. A dispersion-hardened nickel-chromium foil comprising nickel and about 10 to 30% 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 80 millimicrons, said foil being less than 0.010 inch thick and characterized by good room temperature ductility and high temperature strength, and by having both (a) elongated grains having a length-to-thickness ratio greater than about 2 and a grain thickness in the range of about from 15 to 200 microns and (b) equiaxed grains having an average thickness of about from 10 to 80 microns, said equiaxed grains having annealing twins.

2. A product of claim 1 wherein 40 to 60% of the structure is in the form of elongated grains having a grain thickness in the range of about from 20 to 60 microns.

3. A process for preparing foil from a dispersion-hardened nickel-chromium sheet having a grain structure characterized by the presence of a substantial proportion of grains with a length-to-thickness ratio greater than about 2 and a grain thickness in the range of about from 15 to 200 microns, said process comprising (a) annealing the sheet at a temperature in the range of 1800 to 2400° F. and thereafter (b) cold-rolling to a gauge reduction of from 1 to 90 percent and (c) continuing the sequence of annealing and thereafter rolling until the composition has a thickness less than 0.01 inch.

4. A process of claim 3 wherein the temperature of annealing is 2100° F., and the gauge reduction is not more than about 20% on each pass.

References Cited

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 37, the second occurrence of "together" should be cancelled. Column 3, line 47, "to" should be --the--. Column 4, line 37, "1" should be --10--.

SIGNED AND
SEALED

AUG 26 1969

(SEAL)

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