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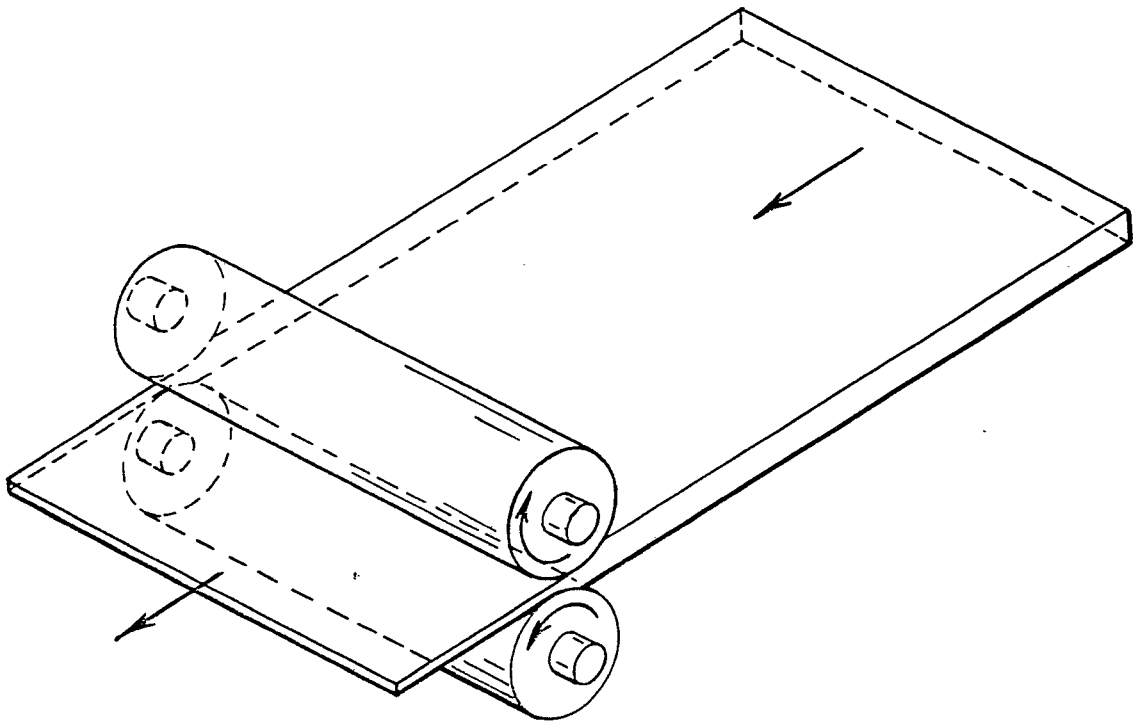

(57) Abstract

Process for producing sheets of dispersion-strengthened precious metal alloys having superior creep resistance. According to this invention dispersion-strengthened precious metal alloys are thermomechanically processed to help develop a creep resistance microstructure.

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D E S C R I P T I O N

THERMOMECHANICAL PROCESSING OF DISPERSION-STRENGTHENED PRECIOUS METAL ALLOYS

TECHNICAL FIELD

This invention relates to thermomechanical processing of dispersion-strengthened precious metal alloys. The present invention can provide alloys containing platinum, palladium, rhodium and gold which are useful in the production of glass fibers.

BACKGROUND ART

One of the most exacting applications of platinum is in the production of glass fibers. Molten glass often at temperatures ranging from 1200 to 1600°C passes through a series of orifices in a bushing. Advances in glass fiber production are demanding both larger bushings and higher operating temperatures.

Structural components such as these at elevated temperatures under constant loads experience continuous dimensional changes or creep during their lives. This creep behavior depends upon the interaction between the external conditions (load, temperature) and the microstructure of the component. In recent times, increased resistance to creep of material systems has been accomplished by using a dispersion of very small, hard particles (called dispersoids) to strengthen the microstructure of the component. These systems have become to be known as dispersion-strengthened metals and alloys and the dispersoids used are usually oxides. A recent

development in dispersion-strengthening is mechanical alloying which uses a high energy ball mill to achieve the intimate mechanical mixing typical of the process. An attritor mill or vibratory mill also can be used.

DISCLOSURE OF THE INVENTION

The present invention provides for the thermomechanical processing of dispersion-strengthened precious metal alloys.

The invention is comprised of a series of mechanical deformation and annealing cycles to help develop a creep resistant microstructure. Specifically, I achieve this by rolling and annealing a powder compact of dispersion-strengthened precious metal. The material may be cross-rolled as well as longitudinally rolled or just longitudinally rolled.

BRIEF DESCRIPTION OF DRAWINGS

FIGURE 1 is a schematic drawing of the rolling operation.

BEST MODE OF CARRYING OUT INVENTION

According to the process of this invention, the procedure used to thermomechanically process the compact was to roll the compact for a 10 percent reduction in area then anneal the rolled specimen. The reduction in area is carried out under a pressure that elongates the rolled specimen without substantially widening it. Generally, the annealing is carried out for a period of time and at a temperature sufficient to develop a specimen with a minimum creep rate. Preferably the annealing is carried out for five minutes at at 1,900°F (1,040°C) before further rolling. The total extent of deformation ranges from 50 to 90 percent reduction in area and generally is approximately an 85 percent reduction in area. This roll/anneal cycle was selected to help develop a creep resistance microstructure. The roll/anneal cycles are continued until the 85 percent reduction in area is accomplished.

There are several high-energy ball mills commercially available either using a stirrer or vibration

to induce mechanical alloying. Stainless steel bearings or grinding media and the powder charge go into the cylindrical container of the mill. The high-energy impacts are affected by the rotating impeller. In the internal arrangement of the attritor mill, impact events occur in the dynamic interstices of the media created by the impeller during stirring.

Dispersion-strengthened precious metals are known in the art and are commercially available. One such material is that available from Johnson, Matthey & Co. Limited, under their designation ZGS. The above indicated ZGS material consists essentially of platinum in which the disperoid is zirconia; the latter is present in an amount of about 0.5% by volume.

The dispersion-strengthened precious metals of this invention generally comprise a precious metal, or precious metal alloy, preferably platinum, as the dispersing medium, or matrix, and a dispersoid of a metal oxide, metal carbide, metal silicide, metal nitride, metal sulfide or a metal boride which dispersoid is present in effective dispersion-strengthening amounts. Usually such amounts will be between about 0.1 percent to about 5.0 percent by volume. Preferably the dispersoid will be an oxide. Exemplary of metal compounds which may be employed as the dispersoid are compounds of metals of Group IIA, IIIA, IIIB (including non-hazardous metals of the Actinide and Lanthanide classes), IVB, VB, VIB and VIIB. More specifically exemplary of suitable metals are the following: Be, Mg, Ca, Ba, Y, La, Ti, Zr, Hf, Mo, W, Ce, Nd, Gd, and Th as well as Al.

Several mechanical alloying experiments were performed using the attritor mill to generate a composite powder for consolidation. Wash heats intended to coat a thin layer of platinum on the internal working surfaces of the attritor mill were carried out. This "conditioning" treatment was intended to prevent iron contamination of subsequent milling experiments, but several washes were

required before the iron contamination was reduced to what was believed to be an acceptable level.

The samples then are consolidated by vacuum hot pressing (VHP) at elevated temperatures and pressures. In the alternative, the samples can be consolidated by first cold pressing at elevated pressures followed by sintering at elevated temperatures. VHP generally is carried out at a temperature ranging from 1300 to 1700°C under a pressure ranging from 500 to 10,000 psi for a time ranging from 10 to 30 minutes. Preferably, the temperature ranges from 1400 to 1500°C under a pressure of 3,000 to 6,000 psi for a time of 15 to 25 minutes. Generally, the cold pressing is carried out at a pressure ranging from 2,000 to 10,000 psi for up to 5 minutes followed by sintering at a temperature ranging from 1200 to 1700°C for 2 to 6 hours.

EXAMPLE I

Approximately one kgm of -325 mesh (-44 micron) platinum sponge from Englehard was blended with an amount of yttria (Y_2O_3) to give nominally 0.65 volume percent (0.15 weight percent) oxide loading in the final compact. The yttria was nominally 200-600 angstrom in size. The platinum matrix starting powder for the experiment consisted of very fine, near spherical particles or chained aggregates. Most of the particles below 2 microns appeared to be single crystals. The starting powder had a fairly high specific surface area.

The powder mixture was charged into the container of the attritor mill while it was running. The grinding media had been previously loaded to give a volume ratio of media to powder of 20:1. The grinding media used was a hardened 400 series stainless steel bearing nominally 3/8 inch (0.953 cm) diameter. The impeller rotational speed was selected at 130 rpm.

Samples of powder were removed at various times to obtain information on the changes in particle morphology and specific surface area with milling time. The first

sample was taken after one hour of milling and indicated that flake generation was in progress.

After milling for three hours, another powder sample was taken for metallographic characterization. While more flakes were generated, the extent of plastic deformation seemed to have increased. Flake cold welding appeared to have taken place as well. The composite flake appeared to have three or four component flakes cold welded together. No edge cracking appeared in the composite flake suggesting that work hardening saturation had not been reached at this point.

After milling for 23 hours, the composite flakes appeared to thicken. This clearly demonstrates the cold welding aspect of the milling action. Along with cold welding, the flake diameter appeared to increase.

The experiment was continued for 71 hours then terminated, and the powder was removed for further processing.

There appeared to be a fairly high initial surface area generation rate. The iron contamination in the milled powder was greatly reduced compared to the previous experiments and reflects the coating action that appeared to minimize wear debris generation during milling. The maximum iron contamination level in the powder was approximately 300 wppm. The milled powder was consolidated by vacuum hot pressing and thermomechanically processing into sheet for creep testing, the details are to follow.

EXAMPLE II

Example I produced a powder of relatively low iron contamination. Since this experiment resulted in small powder lots (nominally 80 gms) taken at various times during the milling experiment, each sample was individually consolidated by vacuum hot pressing (VHP) at 1,450°C under 5,000 psi (34.5 MN/m^2) for twenty minutes. The resultant compacts were nominally 1 inch (2.54 cm) in diameter.

Relative density of specimens are listed.

Specimen	Milling Time (hr.)	Relative Density (%)
A	0	95.2
B	1	98.2
C	2.5	99.8
D	6	99.8

The thermomechanical processing (TMP) used on the compact consisted of several roll/anneal cycles. The basic operation involved rolling a sheet specimen and cropping pieces after various rolling passes for microstructural characterization. The procedure used was to roll the compact for a 10 percent reduction in area then anneal the rolled specimen for five minutes at nominally 1,040°C before further rolling.

Specimen D was the most responsive to the TMP cycles. After the 10th rolling pass, the grain structure was fairly elongated. The lack of oxide clusters during optical metallographic examination suggested that the milling action had worked the yttria into the platinum matrix. A metallographic analysis of the same region showed the development of a moderate grain aspect ratio (grain length to thickness ratio in the viewing plane). As the number of roll/anneal cycles increased, the grain aspect ratio (GAR) increased. At this stage a moderate GAR also had been developed in a transverse direction. The significance of this observation is that the grains took on the shape of a pancake structure thin in a direction perpendicular to the sheet yet extended in the other two directions. Since a GAR seems to extend in two directions in the rolled sheet and the state of stress in a bushing tip plate is biaxial, this transverse GAR development may be very beneficial for good creep resistance in bushing applications.

After the 16th rolling pass, the elongation of the grains had increased significantly. A higher magnification view of the same region revealed the degree of grain elongation and fineness of the grain size. The transverse GAR had also significantly increased. These

elongated grain morphologies are desirable microstructures for good creep resistance.

INDUSTRIAL APPLICABILITY

EXAMPLE III

Creep Testing

All the creep testing was done in air using constant load machines, the elongation was measured by an LVDT connected to a multi-point recorder and a precision digital voltmeter. Specimen temperature was monitored with a calibrated Pt/Pt-Rh thermocouple attached so that the bead was adjacent to the gage section of the creep specimen. The creep specimen was a flat plate type with a gage length of approximately 2.25 inch (5.72 cm). The tensile stress was applied parallel to the rolling direction (longitudinal direction). The general procedure was to hang the specimen in the furnace to reach thermal equilibrium then start the rig timer upon application of the load. Periodic temperature and extension measurements were made either until the specimen failed or the test was terminated (specimen removal or furnace burn-out).

Creep results were obtained from specimens that were processed according to Example II except that these specimens were milled 10 hours and received the above thermomechanical processing treatment of 10% reduction in area per pass with an intermediate anneal at nominally 1040°C for 5 minutes. The extent of deformation was nominally an 85% reduction in area. The first specimen had a varied creep history that started by applying a tensile stress of 1,000 psi (6.89 Mn/m^2) at 2,400°F (1,316°C). The resultant secondary creep rate was too low to adequately measure; therefore, the temperature was increased to 2,600°F (1,427°C) and a secondary creep rate of 4.5×10^{-6} hr^{-1} was observed. After approximately 118 hours the stress was increased to 1,400 psi (9.65 Mn/m^2) and a new secondary creep rate of nominally 3×10^{-5} hr^{-1} was recorded. These creep rates are two orders of magnitude less than that for the previously indicated ZGS under the same

testing conditions. The ZGS material will have a stress rupture life of at least 48 hours when tested at 1400°C and 1000 psi in the rolling direction of the sheet.

The general microstructure of the crept specimen indicated that the grains were highly elongated in the rolling direction (creep stress direction also) and the grain boundries were ragged. There appeared to be evidence of subgrains in the structure as well. The microstructure observed in this specimen was typical of that of a good creep resistant material as evidenced by the exceptionally good creep properties.

C L A I M S

1. A process for producing sheets of dispersion-strengthened precious metal alloys comprising the step of thermomechanically processing compacted dispersion-strengthened precious metal alloys.

2. A process according to claim 1 wherein the thermomechanical processing comprises at least one mechanical deforming/annealing cycle and the cycles are repeated until a 50 to 90 percent reduction in area is achieved.

3. A process according to claim 2 wherein the mechanical deforming is rolling.

4. A process according to claims 2 or 3 wherein mechanical deforming is carried out until a 10 percent reduction in area is achieved before the compact is annealed.

5. A process according to claim 4 wherein the reduction in area is carried out at a pressure that elongates the compact without widening it.

6. A process according to claims 2 or 3 wherein the mechanical deforming/annealing cycles are carried out until approximately an 85 percent reduction in area is achieved.

7. A process according to claims 2 or 3 wherein the dispersion-strengthened precious metal alloy includes (1) platinum or a platinum alloy and (2) at least one metal oxide.

8. A process according to claim 7 wherein the metal oxide is yttria (Y_2O_3).

9. A process according to claim 1 wherein the

dispersion-strengthened precious metal alloy is produced by mechanical alloying.

10. A process for producing sheets of dispersion-strengthened precious metal alloys comprising a series of rolling/annealing cycles wherein each annealing step is carried out for a period of time and at a temperature sufficient to develop a specimen with a minimum creep rate.

11. A process for producing sheets of dispersion-strengthened precious metal alloys comprising the steps of:

(1) mechanically alloying platinum powder and yttria (Y_2O_3) together wherein the yttria is present in effective dispersion-strengthening amounts;

(2) consolidating the resulting powder by vacuum hot pressing at elevated temperatures and pressures; and

(3) carrying out a series of rolling/annealing cycles wherein each annealing step is carried out for a period of time and at a temperature sufficient to develop a specimen with a minimum creep rate.

12. A process according to claim 11 wherein the dispersion-strengthened precious metal alloy includes (1) platinum or a platinum alloy and (2) at least one metal oxide.

13. A process according to claim 12 wherein the metal oxide is yttria (Y_2O_3).

14. A process according to claim 13 wherein the amount of yttria ranges between 0.1 and 5.0 percent by volume.

15. A process according to claims 13 or 14 wherein the amount of yttria is 0.65 percent by volume (0.15 percent by weight).

16. A process according to claim 11 wherein the vacuum hot pressing is carried out at a temperature of 1,450°C under a pressure of 5,000 psi for a time of twenty

minutes and the annealing is carried out for 5 minutes at 1040°C.

17. A process according to claim 11 wherein high energy ball milling is used to achieve the mechanical alloying.

AMENDED CLAIMS
(received by the International Bureau on 20 November 1980 (20.11.1980))

C L A I M S

1. (Amended) A process for producing sheets of dispersion-strengthened precious metal alloys comprising the step of thermomechanically processing compacted dispersion-strengthened precious metal alloys, wherein the dispersion-strengthened precious metal alloys are produced by mechanical alloying.

2. A process according to claim 1 wherein the thermomechanical processing comprises at least one mechanical deforming/annealing cycle and the cycles are repeated until a 50 to 90 percent reduction in area is achieved.

3. A process according to claim 2 wherein the mechanical deforming is rolling.

4. A process according to claims 2 or 3 wherein mechanical deforming is carried out until a 10 percent reduction in area is achieved before the compact is annealed.

5. A process according to claim 4 wherein the reduction in area is carried out at a pressure that elongates the compact without widening it.

6. A process according to claims 2 or 3 wherein the mechanical deforming/annealing cycles are carried out until approximately an 85 percent reduction in area is achieved.

7. A process according to claims 2 or 3 wherein the dispersion-strengthened precious metal alloy includes (1) platinum or a platinum alloy and (2) at least one metal oxide.

8. A process according to claim 7 wherein the metal oxide is yttria (Y_2O_3).

9. (Cancelled)

10. (Amended) A process for producing sheets of dispersion-strengthened precious metal alloys comprising a series of rolling/annealing cycles wherein each annealing step is carried out for a period of time and at a temperature sufficient to develop a specimen with a minimum creep rate, wherein the precious metal alloys are produced by mechanical alloying.

11. (Amended) A process for producing sheets of dispersion-strengthened precious metal alloys comprising the steps of:

(1) mechanically alloying platinum powder and at least one dispersoid together wherein the dispersoid is present in effective dispersion-strengthening amounts;

(2) consolidating the resulting powder by vacuum hot pressing at elevated temperatures and pressures; and

(3) carrying out a series of rolling/annealing cycles wherein each annealing step is carried out for a period of time and at a temperature sufficient to develop a specimen with a minimum creep rate.

12. A process according to claim 11 wherein the dispersion-strengthened precious metal alloy includes (1) platinum or a platinum alloy and (2) at least one metal oxide.

13. A process according to claim 12 wherein the metal oxide is yttria (Y_2O_3).

14. A process according to claim 13 wherein the amount of yttria ranges between 0.1 and 5.0 percent by volume.

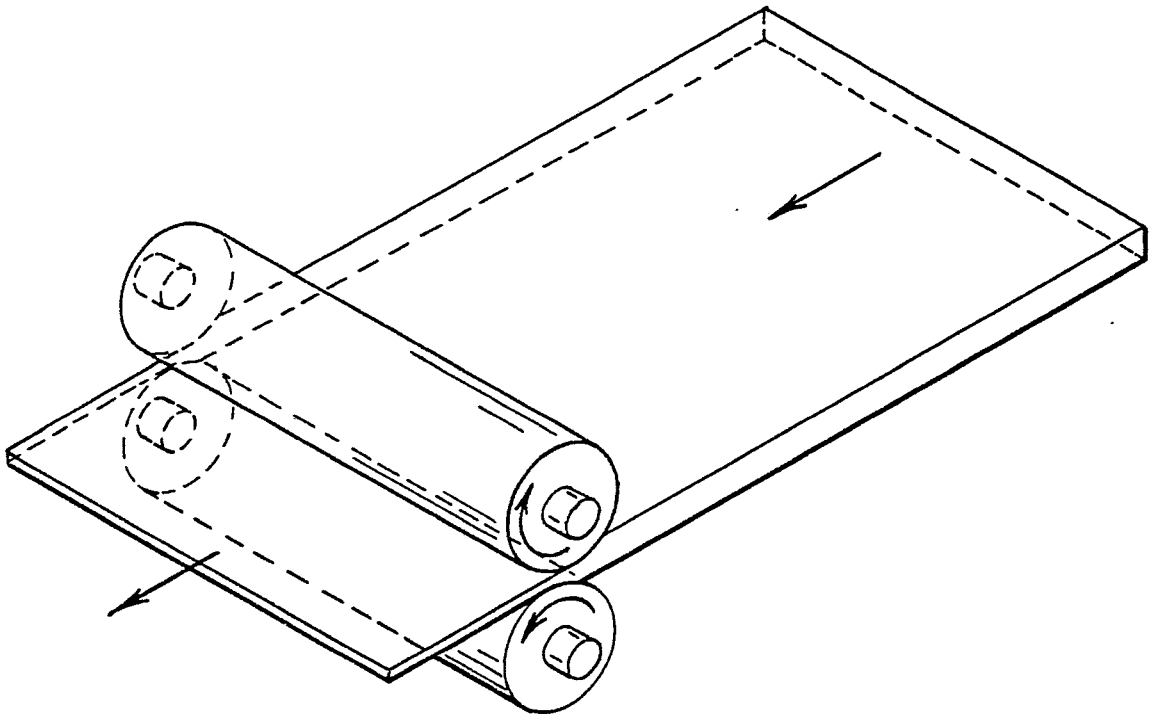
15. A process according to claims 13 or 14 wherein the amount of yttria is 0.65 percent by volume (0.15 percent by weight).

16. A process according to claim 11 wherein the vacuum hot pressing is carried out at a temperature of 1,450°C under a pressure of 5,000 psi for a time of twenty minutes and the annealing is carried out for 5 minutes at 1040°C.

17. A process according to claim 11 wherein high energy ball milling is used to achieve the mechanical alloying.

18. (New) A process according to claim 7 wherein the metal oxide is present in amounts ranging between 0.1 and 5.0 percent by volume.

19. (New) A process according to claim 18 wherein the amount of metal oxide is 0.65 percent by volume.



INTERNATIONAL SEARCH REPORT

International Application No PCT/US 80/01062

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL.3 C22F 1/14
US. CL. 148/11.5P

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
US	148/11.5P 75/172R, 951

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
X	GB,A 1,134,492, Published, 27 November 1968, See Page 5, lines 5-27, Johnson, Matthey and Company Limited.	1-7,9,10
X	CA,A 801,702, Published, 17 December 1968, See Page 8, lines 2-10, Sherritt Gordon Mines Limited.	1-14,17
X	US,A 3,738,817, Published, 12 June 1973, See Column 5, lines 40-52; Column 13, lines 42-45; Column 18, lines 66-75; Column 19, lines 1-10, Benjamin.	1-14,17
A	US,A 3,640,705, Published, 08 February 1972, See Column 2, lines 11, 12, Selman et al	16

* Special categories of cited documents: [15]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
04 NOVEMBER 1980	14 NOV 1980
International Searching Authority [1]	Signature of Authorized Officer [20]
ISA/US	PETER K. SKIFF