

DESCRIPTION

METHOD FOR MANUFACTURING OXIDE DISPERSION STRENGTHENED PLATINUM ALLOY

5

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

[0001]

The present invention relates to a method of producing an oxide-
10 dispersion-strengthened platinum alloy in which oxide is dispersed in
platinum or platinum alloy. In particular, the present invention relates to a
method in which contaminants that could be mixed during production are
reduced.

15 DESCRIPTION OF THE RELATED ART

[0002]

Oxide-dispersion-strengthened platinum materials in which oxide such
as zirconium oxide (zirconia) or yttrium oxide (yttria) is finely dispersed in
platinum or platinum alloy, also called strengthened platinum, have excellent
20 high temperature strength properties, in particular, excellent creep strength,
and are therefore used as a structural material for glass manufacturing
equipment used in a high temperature environment. For such oxide-
dispersion-strengthened platinum alloys, various improvements have been
made to increase, for example, high temperature strength. And there have
25 been many reports of materials in which oxide for dispersion has been
effectively dispersed as a result of the improvement in the production process
(Patent Documents 1, 2).

[Prior Art Documents]

[Patent Documents]

[0003]

[Patent Document 1] Japanese Patent No. 4094959

[Patent Document 2] Japanese Patent No. 4280215

5 [0004]

Here, as a method of producing an oxide-dispersion-strengthened platinum alloy, generally a powder metallurgy process is used. In the process, an alloy powder of platinum and zirconium is first prepared, and the powder is subjected to oxidization so that zirconium in the alloy powder is internally
10 oxidized to form zirconium oxide, thereby preparing a platinum powder in which zirconium oxide is finely dispersed. Then the above is formed into fine powder by milling means such as an attritor or a ball mill, and the resultant is sintered and processed into a platinum material. In the invention described in the above Patent Document 1, production conditions are adjusted based on
15 the above process. Also, in the above Patent Document 2, alloy powder of platinum and zirconium is prepared and then milled with the attritor in water without oxidization, thereby oxidizing zirconium by water, where the formation of oxide and milling of powder are carried out simultaneously, and then the powder is sintered; the invention is also based on the same powder
20 metallurgy process.

SUMMARY OF THE INVENTION

[Problems to be Solved by the Invention]

[0005]

25 Established methods of producing oxide-dispersion-strengthened platinum alloy have intended to disperse oxide particles in a suitable condition, and it can be said that those methods are all useful in that respect. However, all methods had problems with some of the resulting platinum alloy.

The problems include not only poor strength of the alloy but also higher hardness of the alloy than expected (designed) that may affect processing.

Cases of the problems involving processing due to increased hardness

reported include formation of a scaly processed surface due to extremely

5 high hardness of the material to be processed at the time of surface grinding for shaping.

[0006]

Such defective products are not due to the production method itself,

and are also unexpectedly produced even under a stable control including

10 quality control of raw materials. The present invention investigates the cause of the problem and provides a method capable of producing a high quality oxide-dispersion-strengthened platinum alloy in a stable manner.

[Means for Solving the Problems]

[0007]

15 To solve the above problem, the present inventors have thoroughly examined the steps of conventional methods of producing oxide-dispersion-strengthened platinum alloys and studied the properties of defective platinum alloy. As a result, the inventors have found that zirconium oxide having relatively large and uneven particle size is dispersed in the platinum alloy
20 having problems. So the inventors have examined the cause of the mixing of such large particle size zirconia and focused on the structural material of milling equipment in the milling step.

[0008]

25 Milling equipment such as an attritor and a ball mill is provided with a container (pot) for containing a material to be milled, a milling medium (balls, beads) and an agitating rod (agitator). And in the milling equipment for producing an oxide-dispersion-strengthened platinum alloy, zirconia is often used as a milling medium in terms of the hardness. In this regard, the oxide-

dispersion-strengthened platinum alloy is obtained by dispersing oxide such as zirconia, and therefore even if milling medium zirconia is mixed, it is not necessary to regard it as a contaminant, and thus the mixing has not been considered as a problem.

5 [0009]

On the other hand, the present inventors have considered that the mixing of zirconia at the time of milling that has been ignored so far is exactly the problem. It is true that zirconia functions as a dispersion strengthening agent for an oxide-dispersion-strengthened platinum alloy, but in the principle
10 of dispersion strengthening, irregular dispersion of oxide having a particle size larger than that of the original dispersant may cause a material strength different from the designed value. Then the movement of the milling medium during the milling operation is not always predictable, and it is impossible to control the abrasion amount of the medium or the size of fragments
15 separated due to abrasion. It is considered that for this reason, unfavorable zirconia is mixed in some occasion. The present inventors have found the present invention for carrying out a milling operation with suppressing the mixing of zirconia in a milling step.

[0010]

20 Accordingly, the present invention is a method of producing an oxide-dispersion-strengthened platinum alloy, comprising a step of milling a material to be milled composed of platinum alloy in a solvent by means of a milling equipment provided with a container, a milling medium and an agitator, wherein at least the surfaces, coming into contact with the material to be
25 milled, of the container, the milling medium and the agitator are made of platinum or platinum alloy, and the material is milled with a hydrogen peroxide solution introduced into the solvent.

[0011]

In the method of the present invention, for the container, the milling medium and the agitator that have the structural materials of the milling equipment in the milling step, the entire surface that comes into contact with the material to be milled is made of platinum or platinum alloy (hereinafter they may be referred to as a platinum material). When the entire surface that comes into contact with the material to be milled is made of a platinum material as described above, the mixing of zirconia can be inevitably avoided.

[0012]

The present invention is more than mere modification of the structural material of milling equipment. When the material to be milled and the milling equipment are made of a platinum material as in the present invention, it is likely that the material to be milled adheres and is bonded to the agitator or the wall of the container to hinder the progress of milling. Such phenomenon is more likely to occur in a high energy ball mill such as an attritor. In view of this phenomenon, hydrogen peroxide is added to the solvent in the container in the present invention. Addition of hydrogen peroxide generates bubbles in the solvents, and the bubbles serve as a cushioning material to prevent platinum from adhering, enabling smooth milling operation.

[0013]

Hereinafter the present invention will be described in more detail. In the method of the present invention, the steps before and after the step of milling of platinum alloy powder are basically in accordance with conventional methods of producing an oxide-dispersion-strengthened platinum alloy. The preparation of platinum alloy powder before the milling step is also based on the conventional method. For example, as described in the above Patent Document 1, platinum alloy powder is internally oxidized to prepare platinum alloy powder in which zirconia or the like is dispersed, or as in Patent

Document 2, platinum alloy powder which does not contain oxide is prepared without oxidization; either process may be employed.

[0014]

5 In the milling step in the present invention, milling equipment in which the surfaces of the container, the milling medium and the agitator that come into contact with the material to be milled is made of platinum or platinum alloy is used. Here, platinum or platinum alloy may be applied to at least the surfaces which come into contact with the material to be milled. Therefore, equipment in which the full body of the structural materials is made of
10 platinum, or equipment in which some part of the structural materials is made of platinum may be used. A container, for example, whose inner surface is clad with platinum, or a stainless steel container in which a smaller-diameter container made of platinum is inserted, may be used. Likewise, the agitator may be made of solid platinum or the like, or a rod material clad with platinum
15 may also be used. Here, as platinum or platinum alloy constituting the surface that comes into contact with the material to be milled, pure platinum, platinum alloy (platinum-rhodium alloy, platinum-gold alloy, etc) and also strengthened platinum (oxide-dispersion-strengthened platinum alloy) may be used. Strengthened platinum contains oxide such as zirconia, but the
20 absolute quantity is extremely low and if the oxide is in strengthened platinum without any quality problem, minor mixing of the oxide in the material to be milled causes little problem. Therefore, strengthened platinum may also be used.

[0015]

25 The milling step comprises wet milling in which a solvent is used. This is for dispersing the material to be milled adequately. Examples of solvents include pure water, organic solvents such as heptane and alcohol, and mixed solutions thereof. When platinum alloy powder which has not been oxidized

is oxidized in the milling step as in Patent Document 2, water (pure water) is preferably used.

[0016]

It is preferable that hydrogen peroxide is introduced into the solvent to
5 be used so that the concentration of hydrogen peroxide is 0.2 to 1% in the
solvent. This is because a concentration of less than 0.2% results in low
foaming which is less effective, and on the contrary a concentration of more
than 1% causes intense foaming that is difficult to control. It is preferable to
add the hydrogen peroxide solution in the form of an aqueous solution, and
10 the concentration and the amount of addition of the aqueous solution is
adjusted in consideration of the concentration in the solvent described above.
For the timing of the addition of hydrogen peroxide, it may be added at one
time at the start of milling or in several installments during milling.

[0017]

15 The condition of milling (time, temperature) in the milling step may be
determined in the same manner as in conventional methods. So may be the
number of rotations of the agitator.

[0018]

The alloy powder after the milling step may be formed into bulk alloy
20 by shaping and consolidation as in conventional methods. For shaping and
consolidation, a method of sintering with pressurizing as with a hot press is
preferred. Further, the percent compaction of the alloy after shaping and
consolidation can be increased by forging. Furthermore, for processing into a
predetermined shape, plastic processing such as rolling, extrusion and
25 drawing may be carried out.

[Advantageous Effects of Invention]

[0019]

The present invention can prevent mixing of zirconia into the material to be milled that has been occurred in the milling step, and can provide an oxide-dispersion-strengthened platinum alloy which does not contain coarse zirconia. As a result, a strengthened platinum alloy having good processability without unpredictable change in strength can be produced.

[0020]

Also, since a platinum material is used as a milling medium in the present invention, the oxide to be dispersed can be refined and highly dispersed. This is attributable to the fact that the platinum material as a dispersion medium is heavier (has higher specific gravity) than zirconia that has been conventionally used, and therefore the platinum material involves higher kinetic energy in milling than before and thus improves the milling ability. The present invention contributes to the improvement in the quality of platinum alloy in this respect as well.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021]

[Fig. 1] Fig. 1 is a view illustrating the structure of milling equipment (attritor) used in an embodiment.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0022]

Hereinafter a preferred embodiment of the present invention will be described. In this embodiment, first a platinum alloy (platinum - 0.1% by weight zirconium alloy) powder was produced. For producing the platinum alloy powder, a platinum - 0.1% by weight zirconium alloy ingot was prepared by vacuum melting and by using the ingot as an electrode, the platinum alloy powder was produced by a rotating electrode gas atomization process (EIGA

process). The platinum alloy powder has an average particle size of 80 μm (particle size distribution of 1 to 300 μm).

[0023]

Next 4000 g of the above alloy powder was introduced into the attritor shown in Fig. 1. The attritor used in this embodiment is provided with a container in which a pot (inner diameter ϕ 195 $\times$ height 175 mm $\times$ thickness 2 mm, weight 5.8 kg) made of strengthened platinum (trade name: GTH, available from TANAKA KIKINZOKU KOGYO K.K.) produced by the method of Patent Document 1 is inserted in a stainless steel pot, an agitator made of strengthened platinum (GTH) (agitating blade ϕ 16 $\times$ 160 mm $\times$ 4 blades, weight 14 kg), and as a milling medium, a ball made of strengthened platinum (ϕ 5 mm, total 14 kg).

[0024]

The attritor was charged with 2 L of pure water and an aqueous hydrogen peroxide solution was added thereto at 0.5% relative to pure water.

[0025]

For the milling step, after the above preparation, the platinum alloy powder was milled by rotating the agitator of the attritor at 340 rpm for 5 hours. In this Example, the platinum alloy powder was simultaneously oxidized with pure water.

[0026]

After the milling step, the platinum alloy powder was separated by screening and dried. When the platinum alloy powder after drying was precisely weighed, the weight was 4002.7 g, up 2.7 g compared to before milling. When the weight of the structural members of the attritor was measured after the milling step, the weight of the balls, the agitator and the pot was found to be decreased by 1.5 g, 1.0 g, and 0.2 g, respectively. The

weight of the platinum alloy powder increased due to the mixing of platinum alloy in the platinum alloy powder in milling.

[0027]

The platinum alloy powder after the milling step was put in a carbon mold (size: 70 × 70 × 100 (mm)), subjected to degassing in a vacuum oven (1200°C × 3 hours), and then pressurized and sintered at 1100°C at 20 MPa. The platinum alloy after sintering had a size of about 70 mm × 70 mm × 48.4 mm and a density of 16.9 g/cm³. The platinum alloy ingot was subjected to hot forging (1300°C) for several times to have a density of 21.4 g/cm³ (percent compaction 100%). At this stage, the ingot had a size of about 75 mm × 100 mm × 25 mm. Both surfaces of the platinum alloy ingot were ground by a shaper, and the ingot was cold rolled (100 mm × 310 mm × 6 mm), annealed (1250°C, 30 minutes) and then turned 90 degrees and cold rolled again to form a sheet material of 600 mm × 300 mm × 1 mm. A specimen for the creep test described later was punched out of the sheet material.

[0028]

Comparative Example: For comparison, platinum alloy was produced by a conventional milling step. The platinum alloy powder used was the same as that in the embodiment. The attritor used in the milling step is provided with a pot made of zirconia (inner diameter ϕ 200 × height 165 mm, capacity 5L), a stainless steel agitator (with a zirconia cap attached to the tip of the agitating blade, having the same size and shape as those of the embodiment), and as a milling medium, a YZT zirconia ball (ϕ 5 mm, total 7 kg). In the milling step, 4000 g of the platinum alloy powder and 2 L of pure water were introduced to the attritor and milling was carried out under the same conditions as in the embodiment.

[0029]

When the platinum alloy powder after milling and drying was precisely weighed, the weight was 4005.7 g, up 5.7 g compared to before milling.

When the weight of the zirconia balls in the attritor after the milling step was measured, the weight was found to be decreased by 5.7 g.

5 [0030]

The platinum alloy powder after milling was formed into an ingot by sintering by the same process as in the embodiment, and then the ingot was formed into a sheet material by hot forging and rolling. Also, a specimen for the creep test was obtained.

10 [0031]

The oxide-dispersion-strengthened platinum alloys produced in the embodiment and Comparative Example were subjected to quantitative analysis of zirconium content in the alloy and a creep test. In the creep test, 5 specimens were used to measure the rupture time at a test temperature of 1400°C and a stress of 15 MPa and 20 MPa. The results are shown in Table 1.

[0032]

[Table 1]

	Zr content	Creep test		
		Specimen No.	Stress	
			15 Mpa	20 Mpa
Embodiment	0.10 wt%	1	100 hours or more	62 hr
		2	100 hours or more	69 hr
		3	100 hours or more	55 hr
		4	100 hours or more	81 hr
		5	100 hours or more	44 hr
Comparative Example	0.21 wt%	1	41 hr	10 hr
		2	34 hr	8 hr
		3	55 hr	17 hr
		4	29 hr	5 hr
		5	28 hr	14 hr

[0033]

As shown in Table 1, the zirconium content in the platinum alloy of the
5 embodiment is 0.1% by weight, which is the same as the zirconium content in
the raw material platinum alloy powder before milling. This shows that the
mixing of zirconia in the milling step is suppressed. On the other hand, in
Comparative Example the zirconium content in the platinum alloy produced
has increased by 0.11% by weight, showing the mixing of zirconia in the
10 milling step. This is also suggested by the decrease in the weight of the
milling medium (zirconia balls) after the milling step.

[0034]

The results of the creep test show that the platinum alloy of the
embodiment has excellent high temperature strength. More specifically, the

platinum alloy of the embodiment is effective in extending the rupture time by several times compared to Comparative Example as shown in Table 1.

[0035]

The advantageous effect of the embodiment was also seen in the step
5 of producing the above platinum alloy sheet material. More specifically, when both surfaces of the hot forged ingot were ground, the entire surface was smooth and glossy in the embodiment after grinding, while in Comparative Example the surface was partly scaly. From this, it is considered that the method of the embodiment in which the mixing of zirconia is avoided also
10 contributes to the improvement in the processability of platinum alloy.

[0036]

Also, the change in the weight of the platinum alloy powder and the change in the weight of the milling medium (strengthened platinum balls) before and after milling in this embodiment show that a small amount of
15 platinum alloy has been mixed to the platinum alloy powder in the milling step. However, from the results of the creep test, it cannot be said that the mixing has deteriorated the properties of the platinum alloy. Further, even the results of analysis of the zirconium content show that the composition ratio of the oxide-dispersion-strengthened platinum alloy of the embodiment has not
20 changed, and it is considered that the strengthening ability is not reduced.

[Industrial Applicability]

[0037]

As described above, the method of producing an oxide-dispersion-strengthened platinum alloy of the present invention can provide a higher
25 quality platinum alloy than that produced by the conventional method.

WHAT IS CLAIMED IS:

1. A method of producing an oxide-dispersion-strengthened platinum alloy, comprising a step of milling a material to be milled composed of platinum alloy in a solvent with milling equipment provided with a container, a
5 milling medium and an agitator,
wherein at least surfaces, coming into contact with the material to be milled, of the container, the milling medium and the agitator are made of platinum or platinum alloy, and
the material is milled with a hydrogen peroxide solution introduced into
10 the solvent.
2. The method of producing an oxide-dispersion-strengthened platinum alloy according to claim 1, wherein the hydrogen peroxide solution is introduced into the solvent in the container so that the concentration of
15 hydrogen peroxide is 0.2 to 1% in the solvent.