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DISPERSION STRENGTHENING OF PLATINUM-BASE ALLOYS

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This invention relates to the production of high strength precious metals and alloys and, in particular, to dispersion strengthened platinum and platinum-base alloys characterized by high temperature creep strength at temperatures ranging up to about 1100° C. and higher.

Included among the precious metals are platinum, palladium, rhodium, iridium, ruthenium and alloys based on these metals. For the purposes of this invention rhenium and rhenium-base alloys are also included as coming within the purview of precious metals.

Dispersion strengthening consists of dispersing a finely divided, substantially insoluble, refractory oxide phase throughout a metal matrix. This type of strengthening has been studied primarily by means of powder metallurgy techniques using a metal powder as the matrix-forming material which is blended with finely divided refractory oxide particles, such as Al_2O_3, and which is thereafter consolidated by hot working to the desired shape.

Dispersion strengthening has the advantage of promoting high temperature strength and stability unobtainable by other techniques. This is evidenced by increased recrystallization temperatures and the absence of intercrystalline failures in low strain rate tests at high temperatures. The dispersion should preferably be a hard, inert, stable phase, such as a refractory oxide, of sub-micron size. Storage of energy, obtained by a high strain rate deformation process, such as extrusion, produces a strong, stable material at high temperatures. The second phase is not prone towards coalescence as in age-hardenable alloys and, moreover, the particle size and distribution of the dispersoid remain to a large extent fixed.

It would be desirable to produce dispersion-strengthened platinum characterized by high strength properties at both room and elevated temperatures for use in high temperature oxidation resistant devices, such as stirring rods used in glass manufacture, liners in glass furnaces, structural elements for load carrying applications at elevated temperatures, spinnerettes for spinning glass fibers, and other high temperature uses. However, attempts to optimize the high temperature strength properties of platinum have not been too successful. For example, dry blending platinum powder with alumina followed by consolidation to a wrought shape did not always optimize the physical properties as expected. A disadvantage which would arise in utilizing fine platinum or platinum alloy powder, for example powder of minus 325 mesh in size, such as powder ranging up to about 10 or 5 microns in size, but which contained sufficient amount of powder below 2 or 3 microns in size and down into the sub-micron range, was the tendency towards spontaneous ignition during the early processing of the powder mixture. The problem was particularly acute with freshly prepared powder and, where spontaneous ignition occurred during processing, it was difficult to optimize the properties of the final product produced therefrom.

Attempts to add the refractory oxide by utilizing a wet method of adding it in the form of a soluble salt dissolved in a solvent, but decomposable to a refractory oxide after drying followed by heating, also presented a problem in that at times the decomposition would uncontrollably proceed exothermically, whereby the final product would accordingly be limited in its properties.

It is the object of this invention to provide a method for producing dispersion strengthened precious metals and alloys thereof and, in particular, platinum and platinum-base alloys characterized by improved strength properties at room and elevated temperature, including improved resistance to creep at elevated temperatures ranging up to 1100° C. and higher.

Another object is to provide as an article of manufacture a high strength precious metal product characterized by improved resistance to creep at elevated temperatures up to 1100° C. and higher.

These and other objects or features will be more clearly apparent when considered in the light of the following disclosure.

In carrying out the method aspects of our invention, we preferably provide a finely divided platinum or platinum-base metal powder under substantially inert conditions which inhibit spontaneous ignition of said powder. We then provide a solution of a refractory oxide-forming salt, e.g., thorium nitrate dissolved in alcohol, and slowly add the metal powder to it while rapidly stirring said solution and form a thick slurry in order to effect a homogeneous mixture throughout in as short a time as possible, this step likewise being preferably conducted under substantially inert conditions. The rate of stirring should be at least sufficient to avoid isolated heavy concentrations of the solution in the thick mass so as to inhibit as much as possible a high rise of temperature which otherwise occurs exothermically when the mass is not homogeneously mixed. The rate of stirring may go as high as 20,000 r.p.m., or range from about 5,000 to 20,000 r.p.m. After a homogeneous mix has been obtained, the stirring thereafter is continued while evaporating the solvent under substantially inert conditions until a dry residue is obtained comprising the metal powder and the salt. The stirring need be just sufficient to augment the evaporation. The residue is then preferably uniformly distributed over the hearth of a decomposition chamber under a substantially inert atmosphere and the temperature of the chamber raised to a level at least sufficient to decompose the nitrate salt and leave behind a uniform dispersion of a finely divided refractory oxide powder as a coating about the particles. The decomposition tends to proceed exothermically, but it may be controlled by the rate at which heat is applied and by uniformly spreading the powder about the hearth. The powder mixture resulting from this treatment is ready for compaction and extrusion into the desired shape.

In one embodiment of our invention, we are able to achieve a markedly high creep strength at 1100° C. by utilizing thoria decomposed from thorium nitrate.

In applying the principles of our invention, the particle size distribution of the precious metal powder may range as high as 325 mesh and preferably not exceed 10 microns. We prefer for optimum results that the particle size be maintained below about 5 microns and, more preferably, range from about 0.1 to 1 or 2 microns. The invention is applicable to any one of the precious metals

Pt, Pd. Rh, Ru, Ir and Re taken alone or as alloys of at least two of the metals with each other. Thus, in the case of platinum alone, it may comprise at least about 99% Pt and, more preferably, at least about 99.8% Pt, and the balance elements which do not substantially adversely affect the properties of the final composition.

In the case of platinum-base alloys, we prefer those alloys which contain at least about 50% Pt with substantially the balance at least one metal from the precious metal group, with the sum of the platinum and the precious metal constituting at least about 99% of the total composition and, more preferably, at least about 99.8% similarly as for platinum per se above.

With regard to the decomposable refractory oxide-forming salts, we prefer those salts which are soluble in non-residue leaving solvents, such as water, or alcohol or other organic solvents, and which salts will decompose under prevailing conditions into a refractory oxide whose negative free energy of formation is at least about 100,000 calories per gram atom of oxygen at about 25° C. and, more preferably, at least about 120,000 calories. We prefer for our purposes to use soluble, oxygen-containing salts.

The solvent for the salt should be one which evaporates below the decomposition temperature of the salt and does not leave a residue.

We prefer that the soluble salt be one whose decomposition temperature does not exceed about 550° C. and, more preferably, does not exceed about 375° C. Examples of soluble refractory oxide-forming salts which decompose to form dispersions of refractory oxide are

$Th(NO_3)_4 \cdot 4H_2O$; $Al(NO_3)_3 \cdot 9H_2O$; $Al(C_2H_3O_2)_3$; $Al_2(C_2O_4)_3 \cdot 4H_2O$; $2NH_4NO_3Ce(NO_3)_3 \cdot 4H_2O$; $Ce(NO_3)_3 \cdot 6H_2O$; $Ba(NO_3)_2$; $Be(NO_3)_2 \cdot 3H_2O$; $Ca(NO_3)_2 \cdot 4H_2O$; $Gd(NO_3)_3 \cdot 5H_2O$; $La(NO_3)_3 \cdot 6H_2O$; $Mg(C_2H_3O_2)_2 \cdot 4H_2O$; $Nd(NO_3)_3 \cdot 6H_2O$; $Sr(NO_3)_2 \cdot 4H_2O$; $5TiO_2N_2O_5 \cdot 6H_2O$, etc. Certain of the chlorine salts may be employed provided the prevailing conditions are such as to favor formation of oxides. The salts may comprise nitrates, oxalates, acetates, chlorides and the like. The foregoing salts are at least to some extent soluble in water, alcohol or both. The refractory oxides formed by the decomposition of these salts are those which have a negative free energy of formation of at least about 100,000 calories per gram atom of oxygen at about 25° C.

We prefer to use thorium nitrate as the source of the refractory oxide ThO_2 as we have been able to realize execptionally high strength properties with it. In addition, we find thorium nitrate easy to work with because of its high solubility in alcohol.

In order to insure optimum strength properties in the final product, we prefer that the platinum powder be provided as fine as possible. We find the powder to be satisfactory for our purposes when it has been reduced to yield a high specific surface which is generally indicated when the powder shows a high degree of pyrophoricity on exposure to an oxygen-containing atmosphere. However, in order to utilize the advantages of such a powder, particular care must be taken to handle the powder under substantially inert environment or conditions. We prefer when reducing the powder to sizes below 3 microns in an attrition mill to carry out the grinding in alcohol or other suitable liquid in controlled atmosphere, such as argon or other inert gas. The attrition mill we have found suitable for our purposes is one in which the grinding vessel or tank is stationary and in which a ball charge and the powder are kept in constant motion. After grinding to a particle size below about 3 microns and preferably over the range of about 0.1 to 1 or 2 microns, the powder is washed and dried in a substantially inert or protective environment, e.g., in argon, and retained under the inert atmosphere for wet mixing, with the dissolved refractory oxide-forming salt.

Of course, other means may be used to insure an inert or protective environment, such as vacuum, or a liquid medium. A still further method would be to stabilize the finely ground platinum powder during grinding. For example, during wet grinding, sufficient oxygen might be bled into the mill atmosphere so that any oxidation which takes place in the mill environment is controlled in accordance with the prevailing oxygen partial pressure. Thus, the finely ground platinum powder would be stabilized to the extent that its high degree of pyrophoricity would be sufficiently inhibited to render the powder easier to handle in subsequent operational steps. Thus, the terms "inert environment," "protective environment," and "inert conditions" are meant to cover those means for protecting the powder to avoid as far as possible from it markedly undergoing spontaneous ignition.

In producing the finely divided platinum powder by grinding or other means, care should be taken to avoid absorption of certain impurities which might prevail in a grinding mill in amounts which tend to adversely affect the disperse phase in the final wrought product. For example, iron substantially in excess of about 0.5% by weight should be avoided as far as possible where optimum high strength properties of the wrought product are desired in oxygen-containing atmospheres. Preferably, such elements should not exceed 0.2% by weight. It is believed that the presence of certain amounts of iron, silicon, chromium, copper, nickel and cobalt in excess of 0.5% by weight in the form of non-refractory oxides adversely affect the disperse phase in the final wrought product, such as to cause the phase to agglomerate into larger sizes above the preferred sub-micron size range and thereby result in lower strength properties.

As illustrative of the invention, the following examples are given:

EXAMPLE 1

An amount of platinum powder was ground in an attrition mill in ethyl alcohol containing a wetting agent to an average particle size in the neighborhood of about 1 to 2 microns under substantially inert conditions. After grinding, the powder was washed in isopropyl alcohol, while being protected from the atmosphere, and further washed in distilled water and dilute hydrochloric acid solution. The powder was then dried under an argon atmosphere and maintained under this condition for the next step.

Portions of thorium nitrate sufficient to give several oxide loadings ranging from about 8 to 12.5% by volume when mixed with various portions of the ground platinum powder were each dissolved in methyl alcohol. Weight portions of the ground platinum powder were slowly added to each of the nitrate solutions in a rotating blender, for example a Waring Blendor, and a thick slurry of each formed. The mixing was done under an argon atmosphere at a rate of about 15,000 r.p.m. Each batch was then subjected to evaporation in a partial vacuum in argon while continuously being stirred. Thereafter, each batch of dried powder was treated in a decomposition furnace by heating to a temperature of about 205° C. to decompose the thorium nitrate coated about the particles. The decomposition proceeded somewhat exothermically during the evolution of gases and there was a rise in temperature. It was found that where the powder was spread out over a wide area in the decomposition chamber, the reaction was controllable. However, where the powder batches were merely placed in the decomposition in bulk, the decomposition was somewhat violent and tended toward overheating. Best results were obtained in the final product when the powder was uniformly spread over a large area.

Each batch of powder was then compacted into a slug of about 1½ inches in diameter and 2½ inches long at a pressure of about 30,000 p.s.i. and then sintered in dry hydrogen at about 1010° C. for 12 hours. The slug was

then canned in a stainless steel container and extruded at about 1035° C. at an extrusion ratio of about 20/1.

For evaluation purposes, the extruded product was machined into specimens of 0.160" diameter and 1.0" gauge length for determining room temperature tensile tests and stress-rupture tests at elevated temperatures. Creep tests were also run in air at 1100° C.

In using the foregoing method of preparation, three platinum-thoria compositions were prepared from the same batch of ground platinum powder: P–1, P–2 and P–3 containing 8%, 10% and 12.5% by volume of thoria, respectively. Very high room temperature properties were obtained as compared to pure platinum as follows:

Table 1

Alloy No.	Powder Size, μ	Vol. Percent Thoria	Yield Strength 0.2% Offset (p.s.i.)	Tensile Strength	Percent Elong.
P–1	1–2	8	127,000	146,000	4.5
P–2	1–2	10	128,000	164,000	-------
P–3	1–2	12.5	119,000	148,000	6.2
Pure Pt (Wrought)	-------	-------	----------	28–32,000	3.5
Pure Pt (Annealed)	-------	-------	12,000	18–22,000	40.0

Stress rupture tests were run in air at 1100° C. for P–1 and P–3. The stresses to give 1, 10 and 100 hours rupture lives are listed in Table 2.

Table 2

Alloy No.	Vol. Percent Thoria	Rupture Time, Hrs.	Stress to Rupture, p.s.i.
P–1	8	1	4,000
P–3	12.5	1	8,100
Wrought Pt	----------	1	1,900
P–1	8	10	3,400
P–3	12.5	10	7,000
Wrought Pt	----------	10	1,200
P–1	8	100	3,200
P–3	12.5	100	6,400
Wrought Pt	----------	100	620

Alloy P–3 also sustained high loads at 1200° C. and 1300° C. as follows:

Table 3

Temp., ° C.	Stress to Rupture, p.s.i.		
	1 Hr.	10 hrs.	100 hrs.
1,200	5,800	5,100	4,700
1,300	4,100	3,200	2,800

The markedly high stress to rupture properties of alloy P–3 at 1300° C. will be better appreciated when considered with a wrought alloy of 60% Pt–40% Rh which exhibited a 100 hour rupture stress of about 1200 p.s.i. as compared to 2800 p.s.i. for P–3. Thus, alloy P–3 had a stress for 100 hour rupture of over 230% greater than the Pt-Rh alloy.

Similar tests were conducted using a Pt-Rh alloy containing 10% Rh. The powder of this alloy had a particle size of about 2 to 8 microns, with the average size in the neighborhood of about 5 microns. The powder was lightly oxidized in the as-received condition. One batch of powder was first reduced and mixed with a thorium nitrate solution to form a thick slurry (corresponding to 12.5% of thoria) and another batch before reduction PR–5 mixed with another thorium nitrate solution to form a thick slurry (corresponding to 10 v/o thoria). As in Example 1, the processing steps were carried out in argon. After evaporating the alcohol solvent, both mixtures were decomposed as in Example 1. In the case

of PR–5, the decomposed mixture was reduced in hydrogen. Thus, the dry mixes differed in that one was reduced in hydrogen before decomposition (PR–4) and one reduced in hydrogen after decomposition (PR–5). Both mixes in the reduced state exhibited pyrophoricity and had to be handled under inert conditions, e.g., argon.

Wrought extruded products were made from each using the same procedure as Example 1 and test specimens similarly prepared. Room temperature properties obtained are as follows:

Table 4

Alloy No.	Powder Size, μ	Vol. Percent Thoria	Yield Strength 0.2% Offset (p.s.i.)	Tensile Strength	Percent Elong.
PR–4	2 to 8	12.5	87,400	100,700	1.8
PR–5	2 to 8	10.0	87,500	107,100	2.2
Pure Pt Wrought	-------	-------	----------	28–32,000	3.5

Stress-rupture properties were also obtained at 1100° C. These results are given in Table 5 as follows:

Table 5

Alloy No.	Vol. percent Thoria	Rupture Time, Hrs.	Stress to Rupture, p.s.i.
PR–4	12.5	1	6,200
PR–5	10.0	1	5,800
Wrought Pt	----------	1	1,900
PR–4	12.5	10	4,100
PR–5	10.0	10	4,000
Wrought Pt	----------	10	1,200
PR–4	12.5	100	2,600
PR–5	10.0	100	1,900
Wrought Pt	----------	100	620

It is noted that markedly high stress to rupture properties are also obtained for the Pt-Rh alloy matrix. Similar trends are indicated for platinum-base alloys containing up to 40% by weight of at least one metal selected from the platinum-group metals referred to hereinbefore. Likewise, similar trends are also indicated for other refractory oxides, preferably those whose negative free energy of formation exceeds about 120,000 calories per gram atom of oxygen, such as BeO, Al_2O_3, ZrO_2, La_2O_3, Y_2O_3 and the like.

In addition, similar trends are indicated for other of the precious metals, such as palladium and palladium-base alloys. Thus, in dispersion strengthening an alloy containing 60% palladium and about 40% platinum, a powder of the alloy would preferably be ground as in Example 1 to below about 3 microns in size, similarly mixed with a solution of a refractory oxide-forming salt, such as a water solution of cerium nitrate, in an amount sufficient to yield a cerium oxide loading of about 10 volume percent in the final mixture.

After mixing and drying the ingredients as in Example 1, the salt associated with the particles would then be subjected to decomposition in a decomposition furnace between about 200° C. and 300° C. under substantially inert conditions. The decomposed powder mixture would then be prepared for extrusion as in Example 1 for extrusion at a ratio of about 20/1 and at a temperature of about 1100° C. In producing dispersion strengthened rhodium and rhodium-base alloys a similar procedure would be followed.

Generally speaking, the extrusion temperature may range from about 900° C. to 1250° C., and usually from about 1000° C. to 1200° C. for extrusion ratio ranging from about 10/1 to 50/1 and more preferably from about 20/1 to 30/1.

While the starting metal powder should be as fine as possible to insure optimum properties, our wet method

of effecting a homogeneous mixture of metal and refractory oxide is also applicable to particle sizes ranging up to about 325 mesh (up to about 44 microns). Thus, a platinum powder having a particle size distribution of about 1 to 44 microns and an average size of about 25 microns and treated in accordance with Example 1 to form an extruded product containing about 10 volume percent of thoria, exhibited a yield strength of about 48,500 p.s.i. as compared to 12,000 for pure annealed platinum. The extruded product also exhibited a stress for 100 hour rupture life at 1100° C. of over 2000 p.s.i. as compared to 620 p.s.i. for platinum. A test conducted on a platinum product produced from the same size powder but containing 8 volume percent thoria exhibited a yield strength of about 38,400 p.s.i. as compared to the much lower value for pure platinum.

Summarizing the foregoing, whole alloys fabricated from the minus 325 mesh powder do not exhibit the somewhat higher level of improvement obtained with the finer powders, nevertheless, they are a marked improvement over pure platinum.

The material fabricated from the very fine platinum powder, e.g., 1 to 2 microns, exhibited unexpectedly high yield strength ranging from about 119,000 to 128,000 p.s.i. Alloy No. P–3 (12.5 v/o ThO_2) in particular exhibited an extremely low creep rate under a load of 2000 p.s.i. at 1100° C. of less than 10^{-5}%/hr. as compared to 3.7×10^{-3}%/hr. obtained for a Pt–40% Rh alloy at the same temperature but under a lower stress of 1600 p.s.i.

It is apparent that by associating a decomposable refractory oxide-forming salt with the surface of otherwise pyrophoric metal particles that dispersion strengthening of a very high order is obtainable, particularly where the decomposable salt is thorium nitrate and the disperse phase produced therefrom is thoria. We have found that with this method of producing the disperse phase, we obtain a sub-micron particle size ranging up to an average of about 0.5 micron, but, more preferably, an average size ranging from about 0.01 to 0.3 micron.

The amount of salt employed should be sufficient to yield an oxide loading in the product ranging from about 6 to 20 volume percent and, more preferably from about 8 to 15 volume percent. We find that when we employ oxide loadings in the preferred range, we are able to obtain platinum dispersion strengthened with thoria having at least a 100 hour rupture life at 1100° C. at an applied stress of at least about 2000 p.s.i. and more likely of 5000 to 6000 p.s.i.

Generally speaking, in producing an alloy from the precious metal group, we prefer a platinum-base alloy, that is an alloy containing at least about 50% by weight of platinum and substantially the balance one or more metals of the group. Examples of such alloys are 60% Pt and 40% Pd; 50% Pt and 50% Pd; 3.5 to 40% Rh and the balance Pt; 5 to 30% Ir and the balance Pt; 84% Pt, 10% Pd and 6% Ru; up to 10% Ru and the balance Pt; 5 to 15% Re and the balance Pt, etc.

While it has been indicated that the refractory oxide referred to should have a negative free energy of formation of at least about 100,000 calories per gram atom of oxygen at about 25° C. and, preferably 120,000 calories, it is also preferred that the melting point of such refractory oxide be at least about 1600° C.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and the appended claims.

What is claimed is:

1. A method for producing a precious metal powder product selected from the group consisting of Pt, Pd, Rh, Ir, Ru and Re and alloys of at least two of these metals with each other for use in forming by powder metallurgy a high strength precious metal characterized by high creep resistance at elevated temperatures which comprises, providing under substantially inert conditions finely divided powder of said precious metal of average size which under normal conditions would be pyrophoric, providing a solution of a refractory oxide-forming salt in a non-residue leaving solvent, said salt being one capable of decomposing on heating to a refractory oxide whose negative free energy of formation is at least about 100,000 calories per gram atom of oxygen at about 25° C., slowly adding said metal powder in said solution under substantially inert conditions while rapidly stirring the solution to form a thick slurry, evaporating said solvent under said substantially inert conditions until a substantially dry residue is obtained in which the salt is associated at least with the surface of the powder, and uniformly spreading said dry residue in a decomposition chamber and subjecting it to heating at an elevated temperature at least sufficient to decompose the contained salt to a refractory oxide dispersion, whereby a precious metal powder product is obtained having a substantially uniform dispersion of refractory oxide throughout.

2. The method of claim 1 wherein the amount of refractory oxide-forming salt mixed with the metal powder corresponds to about 6% to 20% by volume of its corresponding refractory oxide taken on the dry basis of the metal powder mixture.

3. The method of claim 2 wherein the refractory oxide-forming salt is a thorium salt which decomposes to thoria.

4. The method of claim 3 wherein the thorium salt is thorium nitrate and wherein the amount of thorium salt present corresponds to about 8% to 15% by volume of thoria taken on the dry basis of the metal powder mixture.

5. The method of claim 4 wherein the previous metal contains at least about 50% platinum by weight and wherein the particle size of the powder does not exceed about 10 microns.

6. The method of claim 5 wherein the precious metal powder consists essentially of platinum.

7. A method for producing by powder metallurgy a high strength wrought precious metal selected from the group consisting of Pt, Pd, Rh, Ir, Ru and Re and alloys of at least two of these metals with each other characterized by high creep resistance at elevated temperatures which comprises, providing under substantially inert conditions finely divided precious metal powder of average size which under normal conditions would be pyrophoric, providing a liquid solution of a refractory oxide-forming salt in a non-residue leaving solvent, said salt being one capable of decomposing on heating to a refractory oxide whose negative free energy of formation is at least about 100,000 calories per gram atom of oxygen at about 25° C., slowly adding said metal powder therein under substantially inert conditions while rapidly stirring said solution to form a thick slurry, evaporating said solvent while stirring said slurry under said substantially inert conditions until a substantially dry residue is obtained in which the salt is associated at least with the surface of the powder, uniformly spreading the powder residue in a decomposition chamber, and subjecting said powder residue to heating under substantially inert conditions at an elevated temperature at least sufficient to decompose the contained salt to a refractory oxide dispersion throughout said precious metal powder, and consolidating said powder into a wrought metal shape.

8. The method of claim 7 wherein the refractory oxide-forming salt mixed with the metal powder is a thorium salt which decomposes to thoria and corresponds in amount to about 6% to 20% by volume equivalent of thoria of the wrought metal product.

9. The method of claim 8 wherein the thorium salt is thorium nitrate and wherein the amount of thoria

obtained by decomposition ranges from about 8% to 15% by volume of the wrought metal product.

10. The method of claim 9 wherein the precious metal contains at least about 50% platinum by weight, wherein the average particle size of the metal powder does not exceed 10 microns, and wherein the powder after decomposition is sintered into a compact and the compact thereafter is hot extruded into a wrought metal shape.

11. The method of claim 10 wherein the precious metal consists essentially of platinum.

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