United States Patent [19]

Selman et al.

[11] **3,709,667**

[45] **Jan. 9, 1973**

[54] DISPERSION STRENGTHENING OF PLATINUM GROUP METALS AND ALLOYS

[75] Inventors: **Gordon Leslie Selman; Alan Sidney Darling,** both of London E.C.1, England

[73] Assignee: **Johnson, Matthey & Co., Limited,** London, England

[22] Filed: **Jan. 19, 1971**

[21] Appl. No.: **107,812**

[52] **U.S. Cl.**.....**29/182.5,** 29/192 R, 75/206, 75/211

[51] **Int. Cl.**.....**C22c 31/04**

[58] **Field of Search** 75/206, 213, 211; 29/182.5; 264/111; 29/192

[56] **References Cited**

UNITED STATES PATENTS

3,578,443	5/1971	Grant et al.	75/206
3,166,417	1/1965	Gainsbury	75/206

FOREIGN PATENTS OR APPLICATIONS

645,681	11/1950	Great Britain	75/206

Primary Examiner—Carl D. Quarforth
Assistant Examiner—R. E. Schafer
Attorney—Cushman, Darby & Cushman

[57] **ABSTRACT**

This specification describes a method of producing dispersion strengthened metals or alloys by alloying the metal or alloy with a minor amount of a material capable of forming a stable refractory compound. The so formed alloy is converted to granular or powder form and the powder is then cold worked prior to exposing the cold worked and so deformed granules to a gas at a temperature so as to form a stable refractory compound within the metal or alloy. Thereafter the metal or alloy particles are compacted and sintered to form an ingot.

20 Claims, 4 Drawing Figures

PATENTED JAN 9 1973

3,709,667

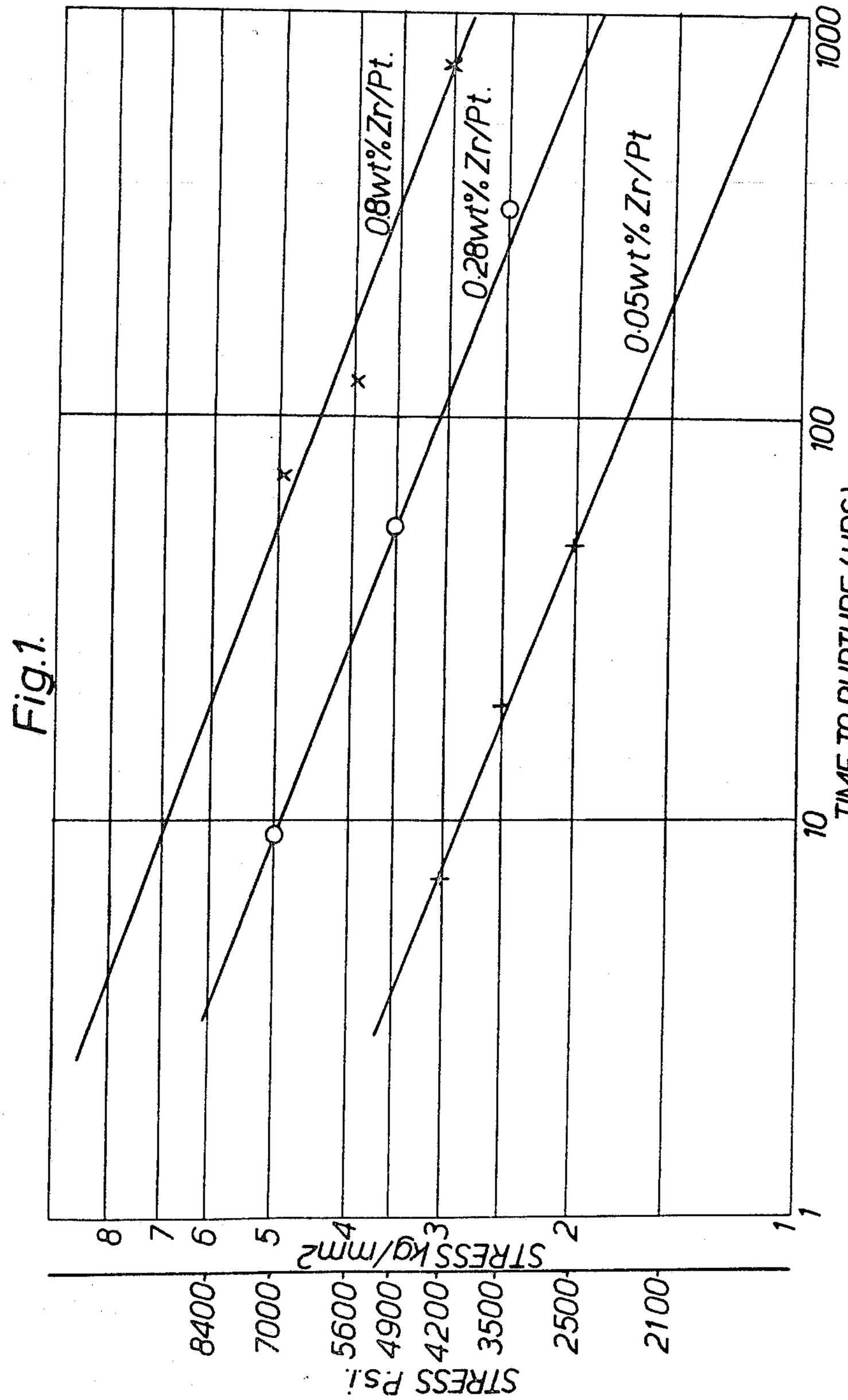
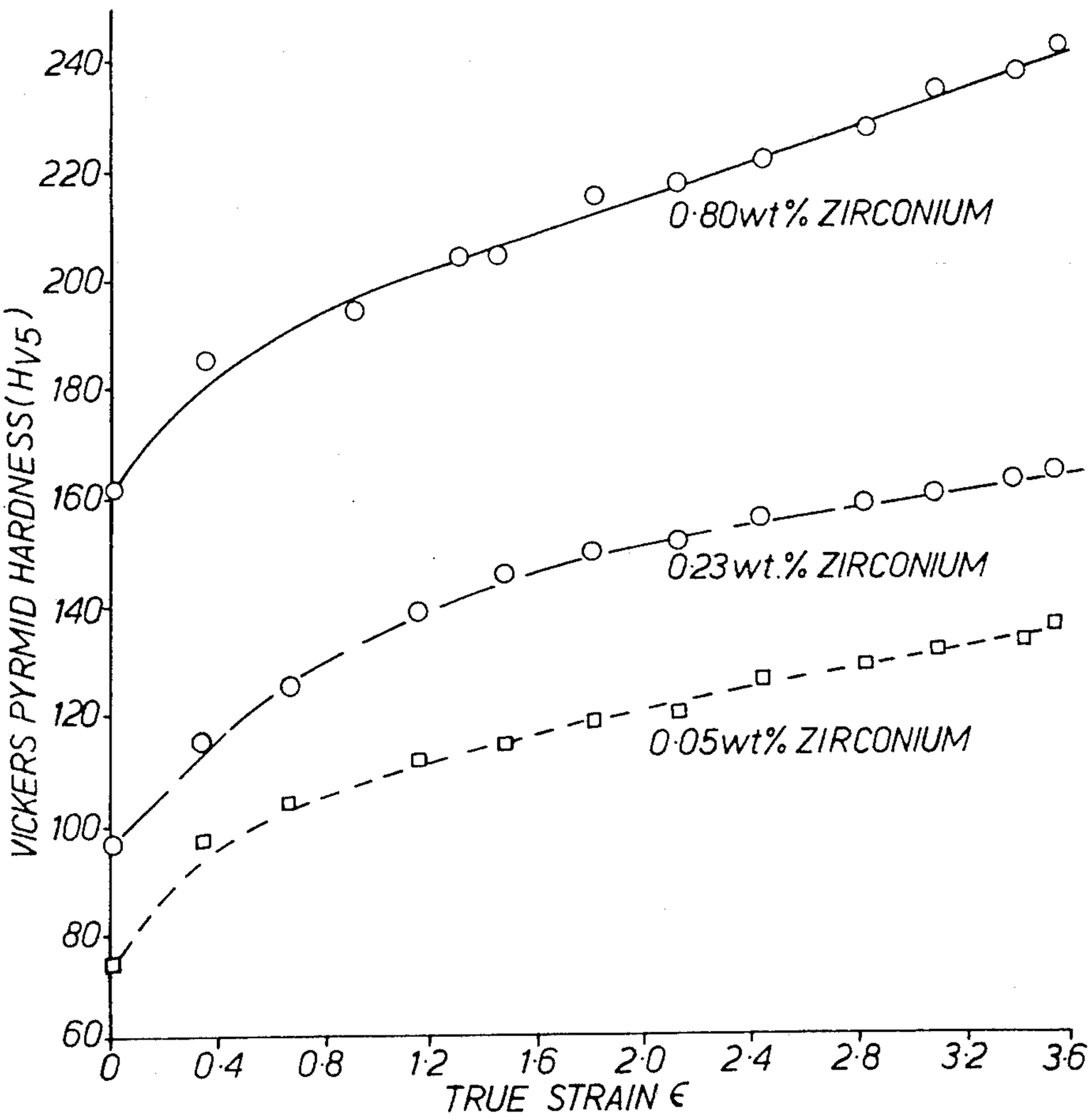


Fig.1.



$\epsilon = \ln\left(\frac{1}{1-\frac{l}{L}}\right)$ Fig. 2.

Rate of Oxidation of Platinum-Zirconium Alloys containing nominally 0·3 and 0·6% of Zirconium at 700°C in air in the Fluidised Bed arrangement

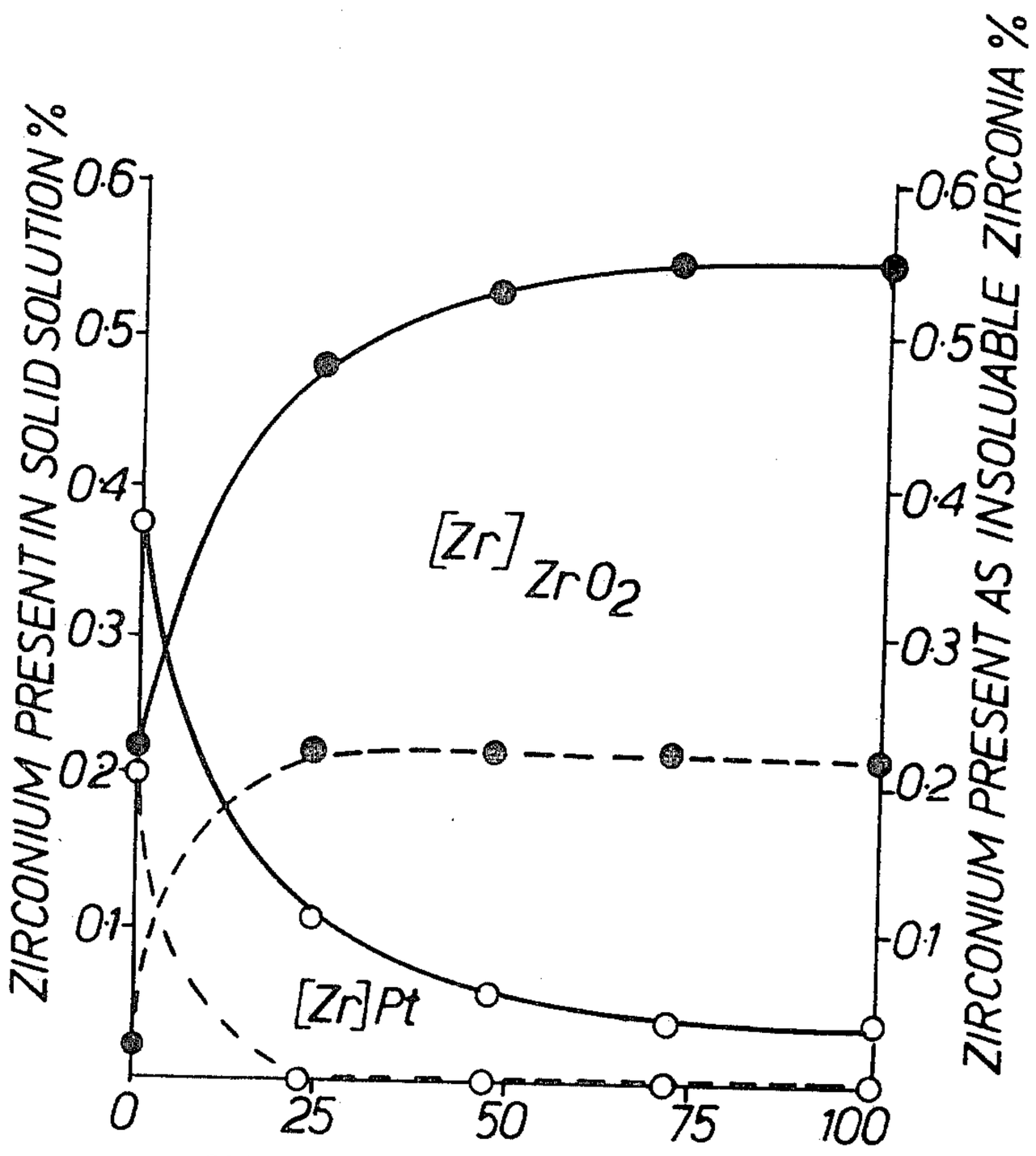


Fig.3.

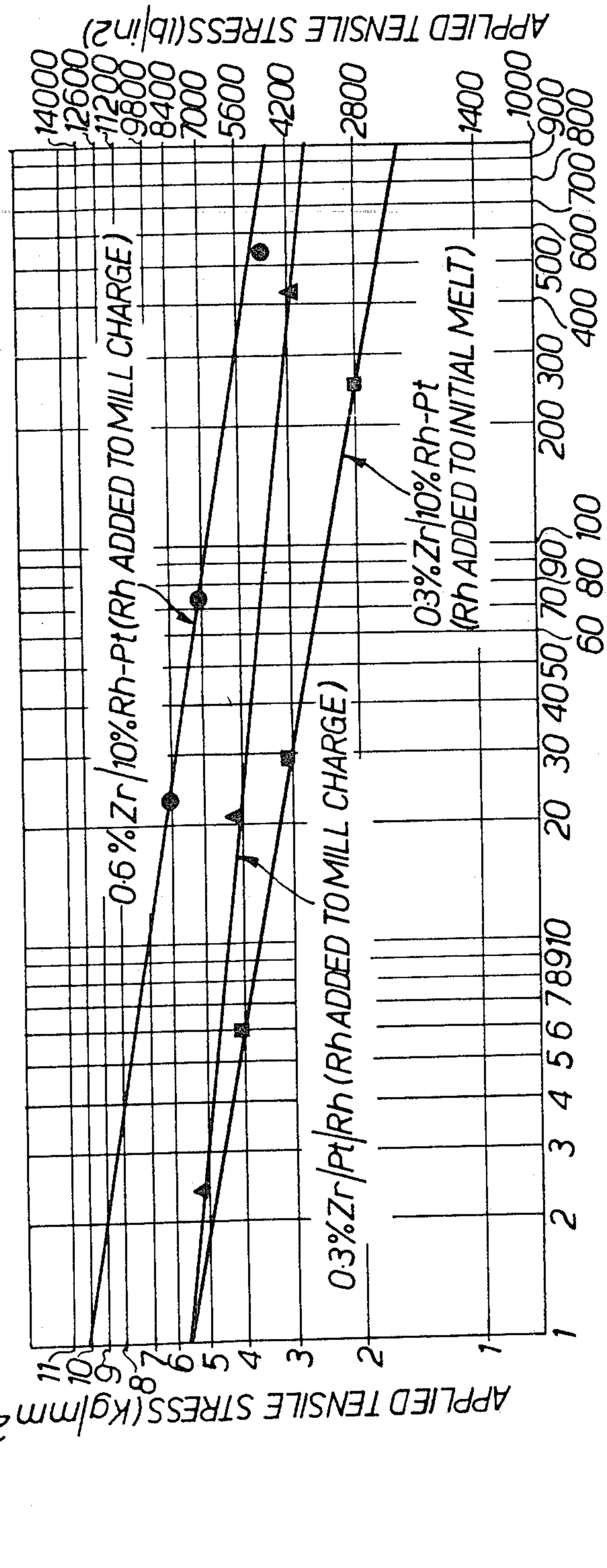

APPLIED TENSILE STRESS(lb/in2)
14000
12600
11200
9800
8400
7000
5600
4200
2800
1400
1000
900
800
700
600
500
400
300
200
100
80
60
50
40
30
20
10
9
8
7
6
5
4
3
2
1
0·6%Zr/10%Rh-Pt (Rh ADDED TO MILL CHARGE)
0·3%Zr/Pt/Rh (Rh ADDED TO MILL CHARGE)
0·3%Zr/10%Rh-Pt (Rh ADDED TO INITIAL MELT)
TIME TO RUPTURE IN HOURS
APPLIED TENSILE STRESS(kg/mm2)

Fig.4.

DISPERSION STRENGTHENING OF PLATINUM GROUP METALS AND ALLOYS

This invention relates to the dispersion strengthening of high temperature metals and alloys. Such metals and alloys include platinum group metals and alloys containing a major proportion of one or more of these metals; gold, silver and alloys of these metals, and materials such as those sold under the Registered Trade Marks NICHROME and NIMONIC. The invention is particularly, but not exclusively, concerned with an improved method of dispersion strengthening the above metals and alloys by internal oxidation.

The process of dispersion strengthening metals and alloys by internal oxidation is well established and widely practised. It is generally carried out by preparing an alloy comprising a major proportion of the metal or alloy to be strengthened and a minor proportion of one or more metals whose oxides have a relatively high free energy of formation and then subjecting the alloy to an oxidizing treatment. This causes the metal or metals forming the minor proportions of the alloy to be oxidized *in situ* so that particles of the oxide are formed within the body of the alloy.

One of the difficulties often encountered in carrying out the process of internal oxidation as described above is that the form, size and distribution of the oxide particles produced are not such as to produce the maximum strengthening effect. For example, when an ingot of platinum-zirconium alloy containing 1% by weight of zirconium is heated in air for 120 hours at 1,400° C., it is found that the particles of zirconium oxide produced are relatively coarse and are concentrated often as agglomerates, near the surface of the ingot and along the grain boundaries where these penetrate into the body of the ingot from points at or near the surface. The strengthening effect of this oxide distribution is not very marked, the surface hardness of the ingot, in a typical case, being only 128 Hv compared with 115 Hv for the unoxidized alloy and 37 Hv for pure platinum.

We have now found that dispersion strengthened metal or alloy, which is significantly stronger than that made by the simple oxidation process just described, may be made by a process comprising alloying the metal or alloy with a minor amount of a material capable of forming a stable refractory compound, converting the so-formed alloy to granules or powder, deforming the granules or the particles of said powder by cold working, exposing the deformed granules or particles to a gas adapted at a suitable temperature to form the stable refractory compound within the metal or alloy, and then compacting and sintering the so-treated granules or particles. Preferably:

1. the alloy is converted to powder by forming it into wire and then flame-spraying the wire into a non-volatile liquid, for example, distilled water.

2. the stable refractory compound is an oxide and is formed by heating the deformed granules or particles containing the material in air or oxygen at a relatively low temperature. The stable refractory compound formed may be an oxide of beryllium, magnesium, aluminum, silicon, thorium, uranium, a metal in the first transition series comprising the elements calcium to manganese, a metal in the second transition series, comprising the elements strontium to niobium, or a metal in third transition series comprising the elements barium to tantalum.

3. the oxide has a high negative free energy of formation preferably for example greater than — 160 K.cal./gm.mole.

4. the granules or powder particles are deformed into flakes in a ball mill.

5. the degree of cold-working to which the granules or particles are subjected and the quantity of oxidizable material within the alloy is such that on subsequently heating at a suitably adjusted low temperature in air or oxygen, the processes of internal oxidation and recrystallization proceed simultaneously in the deformed granules or particles.

One way in which the invention has been put into effect, for the preparation of dispersion strengthened platinum and the improved physical properties of the resultant material will now be described by way of example, with reference to the attached drawings of which:

FIG. **1** is a graph showing the stress-rupture characteristics of wire made from dispersion strengthened platinum according to the invention;

FIG. **2** is a graph showing the work hardening characteristics of dispersion strengthened platinum according to the invention;

FIG. **3** shows a further graph indicating the progress of oxidation of different alloys during production;

FIG. **4** is a graph showing stress-rupture values of a dispersion-strengthened 10 percent rhodium-platinum alloy.

An ingot of platinum containing approximately 1 percent by weight of zirconium was made up by vacuum melting and casting. This ingot was cold rolled and drawn to wire 1.5 mm. in diameter which was then fed into an oxy-acetylene spray gun. Compressed air was used as a carrier gas for the spraying operation and the atomized metal was directed against the surface of a bath of distilled water approximately 36 inches away from the gun. By this method, spherical powder particles ranging in diameter from 10 to 200 microns were obtained. Approximately 40 percent by weight of the particles fell in the size range 75 to 125 microns with the air pressure at 60 p.s.i. and a wire speed of 42 inches/min. Gas content and X-ray diffraction measurements showed that approximately 15 percent of the total zirconium content of the alloy had been oxidized during the process of spraying, the remainder being retained by the platinum in solid solution.

A 50 ounce charge of powder formed as described above was dry-milled for 12 hours in an 11 inch bore, poly-propylene-lined ball-mill containing ½ inch diameter steel balls. This treatment converted the powder into flakes ranging in thickness from 3–6 microns. The small quantity of polypropylene incorporated into the flakes was removed by oxidation at 200° C for 2 hours in a current of oxygen.

The flaked material was then internally oxidized by loading it into open silica trays and heating it in air for 100 hours at 700° C. At the same time, a 50 gm. sample of the unmilled powder consisting of substantially spherical particles was internally oxidized by subjecting it to exactly the same oxidizing treatment. Subsequent examination of the two samples showed that the total oxygen content of the flaked material was 0.33 wt. % whereas that of the unmilled powder was only 0.25 wt.%.

Further, the nature of the oxide particles within the flakes was entirely different from that within the particles of unmilled powder. The particles of oxide within the flakes were so fine that they were incapable of resolution with an optical microscope whereas those within the spherical particles were coarse and bulky and were located largely near the surfaces of the particles where grain boundaries were present.

Sample quantities of internally oxidized flakes and of internally oxidized unmilled powder were then consolidated by pressing in steel dies under a pressure of 8 tons per sq. inch to produce compacts 5/16 × 5/16 × 3½ inches which were then sintered in a vacuum of better than 5×10^{-4} Torr for 5 hours at 1400° C.

The "flake" compact sintered in this way exfoliated slightly and was therefore repressed in its steel die and resintered as described. This treatment yielded a bar having a density of approximately 80 percent of the theoretical value while that of the bar formed from pressed and sintered unmilled powder, which had not exfoliated and which had been sintered once only, was 63 percent.

Both bars were then hot forged between 1200° C. and 1,300° C. Full densification was obtained during forging when the ingots were reduced by about 50 percent in cross-sectional area. After forging the ingots were annealed in air for 30 minutes at 1400° C. and then cold rolled, swaged and drawn to wires 1 mm. in diameter.

Constant load, stress rupture tests on the wires formed as described above yielded the results shown in Table 1.

TABLE 1

	Wire made from flaked oxidized Pt + 1 wt% Zr flame sprayed powder	Wire made from unflaked oxidized Pt + 1 wt% Zr flames sprayed
Life at 2800 p.s.i. 1400°C.	1000 hrs. unbroken	90 hrs.
Life at 3500 p.s.i. 1400°C.	1000 hrs. unbroken	72 hrs.
Life at 4200 p.s.i. 1400°C.		11 hrs.
Life at 4900 p.s.i. 1400°C.	881	

These results demonstrate the outstanding improvements which are obtained by flaking the platinum alloy powder before internal oxidation.

We have found by experiment that, as would be expected, the strength of platinum, dispersion strengthened with zirconium oxide and made in accordance with the invention, is reduced when the proportion of zirconium is reduced. Nevertheless the strength of the material made from an alloy containing 0.8 wt% of zirconium is not greatly inferior to that made from an alloy containing 1 wt% Zr and a substantial proportion of the strength of this material is retained even when the zirconium content of the starting material is reduced to 0.23 wt%.

The above is illustrated in FIG. 1 and by the results (given in Table 2), which have been derived from FIG. 1, which are plotted against constant load stress rupture tests made on 1 mm. diameter wires stressed in tension in air at 1400° C. In each case the wires were prepared from internally oxidized flake in exactly the same way as the wire made from alloy containing 1 wt% zirconium previously described except that the proportions of zirconium in the starting alloy were respectively 0.8 wt%, 0.23 wt% and 0.05 wt%.

TABLE 2

Composition	10 hour stress rupture strength	100hour stress rupture strength	1000 hour stress rupture strength
0.80 wt% Zr	9750 p.s.i.	6280 p.s.i.	3850 p.s.i.
0.50 wt% Zr*	8400 p.s.i.	5300 p.s.i.	3400 p.s.i.
0.23 wt% Zr	6800 p.s.i.	4250 p.s.i.	2700 p.s.i.
0.05 wt% Zr	3950 p.s.i.	2450 p.s.i.	1500 p.s.i.

*Tests on this composition alloy not yet completed, results quoted being deduced by extrapolation of a composition vs rupture stress curve compiled from the other results.

The quantity of zirconium present in a platinum-zirconium alloy may be between 0.05 and 5 wt.% and preferably between 0.5 and 2 wt.%

The reduction in zirconium content has the advantage that it results in an increase in the ductility of the dispersion strengthened material. This material with a suitably low zirconium content would thus be useful for the manufacture of platinum vessels and other apparatus which, in addition to high temperature strength are required to have good resistance to deformation and tolerance of accidental mishandling.

The work hardening characteristics of samples of dispersion strengthened platinum according to the invention are shown in FIG. 2. The graphs here are based on tests carried out on sheet made by compacting, sintering and rolling internally oxidized flake prepared from platinum zirconium alloys containing 0.8 wt%, 0.23 wt% and 0.05 wt% zirconium respectively. The sheet was forged to achieve full densification, annealed, progressively rolled to a narrower gauge and the hardness measurements were made at suitable stages during the rolling operations.

We have found that when a work hardened sample of dispersion strengthened platinum made according to the invention from platinum-zirconium alloy containing 0.23 wt% of zirconium is annealed for a few minutes at 1,400° C., it develops a stable, recrystallized microstructure with large elongated grains highly aligned with the original direction of working. This recrystallization texture appears to improve the high temperature strength of the material as the fibrous structure discourages failure due to grain boundary shear and sliding across the sample. The high aspect ratio of the grains also reduces considerably the proportion of the grain boundary area subjected either to shear or tension. Dispersion strengthened metals and alloys made in accordance with this invention may be still further improved by following the teaching of our British Pat. No. 1,134,492.

Close microscopic study has, however, failed to provide evidence of recrystallization when samples of work hardened dispersion strengthened platinum made, according to the invention, from an alloy containing 0.8 percent or more of zirconium were annealed, even for 5 hours at 1700° C. or 100 hours at 1500° C. Although small, highly oriented grains could be observed after annealing, the general appearance of the microstructure was very similar to that of the work hardened samples.

Although the invention has been described with reference to the preparation of platinum, dispersion strengthened with zirconium oxide, it is not, of course, so limited.

Certain physical properties of platinum dispersion-strengthened according to the method of the invention are set out in the following tables.

TABLE 3

Mechanical Properties of Flame Sprayed Milled and Internally Oxidized Platinum-Zirconium Powder Materials.

1. Vickers Pyramid Hardness — HV5

Composition	Hardness HV5 Annealed	Hardness HV5 Cold Worked
0.80 wt%. Zirconium	149	243
0.50 wt%. Zirconium	110	194
0.23 wt%. Zirconium	93	161
0.05 wt%. Zirconium	74	138

Annealed — 30 mins at 1400° C
Cold worked — 97 percent cold reduction of area

2. Ultimate Tensile Strength & Ductility at 1400° C. of Fully Annealed Materials

Composition	Ultimate Tensile Strength	% Reduction of Area
0.80 wt%. Zirconium	10,300 p.s.i.	55.0
0.23 wt% Zirconium	9,100 p.s.i.	68.0
0.05 wt% Zirconium	6,600 p.s.i.	86.0

Fully annealed — 100 hrs. at 1400° C.

Results for 0.50 wt%. zirconium composition not available but by extrapolation of graph of above results the values should be approximately: a. U.T.S. = 9700 p.s.i.

b. % Reduction of area = 63.0%

TABLE 4

Room Temperature Tensile Properties of Materials of Various Composition

Composition	As Drawn[1]	Ultimate Tensile Strength Fully Annealed[2]
0.80 wt%. zirconium	128,000 p.s.i.	59,500 p.s.i.
0.50 wt%. zirconium	103,500 p.s.i.	43,000 p.s.i.
0.23 wt%. zirconium	87,000 p.s.i.	33,000 p.s.i.
0.05 wt%. zirconium	76,000** p.s.i.	26,500* p.s.i.

** Tests on this composition alloy were not conducted and the values quoted were deduced by extrapolation of a composition vs ultimate tensile strength curve compiled from the other results.

1. "**As Drawn**" **indicates after** 97 percent cold reduction of area to 0.040 inch dia. wire.

2. "**Fully Annealed**" **indicates** 0.040 inch dia.wire annealed for 100 hrs. at 1400° C.

Further experiments have been undertaken with regard to alloys containing different percentages by weight of zirconium and to modifications in the basic process of production. For example, a number of tests have been made on platinum alloys containing 0.3 and 0.6 weight percent of zirconium respectively.

It was believed following the earlier tests outlined above that the oxidation of the milled alloy flake in shallow silica trays exposed to heat treatment up to 700° C. might be improved by utilizing an arrangement somewhat similar to a "fluidized bed." Accordingly the flakes were supported on a porous sintered silica disc welded within a high purity quartz tube, the assembly being housed within a vertical tube furnace and clean dry air being fed into the lower end of the quartz tube at a constant rate. Although this method does not produce true fluidization a greatly increased intimacy between the air and the flakes is obtained.

The curves shown in FIG. 3 indicate the progress of oxidation for the two alloys containing nominally 0.3 and 0.6 percent zirconium respectively in the vertical tube furnace at 700° C. The curves differentiate between zirconium present in solid solution and zirconium present as insoluble zirconia. As will be noted, oxidation is complete in the case of the 0.3 wt% zirconium alloy after only 25 hours, as compared with the 100 hours required when the flakes were exposed in shallow trays at the same temperature. After oxidation, analysis showed that the quantity of zirconium present in the two alloys was 0.24 percent and 0.59 percent respectively.

The earlier described oxidation treatment followed the removal, by oxidation, of polypropylene incorporated in the flakes during the milling treatment in a poly-propylene lined ball mill which oxidation took about two hours. It has now been determined that the volatile products of the organic impurities may be removed during the oxidation treatment at 700° C. if this step is carried out in the vertical tube arrangement described above. Materials processed in the manner described with and without a separate volatilization step have exhibited similar properties.

It has also been determined that the double pressing and sintering cycle of the compacts may be replaced by a single four hour vacuum sintering treatment at 1400° C. since the zirconia-containing flakes release very little gas during sintering. Table 5 compares the high temperature creep properties of wires processed from compacts given a single four hour vacuum sintering treatment at 1400° C. with those of material processed with the use of the two-stage pressing and sintering technique above described.

TABLE 5

Effect of sintering time at 1400°C. upon the creep properties of wires processed from oxidized 0.3% and 0.6% zirconium-platinum alloy flakes.

Alloy	Sintering treatment	Stress to rupture (psi) in time t(hrs) at 1400°C.			
		$t = 1$	10	100	1000
0.3% Zr/Pt	5 hr 1400°C-repress-5hrs 1400°C	—	6800	4250	2700
0.3% Zr/Pt	4 hrs 1400°C	11800	9300	7300	5800
0.6% Zr/Pt	5 hrs 1400°C-repress-5hrs 1400°C	—	8500	5200	3300
0.6% Zr/Pt	4 hrs 1400°C	14500	11500	9200	7200

The marked improvements obtained by thus shortening the sintering process are obvious and the modified process results in an increased rate of work hardening during cold deformation and improves the resistance of the products to recrystallization at high temperatures.

In order to determine the reproducibility of the process on a reasonable scale tests have been made with ten 300 gram batches of wire each individually

processed from 0.3 wt% and 0.6 wt% zirconium platinum alloys respectively in an identical manner and according to the method hereinbefore described. In preparing these batches part of the platinum used was pure whereas the remainder was scrap platinum from the production of the first batches and from previous tests. This provided batches of zirconium strengthened platinum of which half were processed from pure platinum and the other half from scrap to enable an assessment to be made of the possibilities for recycling process scrap alloy.

In these tests it was found that during melting approximately 7 percent of the zirconium addition was lost from the 0.3 wt% zirconium alloy and approximately 17 percent from the 0.6 percent zirconium alloy. The losses occurring in melts and remelts were substantially identical thus indicating that the initial alloy compositions could be readily controlled.

Creep tests were performed at 1400° C. in air on wires processed from each of the twenty 300 gram batches of sprayed milled and oxidized flake and the detailed results are shown in Table 6 below. It will be seen that both alloy compositions yield a remarkably uniform product, the high temperature strength of which varies little from batch to batch, with the 0.6 wt% zirconium platinum alloy clearly producing the better wire. This table also shows that the properties of wires made from remelted scrap are indistinguishable from those of wires produced from new platinum sponge, which adds considerably to the value of the process.

TABLE 6

Stress rupture properties of 1 mm diameter zirconia strengthened platinum wires prepared from the nominal alloy compositions

0.3% and 0.6% zirconium-platinum.

Nominal Composition	Cast No.	Charge (gm)	Batch No.	Stresses giving 1, and 100 hours. Constant load endurance at 1400°C (p.s.i.) 1 hr	10 hr	100 hr
0.3 wt% zirconium platinum	675A Made from virgin metal	1650	675A1	8,400	6,400	5,000
			675A2	9,700	7,500	5,800
			675A3	10,700	7,800	5,800
			675A4	9,300	7,400	5,900
			675A5	9,000	7,200	5,800
0.3 wt% zirconium platinum	675B Made from scrap	1650	675B1	9,000	7,100	5,600
			675B2	10,400	8,000	6,200
			675B3	11,000	8,000	5,800
			675B4	9,300	6,900	5,200
			675B5	10,400	7,800	5,900
0.6 wt% zirconium platinum	696F Made from virgin metal	1700	696F1	11,900	9,400	7,500
			696F2	14,100	9,900	6,900
			696F3	11,700	9,100	7,100
			696F4	13,800	9,500	6,500
			696F5	14,100	10,300	7,600
0.3 wt% zirconium platinum	696G Made from scrap	1700	696G1	13,200	9,700	7,100
			696G2	14,500	10,800	8,000
			696G3	14,500	10,500	7,400
			696G4	11,800	9,000	7,200
			696G5	14,200	10,100	7,200

Tests undertaken to determine the hardness values during annealing at temperatures up to 1400° C. show a strong correlation between the annealed hardness of the different wire batches and the stress rupture properties at high temperatures. It was significant that there was considerably less variation in the work hardening and annealing behavior of the batches of wire processed from the 0.6 wt% zirconium platinum alloy than in those prepared from the 0.3 wt% zirconium platinum alloy.

Tests have also been carried out on the production of a dispersion strengthened 10 percent rhodium-platinum alloy using similar procedures to those employed for the production of the zirconium strengthened platinum products and described above.

The addition of rhodium to the alloy was made in one or other of two ways. The first procedure comprised the production by argon arc melting of a zirconium-rhodium-platinum solid solution alloy which was drawn to form wire and was then sprayed, milled and oxidized in the manner described above.

The second method was to add the requisite quantity of rhodium sponge to sprayed zirconium-platinum alloy powder at the commencement of the milling operation. Irrespective of which manner of production outlined above was used, the alloy flakes were found to be extremely hard after oxidation at 700° C. and could not be pressed to form bars until and unless the flakes were annealed for 30 minutes at 1100° C.

Three 150 gram batches of wire thus produced were tested to obtain stress-rupture values and the results thereof are shown on the graph of FIG. 4. The best results are comparable with those of the equivalent zirconia strengthened platinums at the higher stress levels, but become inferior at lower stresses. It is of interest to note that in general better properties were produced when the rhodium addition was made, at the milling stage, rather than at the melting stage. Microexamination has shown that wires prepared by the latter procedure contain a larger proportion of coarse, optically visible particles.

What we claim is:

1. A method of producing a dispersion strengthened metallic material which at least prior to dispersion strengthening is resistant to oxidation and diffusion of gaseous oxygen therethrough and which is selected from the group consisting of platinum group metals, platinum group metal alloys, gold, gold alloys and alloys containing nickel and chromium, the method comprising alloying the said metallic material with a minor amount of an additive material capable of forming a stable refractory compound, converting the alloy thus formed into particles, deforming the said particles by cold working, recrystallizing said deformed particles to form a fine grained structure having a lace-work of grain boundaries and exposing the deformed particles to a gas which enters the deformed particles along the lace-work of the grain boundaries and which is adapted to form said stable refractory compound at least within the deformed particles, and thereafter, compacting and sintering the treated particles.

2. A method according to claim 1 wherein the stable refractory compound formed comprises an oxide.

3. A method according to claim 2 wherein the stable refractory oxide is formed by heating the deformed particles containing the additive material in an oxygen containing atmosphere at a relatively low temperature.

4. A method according to claim 3 wherein the particles are heated in the atmosphere which is a constant stream of oxygen-containing gas passing through the particles.

5. A method according to claim 2 wherein the stable refractory compound formed is selected from an oxide of beryllium, magnesium, aluminum, silicon, thorium, uranium, a metal in the first transition series comprising the elements calcium to manganese, a metal in the second transition series comprising the elements strontium to niobium, and a metal in the third transition series comprising the elements barium to tantalum.

6. A method according to claim 2 wherein the oxide formed has a high negative free energy of formation of the order of —160K.cal./gm. mole.

7. A method according to claim 1 wherein the granules or particles are deformed into flakes in a ball-mill.

8. A method according to claim 1 wherein the degree of cold working to which the granules are subjected and the quantity of additive oxidizable material contained within the alloy are such as on subsequent heating to provide for simultaneous processes of internal oxidation and recrystallization in the deformed granules.

9. A method according to claim 1 wherein the particles are made from an alloy of platinum and zirconium.

10. A method according to claim 9 wherein the platinum-zirconium alloy contains between 0.05 and 5 wt.% zirconium.

11. A method according to claim 10 wherein the platinum-zirconium alloy contains between 0.5 and 2 wt.% zirconium.

12. A method according to claim 1 which includes the additional step of forging the sintered compact at an elevated temperature to increase the density thereof.

13. A method according to claim 12 wherein the compact is sintered at a temperature between 1200° C. and 1300° C.

14. A method according to claim 1 wherein the conversion of the alloy into particles is effected by forming the alloy into wire and subsequently flame-spraying the wire into a non-volatile liquid such as distilled water.

15. A method according to claim 1 wherein recrystallization is caused with or without the addition of heat.

16. A dispersion strengthened metal of the platinum group or an alloy thereof comprising an internally oxidized mass of granules of said metal or alloy alloyed with a stable refractory oxide.

17. The dispersion strengthened metal of claim 16 wherein the metal is platinum alloyed with a minor quantity of zirconia.

18. A dispersion strengthened metal or alloy as claimed in claim 16 and forged into bar form to increase the density of the sintered granules.

19. The metal of claim 16 wherein the internally oxidized granules are in a compacted and sintered form after the said internal oxidation.

20. A method of dispersion strengthening a metallic material which at least prior to dispersion strengthening is resistant to oxidation and diffusion of gaseous oxygen therethrough and which is selected from the group consisting of platinum group metals, platinum group metal alloys, gold, gold alloys and alloys containing nickel and chromium, by internal oxidation which consists in alloying the metallic material with a minor amount of an additive metal capable of forming a stable refractory oxide, converting the so-formed alloy into granules, deforming the granules by cold working, heating the deformed granules in an atmosphere containing oxygen at a temperature such as to form said stable refractory oxide within the metal granules and compacting and sintering the treated granules.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,709,667 Dated January 9, 1973

Inventor(s) Gordon Leslie Selman et al

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

(1) In the heading Foreign Application Priority Data should be added as follows:

January 23, 1970 Great Britain 3425/70

Signed and sealed this 25th day of December 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents

USCOMM-DC 60376-P69
* U.S. GOVERNMENT PRINTING OFFICE 1969 O—366-334