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(54) Title: RHODIUM ALLOYS

As Drawn

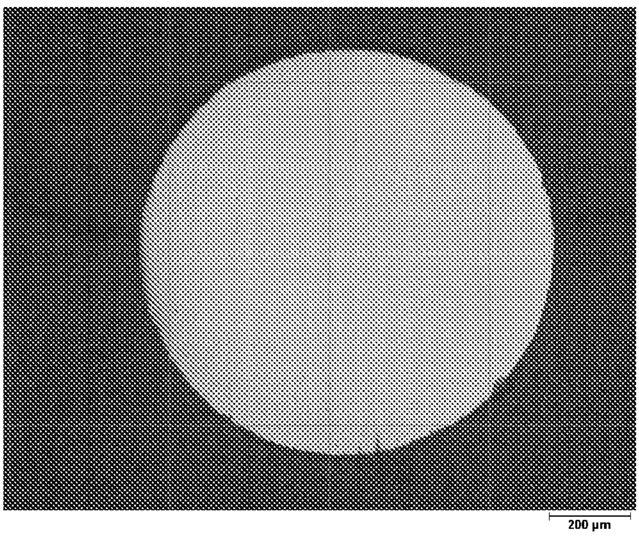

FIGURE 1

(57) **Abstract**: The present invention provides an electrode comprising a rhodium alloy, wherein the rhodium alloy comprises: i) rhodium; and ii) nickel; wherein the alloy comprises a greater quantity of rhodium as compared to any other individual element of the alloy.

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Rhodium Alloys

Field of the Invention

The present invention relates to rhodium alloys comprising nickel, and to the use of the alloys, in particular, as spark ignition electrodes.

Background

US2007/194681 (to Denso Corporation) describes a spark plug for an internal combustion engine wherein at least one of the centre or ground electrodes comprises rhodium and an additive 0.3% to 2.5% by weight of one or more selected from earth rare elements, IVA elements, and VA elements, as listed in the periodic table of elements. US2007/194681 does not describe alloys comprising nickel or a second platinum group metal (PGM).

EP2738892A (to NGK Sparkplug Co. Ltd.) describes a spark plug which includes a tip. The tip of the spark plug contains an element group M (M consists of at least one species of Pt or Rh) in an amount of 3 mass% to 35 mass%, and an element group L (L consists of at least one species of Ir, Ru, and Pt) in an amount of 0 mass% to 15 mass%. The total amount of the element group M and the element group L is 3 mass% to 35 mass%, and the total amount of Ni, the element group M, and the element group L is at least 94 mass%. The amount of Ni, therefore, is 59 mass% to 97 mass%.

J. R. Handley (Platinum Metals Review, 1989, 33, (2), 64-72 and 1990, 34, (4), 192-204) describes binary, ternary and complex rhodium alloys. Neither journal article describes the alloys of the present invention nor the use of rhodium alloys as spark ignition electrodes.

Summary of the Invention

The present inventors have developed rhodium alloys which have enhanced resistances to wear, such as those arising from exposure to sparks. In certain embodiments, the alloys are also easy to manufacture. In certain embodiments, the alloys demonstrate good to very good formability i.e. they are able to undergo plastic deformation without being significantly damaged through fracturing or tearing. In certain embodiments, the alloys exhibit the ability to be welded.

In one aspect, therefore, the present invention provides a spark ignition electrode comprising a rhodium alloy, wherein the rhodium alloy comprises:

i) rhodium; and
ii) nickel;

wherein the alloy comprises a greater quantity of rhodium as compared to any other individual element of the alloy.

In another aspect, the invention provides a spark plug comprising an electrode as defined herein.

In yet another aspect, the invention provides the use of the rhodium alloys as defined herein in an electrode or spark plug.

In another aspect, the invention provides a rhodium alloy comprising:
i) rhodium;
ii) nickel; and
iii) one or more elements selected from the group consisting of yttrium, zirconium and samarium;
wherein the alloy comprises a greater quantity of rhodium as compared to any other individual element of the alloy.

Detailed Description

As described above, the present invention provides a spark ignition electrode comprising a rhodium alloy, wherein the rhodium alloy comprises:
i) rhodium; and
ii) nickel; and
wherein the alloy comprises a greater quantity of rhodium as compared to any other individual element of the alloy.

It will be understood that whilst the amounts of each element are given assuming that the base alloy is pure rhodium, in practical terms, the rhodium and the alloying elements may contain impurities at levels which would be normally expected for such metals.

Rhodium is a platinum group metal (PGM) which exhibits high melting and boiling points, as well as excellent oxidation and corrosion resistances. Rhodium also displays a low vapour pressure and high thermal conductivity which, when allied with the above properties, suit its potential for use as a spark ignition electrode. However, rhodium metal itself cannot be adequately exploited as a spark ignition electrode due to its relatively poor mechanical properties and relatively low density. The present inventors have found that the properties of rhodium which make it a poor spark ignition electrode can be improved by selective alloying. In this respect, the rhodium alloy as described herein comprises rhodium as the main element in the alloy. Rhodium therefore is present in the alloy in the greatest quantity (as expressed as a percentage by weight (wt%)) as compared to any other individual element of the alloy (also expressed as a percentage by weight (wt%)). Any other element of the alloy is individually a minor element as compared to rhodium.

While each element or a combination of elements in the alloy may be expressed as a range, the total wt% of the rhodium alloy adds up to 100 wt%.

The rhodium alloy may comprise about ≥ 30 wt% of rhodium, such as about ≥ 40 wt% of rhodium, such as about ≥ 50 wt% of rhodium. In one embodiment, the rhodium alloy may comprise about 30 to 99 wt% of rhodium, such as about 30 to about 95 wt% of rhodium, for example about about 40 to about 90 wt% of rhodium. In one preferred embodiment, the rhodium alloy comprises about 40 to about 99 wt% of rhodium, such as about 45 to about 95 wt%, for example about 47 to about 90 wt%.

The rhodium may be alloyed with at least one of iridium, platinum or palladium. In this respect, up to about 49.99 wt% (e.g. about 0.01 to about 49.99 wt%) each of one or more elements selected from the group consisting of iridium, platinum and palladium may be present. Iridium, platinum and palladium have excellent solid solubilities with rhodium and, as such, are suitable as alloying elements in preparing rhodium alloys. In one embodiment, the rhodium alloy may comprise up to about 49.99 wt% of iridium, such as 0 to about 40 wt %, for instance about 0.01 to about 25 wt %, for example about 0.1 to about 20 wt% or about 0.5 to about 15 wt% of iridium. In another embodiment, the rhodium alloy may comprise up to about 49.99 wt% of platinum, such as 0 to about 40 wt %, for instance about 0.01 to about 25 wt %, for example about 0.1 to about 20 wt%. In another embodiment, the rhodium alloy may comprise up to about 49.99 wt% of palladium, such as 0 to about 40 wt%, for instance about 0.01 to about 25 wt%, for example about 0.1 to about 20 wt%.

When present in the rhodium alloy, ruthenium may be present in up to about 35 wt%. In this regard, it is generally desirable to limit the quantity of ruthenium to about ≤ 35 wt% as the solid solubility of ruthenium in rhodium is good within this range whilst retaining a single phase solid solution. Ruthenium is suitable as an alloying element as its corrosion resistance is similar to that of iridium. The presence of ruthenium (and/or iridium), therefore, improves the corrosion resistance of the rhodium alloy as compared to rhodium metal alone. Ruthenium also exhibits high melting/boiling points, high atomic weight and high thermal conductivity, all characteristics which are favourable for resistance to spark erosion. The rhodium alloy may comprise no ruthenium i.e. 0 wt% ruthenium. Alternatively, the rhodium alloy may comprise about 0.01 to about 35 wt% ruthenium, such as about 0.1 to about 34 wt%, for instance about 1 to about 32 wt%, for example about 5 to about 31 wt%.

The rhodium alloy may comprise about 0.01 to about 49.99 wt% of nickel. Nickel has an excellent solid solubility in rhodium and is suitable as an alloying element in preparing rhodium alloys. The presence of nickel offers an improved compatibility for any welding process used to join a sparking tip with the body of an ignition electrode. In addition, visual observation made during testing suggests that the power of the spark emitted by the electrode is increased as electrical resistivity of the alloy is increased by the addition of nickel. The rhodium alloy may comprise about 1 to about 48 wt% of nickel, such as about 5 to about 45 wt%, e.g. about 6 to about 45.5 wt%, for instance about 7 to about 44 wt%, for example about 8 to about 43 wt%.

The rhodium alloy may also comprise up to about 5 wt% (such as about 0 to about 5 wt%) each of any one of more elements selected from the group consisting of niobium, tantalum, titanium, chromium, molybdenum, cobalt, rhenium, vanadium, aluminium, hafnium and tungsten, preferably niobium, tantalum, titanium, chromium, molybdenum, cobalt, rhenium and tungsten, more preferably chromium, tungsten and/or molybdenum e.g. chromium and/or tungsten. Without wishing to be bound by theory, it is believed that the inclusion of these elements may ductilise the alloys i.e. make the alloys more tolerant to deformation and ease of manufacture. The rhodium alloy may comprise ≥ about 0.01 wt%, such as, ≥ about 0.05 wt%, ≥ about 0.1 wt%, ≥ about 0.15 wt% or ≥ about 0.2 wt% each of the elements selected from the group consisting of niobium, tantalum, titanium, chromium, molybdenum, cobalt, rhenium, vanadium, aluminium, hafnium and tungsten, preferably niobium, tantalum, titanium, chromium, molybdenum, cobalt, rhenium and tungsten. The rhodium alloy may comprise ≤ about 4.5 wt%, such as ≤ about 4.0 wt%, ≤ about 3.5 wt%, ≤ about 3.0 wt%, ≤ about 2.5 wt%, ≤ about 2.0 wt%, ≤ about 1.5 wt%, ≤ about 1.0 wt%, ≤ about 0.5 wt%, ≤ about 0.4 wt% or ≤ about 0.3 wt% each of the elements selected from the group consisting of niobium, tantalum, titanium, chromium, molybdenum, cobalt, rhenium, vanadium, aluminium, hafnium and tungsten, preferably niobium, tantalum, titanium, chromium, molybdenum, cobalt, rhenium and tungsten. In one embodiment, about 0.01 to about 5 wt% each may be present, such as about 0.05 to about 2.5 wt%, for example, about 0.1 to about 1.0 wt %. When chromium is present, it may be present in 0 to about 5 wt%, such as about 2.5 to about 5 wt%, e.g. about 3 to about 5 wt% or 0 to about 1 wt%, such as about about 0.2 wt%. When tungsten is present, it may be present in about 0.1 to about 0.5 wt%, such as about 0.1 to about 0.3 wt%.

The rhodium alloy may comprise one or more elements selected from the group consisting of yttrium, zirconium and samarium, preferably zirconium. Without wishing to be bound by theory, it is believed that the inclusion of these elements may ductilise the alloys as described above. It is also believed that the elements (in particular zirconium) may hinder dislocation movement through grain boundaries (i.e. the boundaries between crystal lattices at different orientations) and hence limit or slow grain growth. Grain growth therefore appears to be reduced at temperature ensuring a fine grain structure is retained. The rhodium alloy may comprise about 0.01 to about 1 wt% (such as about 0.01 to about 0.50 wt%) each of any one or more elements selected from the group consisting of yttrium, zirconium and samarium. The rhodium alloy may comprise ≥ about 0.015 wt%, ≥ about 0.02 wt%, ≥ about 0.025 wt% or ≥ about 0.030 wt% each of any one or more elements selected from the group consisting of yttrium, zirconium and samarium. The rhodium alloy may comprise ≤ about 0.45 wt%, ≤ about 0.40 wt%, ≤ about 0.35 wt%, ≤ about 0.30 wt%, ≤ about 0.25 wt%, ≤ about 0.20 wt%, ≤ about 0.15 wt%, ≤ about 0.10 wt%, ≤ about 0.05 wt% or ≤ about 0.04 wt% each of any one or more elements selected from the group consisting of yttrium, zirconium and samarium.

In one embodiment, the rhodium alloy may comprise about 0.01 to about 0.50 wt% of zirconium. The rhodium alloy may comprise ≥ about 0.015 wt%, ≥ about 0.02 wt%, ≥ about 0.025 wt% or ≥ about 0.030 wt% of zirconium. The rhodium alloy may comprise ≤ about 0.45 wt%, ≤ about 0.40 wt%, ≤ about 0.35 wt%, ≤ about 0.30 wt%, ≤ about 0.25 wt%, ≤ about 0.20 wt%, ≤ about 0.15 wt%, ≤ about 0.10 wt%, ≤ about 0.05 wt% or ≤ about 0.04 wt% of zirconium.

In another embodiment, the rhodium alloy may comprise about 0.01 to about 0.50 wt% of yttrium. The rhodium alloy may comprise ≥ about 0.015 wt%, ≥ about 0.02 wt%, ≥ about 0.025 wt% or ≥ about

0.030 wt% of yttrium. The rhodium alloy may comprise ≤ about 0.45 wt%, ≤ about 0.40 wt%, ≤ about 0.35 wt%, ≤ about 0.30 wt%, ≤ about 0.25 wt%, ≤ about 0.20 wt%, ≤ about 0.15 wt%, ≤ about 0.10 wt%, ≤ about 0.05 wt% or ≤ about 0.04 wt% of yttrium.

In yet another embodiment, the rhodium alloy may comprise about 0.01 to about 0.50 wt% of samarium. The rhodium alloy may comprise ≥ about 0.015 wt%, ≥ about 0.02 wt%, ≥ about 0.025 wt% or ≥ about 0.030 wt% of samarium. The rhodium alloy may comprise ≤ about 0.45 wt%, ≤ about 0.40 wt%, ≤ about 0.35 wt%, ≤ about 0.30 wt%, ≤ about 0.25 wt%, ≤ about 0.20 wt%, ≤ about 0.15 wt%, ≤ about 0.10 wt%, ≤ about 0.05 wt% or ≤ about 0.04 wt% of samarium.

It will be appreciated that elemental yttrium, zirconium and/or samarium is utilised and not e.g. oxides of yttrium, zirconium and/or samarium. In this respect, the oxides are typically added to an alloy which has already been prepared and is mechanically mixed with it. This is in contrast to elemental yttrium, zirconium and/or samarium which are dissolved in the continuous solution formed during the alloy's synthesis. Yttrium, zirconium and/or samarium, therefore, are alloying constituents.

In one preferred embodiment, the rhodium alloy may comprise about 0.02 to about 0.20 wt% each of any one or more elements selected from the group consisting of yttrium, zirconium and samarium. In another preferred embodiment, the rhodium alloy may comprise about ≥ 0.03 wt% each of any one or more elements selected from the group consisting of yttrium, zirconium and samarium, such as about ≥ 0.04 wt%. In yet another preferred embodiment, the rhodium alloy may comprise about ≤ 0.175 wt% of any one or more elements selected from the group consisting of yttrium, zirconium and samarium, such as about ≤ 0.15 wt%, for example, about ≤ 0.125 wt% or ≤ 0.1 wt%

In one embodiment, the rhodium alloy comprises:

a) about 70 wt% or more of rhodium, such as about 75 wt%;
b) 0 wt% each of any one or more elements selected from the group consisting of iridium, platinum and palladium;
c) 0 wt% of ruthenium;
d) about 0.01 to about 35 wt% of nickel, e.g. about 0.01 to about 25 wt%;
e) up to about 5 wt% each of any one of more elements selected from the group consisting of niobium, tantalum, titanium, chromium, molybdenum, cobalt, rhenium, vanadium, aluminium, hafnium and tungsten; and
f) optionally about 0.01 to about 0.50 wt% each of any one or more elements selected from the group consisting of yttrium, zirconium and samarium; and

wherein the total wt% of the rhodium alloy adds up to 100 wt%.

In one preferred embodiment, the rhodium alloy may comprise about ≥ 72 wt% of rhodium, for instance ≥ 76 wt% for example about ≥ 77 wt%, such as about ≥ 78 wt% or about ≥ 79 wt%. In another preferred embodiment, the rhodium alloy may comprise about ≤ 94 wt% of rhodium, for example about ≤ 93 wt%, such as about ≤ 92 wt% or about ≤ 91 wt%. In one preferred embodiment, the rhodium alloy comprises about 80 wt% of rhodium. In another preferred embodiment, the rhodium alloy comprises about 90 wt% of rhodium.

In one preferred embodiment, the rhodium alloy comprises about 10 to about 35 wt% of nickel, such as about 15 to about 25 wt%. In one preferred embodiment, the rhodium alloy may comprise about ≥ 16 wt% of nickel, for example about ≥ 17 wt%, such as about ≥ 18 wt% or about ≥ 19 wt%. In another preferred embodiment, the rhodium alloy may comprise about ≤ 35 wt% of nickel, for example about ≤ 34 wt%, such as about ≤ 33 wt%, about ≤ 32 wt% or about ≤ 31 wt%. In another preferred embodiment, the rhodium alloy may comprise about ≤ 24 wt% of nickel, for example about ≤ 23 wt%, such as about ≤ 22 wt%, about ≤ 21 wt% or about ≤ 20 wt%. In one particularly preferred embodiment, the rhodium alloy comprises about 19.86 wt% nickel. In one particularly preferred embodiment, the rhodium alloy comprises about 20 wt% nickel. In one particularly preferred embodiment, the rhodium alloy comprises about 30.5 wt% nickel.

In one preferred embodiment, the rhodium alloy may comprise about 0.01 to about 5 wt% of niobium. In another preferred embodiment, the rhodium alloy may comprise about 0.01 to about 5 wt% of tantalum. In yet another preferred embodiment, the rhodium alloy may comprise about 0.01 to about 5 wt% of titanium. In another preferred embodiment, the rhodium alloy may comprise about 0.01 to about 5 wt% of chromium. In yet another preferred embodiment, the rhodium alloy may comprise about 0.01 to about 5 wt% of molybdenum. In another preferred embodiment, the rhodium alloy may comprise about 0.01 to about 5 wt% of cobalt. In yet another preferred embodiment, the rhodium alloy may comprise about 0.01 to about 5 wt% of rhenium. In another preferred embodiment, the rhodium alloy may comprise about 0.01 to about 5 wt% of vanadium. In yet another preferred embodiment, the rhodium alloy may comprise about 0.01 to about 5 wt% of aluminium. In another preferred embodiment, the rhodium alloy may comprise about 0.01 to about 5 wt% of hafnium. In yet another preferred embodiment, the rhodium alloy may comprise about 0.01 to about 5 wt% of tungsten. When the rhodium alloy comprises tungsten, the tungsten may be present in about 0.05 to about 2.5 wt%, such as about 0.06 to about 1.5 wt%, for example, about 0.07 to about 1 wt% e.g. about 0.1 to about 0.3 wt%.

In one preferred embodiment, the rhodium alloy comprises about 0.01 to about 5 wt% each of any one or more elements selected from the group consisting of niobium, tantalum, titanium, chromium, molybdenum, cobalt, rhenium, vanadium, aluminium, hafnium and tungsten, preferably niobium, tantalum, titanium, chromium, molybdenum, cobalt, rhenium and tungsten, more preferably chromium and/or tungsten. The rhodium alloy may comprise about ≥ 0.025 wt% each of any one or more elements selected from the group consisting of niobium, tantalum, titanium, chromium, molybdenum, cobalt, rhenium, vanadium, aluminium, hafnium and tungsten, for example about ≥ 0.05 wt%, such as about ≥ 0.075 wt% or about ≥ 0.10 wt%. The rhodium alloy may comprise about ≤ 5.0 wt% each of any one or more elements selected from the group consisting of niobium, tantalum, titanium, chromium, molybdenum, cobalt, rhenium, vanadium, aluminium, hafnium and tungsten, for instance about ≤ 2.50 wt%, for example about ≤ 2.00 wt%, such as about ≤ 1.50 wt% or about ≤ 1.00 wt%. In one particularly preferred embodiment, the rhodium alloy comprises about 2.5 wt% of molybdenum. In another particularly preferred embodiment, the rhodium alloy comprises about 3.4 wt% or about 5.0 wt% of chromium. In another particularly preferred embodiment, the rhodium alloy comprises about 3.0 wt% of aluminium.

In one embodiment, the rhodium alloy does not comprise zirconium, yttrium or samarium.

In another embodiment, the rhodium alloy may comprise about 0.01 to about 0.50 wt% of zirconium. In another preferred embodiment, the rhodium alloy may comprise about 0.01 to about 0.50 wt% of yttrium. In yet another preferred embodiment, the rhodium alloy may comprise about 0.01 to about 0.50 wt% of samarium.

In one preferred embodiment, the rhodium alloy may comprise about 0.02 to about 0.20 wt% each of any one or more elements selected from the group consisting of yttrium, zirconium and samarium. In another preferred embodiment, the rhodium alloy may comprise about ≥ 0.03 wt% each of any one or more elements selected from the group consisting of yttrium, zirconium and samarium, such as about ≥ 0.04 wt%. In yet another preferred embodiment, the rhodium alloy may comprise about ≤ 0.175 wt% each of any one or more elements selected from the group consisting of yttrium, zirconium and samarium, such as about ≤ 0.15 wt%, for example, about ≤ 0.125 wt%.

In one embodiment, the rhodium alloy comprises:

a) about 50 to about 95 wt% or more of rhodium;
b) up to about 25 wt% each of any one or more elements selected from the group consisting of iridium, platinum and palladium;
c) up to about 35 wt% of ruthenium;
d) about 0.01 to about 49.99 wt% of nickel;
e) up to about 5 wt% each of any one of more elements selected from the group consisting of niobium, tantalum, titanium, chromium, molybdenum, cobalt, rhenium, vanadium, aluminium, hafnium and tungsten; and
f) optionally about 0.01 to about 0.50 wt% each of any one or more elements selected from the group consisting of yttrium, zirconium and samarium;

wherein the rhodium alloy comprises at least one of iridium, platinum, palladium or ruthenium; and

wherein the total wt% of the rhodium alloy adds up to 100 wt%.

In one preferred embodiment, the rhodium alloy may comprise about ≥ 51 wt% of rhodium, for example about ≥ 52 wt%, such as about ≥ 53 wt%, about ≥ 54 wt% or about ≥ 55 wt%. In another preferred embodiment, the rhodium alloy may comprise about ≤ 80 wt% of rhodium, for example about ≤ 79 wt%, such as about ≤ 78 wt%, about ≤ 77 wt%, about ≤ 76 wt% or about ≤ 75 wt%. In one particularly preferred embodiment, the rhodium alloy comprises about 55 wt% rhodium. In another particularly preferred embodiment, the rhodium alloy comprises about 74 wt% rhodium. In yet another particularly preferred embodiment, the rhodium alloy comprises about 75 wt% rhodium. In another particularly preferred embodiment, the rhodium alloy comprises about 65 wt% rhodium. In yet another particularly preferred embodiment, the rhodium alloy comprises about 50 wt% rhodium. In another particularly preferred embodiment, the rhodium alloy comprises about 60 wt% rhodium. In another particularly preferred embodiment, the rhodium alloy comprises about 75 wt% rhodium. In another particularly preferred embodiment, the rhodium alloy comprises about 57.5 wt% rhodium. In another particularly preferred embodiment, the rhodium alloy comprises about 54.5 wt% rhodium. In another particularly preferred embodiment, the rhodium alloy comprises about 63.1 wt% rhodium.

In this embodiment, the rhodium alloy comprises at least one of iridium, platinum, palladium or ruthenium. The rhodium alloy may comprise up to about 25 wt% (e.g. about 0.01 to about 25 wt%) each of one or more elements selected from the consisting of iridium, platinum and palladium, preferably about 0.1 to about 20 wt% and more preferably about 1 to about 15 wt%. In one preferred embodiment, the rhodium alloy comprises about 0.01 to about 25 wt% of iridium, preferably about 0.1 to about 20 wt% and more preferably about 1 to about 15 wt%. In another preferred embodiment, the rhodium alloy comprises about 0.01 to about 25 wt% of platinum, preferably about 0.1 to about 20 wt% and more preferably about 1 to about 15 wt%. In yet another preferred embodiment, the rhodium alloy comprises about 0.01 to about 25 wt% of palladium, preferably about 0.1 to about 20 wt% and more preferably about 1 to about 15 wt%.

In one particularly preferred embodiment, the rhodium alloy may comprise about ≥ 0.1 wt% each of any one or more elements selected from the group consisting of iridium, platinum and palladium, for example about ≥ 0.5 wt%, such as about ≥ 0.6 wt% or about ≥ 0.7 wt%. In another preferred embodiment, the rhodium alloy may comprise about ≤ 20 wt% each of any one or more elements selected from the group consisting of iridium, platinum and palladium, for example about ≤ 15 wt%, such as about ≤ 10 wt%.

In one preferred embodiment, the rhodium alloy may comprise about 0.01 to about 35 wt % ruthenium, such as about 2.5 to about 33 wt %, for example about 5.0 to about 31 wt%. In one particularly preferred embodiment, the rhodium alloy comprises about 5 to about 10 wt% ruthenium, for example about 7.5 wt%. In another particularly preferred embodiment, the rhodium alloy comprises about 15 to about 25 wt % of ruthenium, such as about 20 wt% (e.g. 19.86 wt%). In yet another particularly preferred embodiment, the rhodium alloy comprises about 25 to about 35 wt % of ruthenium, such as about 30 wt% (e.g. 29.86 wt%).

In another preferred embodiment, the rhodium alloy may comprise no ruthenium i.e. 0 wt% ruthenium.

In one preferred embodiment, the rhodium alloy comprises about 5 to about 45 wt% of nickel. In one preferred embodiment, the rhodium alloy may comprise about ≥ 6 wt% of nickel, for example about ≥ 7 wt%, such as about ≥ 8 wt%, about ≥ 9 wt% or about ≥ 10 wt%. In another preferred embodiment, the rhodium alloy may comprise about ≤ 44 wt% of nickel, for example about ≤ 43 wt%, such as about ≤ 42 wt%. In one particularly preferred embodiment, the rhodium alloy comprises about 42 wt% of nickel. In another particularly preferred embodiment, the rhodium alloy comprises about 15.5 wt% of nickel. In yet another particularly preferred embodiment, the rhodium alloy comprises about 25 wt% of nickel. In another particularly preferred embodiment, the rhodium alloy comprises about 30 wt% of nickel. In yet another particularly preferred embodiment, the rhodium alloy comprises about 10 wt% of nickel. In yet another particularly preferred embodiment, the rhodium alloy comprises about 5 wt% of nickel. In yet another particularly preferred embodiment, the rhodium alloy comprises about 45 wt% of nickel. In yet another particularly preferred embodiment, the rhodium alloy comprises about 30 wt% of nickel. In yet another particularly preferred embodiment, the rhodium alloy comprises about 41.5 wt% of nickel. In yet another particularly preferred embodiment, the rhodium alloy comprises about 42 wt% of nickel.

In one preferred embodiment, the rhodium alloy may comprise about 0.01 to about 5 wt% of niobium. In another preferred embodiment, the rhodium alloy may comprise about 0.01 to about 5 wt% of tantalum. In yet another preferred embodiment, the rhodium alloy may comprise about 0.01 to about 5 wt% of titanium, such as about 0.5 to about 2.5 wt%, e.g. about 1 wt%. In another preferred embodiment, the rhodium alloy may comprise about 0.01 to about 5 wt% of chromium. In yet another preferred embodiment, the rhodium alloy may comprise about 0.01 to about 5 wt% of molybdenum. In another preferred embodiment, the rhodium alloy may comprise about 0.01 to about 5 wt% of cobalt. In yet another preferred embodiment, the rhodium alloy may comprise about 0.01 to about 5 wt% of rhenium. In another preferred embodiment, the rhodium alloy may comprise about 0.01 to about 5 wt% of vanadium. In yet another preferred embodiment, the rhodium alloy may comprise about 0.01 to about 5 wt% of aluminium. In another preferred embodiment, the rhodium alloy may comprise about 0.01 to about 5 wt% of hafnium. In yet another preferred embodiment, the rhodium alloy may comprise about 0.01 to about 5 wt% of tungsten. When the rhodium alloy comprises tungsten, the tungsten may be present in about 0.05 to about 2.5 wt%, such as about 0.06 to about 1.5 wt%, for example, about 0.07 to about 1 wt% e.g. about 0.1 to about 0.3 wt%.

In one preferred embodiment, the rhodium alloy may comprise about 0.01 to about 5 wt% each of any one or more elements selected from the group consisting of niobium, tantalum, titanium, chromium, molybdenum, cobalt, rhenium, vanadium, aluminium, hafnium and tungsten, preferably niobium, tantalum, titanium, chromium, molybdenum, cobalt, rhenium and tungsten, more preferably chromium and/or tungsten. The rhodium alloy may comprise about ≥ 0.025 wt% each of any one or more elements selected from the group consisting of niobium, tantalum, titanium, chromium, molybdenum, cobalt, rhenium, vanadium, aluminium, hafnium and tungsten, for example about ≥ 0.05 wt%, such as about ≥ 0.075 wt% or about ≥ 0.10 wt%. The rhodium alloy may comprise about ≤ 2.50 wt% each of any one or more elements selected from the group consisting of niobium, tantalum, titanium, chromium, molybdenum, cobalt, rhenium, vanadium, aluminium, hafnium and tungsten, for example about ≤ 2.00 wt%, such as about ≤ 1.50 wt% or about ≤ 1.00 wt%.

In one embodiment, the rhodium alloy does not comprise zirconium, yttrium or samarium.

In one preferred embodiment, the rhodium alloy may comprise about 0.01 to about 0.50 wt% of zirconium. In another preferred embodiment, the rhodium alloy may comprise about 0.01 to about 0.50 wt% of yttrium. In yet another preferred embodiment, the rhodium alloy may comprise about 0.01 to about 0.50 wt% of samarium.

In another preferred embodiment, the rhodium alloy may comprise about 0.02 to about 0.40 wt% each of any one or more elements selected from the group consisting of yttrium, zirconium and samarium. In another preferred embodiment, the rhodium alloy may comprise about ≥ 0.03 wt% each of any one or more elements selected from the group consisting of yttrium, zirconium and samarium, such as about ≥ 0.04 wt%. In yet another preferred embodiment, the rhodium alloy may comprise about ≤ 0.35 wt% each of any one or more elements selected from the group consisting of yttrium, zirconium and samarium, such as about ≤ 0.30 wt%.

Rhodium alloys according to the present invention may be selected from the group consisting of:

Alloy	Rh (wt%)	Ir (wt%)	Ru (wt%)	Ni (wt%)	Mo (wt%)	Cr (wt%)	Ti (wt%)	Al (wt%)	W (wt%)	Zr (wt%)	Y (wt%)
A	80	0	0	19.86	0	0	0	0	0.1	0.04	0
B	55	2.86	0	42	0	0	0	0	0.1	0.04	0
C	74	0.86	0	25	0	0	0	0	0.1	0.04	0
D	75	1.86	7.5	15.5	0	0	0	0	0.1	0.04	0
E	65	9.86	0	25	0	0	0	0	0.1	0.04	0
F	50	0	19.86	30	0	0	0	0	0.1	0.04	0
G	60	0	29.86	10	0	0	0	0	0.1	0.04	0
H	72.4	0	0	20	2.5	5	0	0	0	0	0.1
I	75	20	0	5	0	0	0	0	0	0	0
J	50	5	0	45	0	0	0	0	0	0	0
K	57.5	12.5	0	30	0	0	0	0	0	0	0
L	54.5	3	0	41.5	0	0	1	0	0	0	0
M	55	3	0	42	0	0	0	0	0	0	0
N	63.1	0	0	30.5	0	3.4	0	3	0	0	0

In certain embodiments, the rhodium alloy does not comprise Alloy D. In certain embodiments, the rhodium alloy does not comprise Alloy E. In certain embodiments, the rhodium alloy does not comprise Alloy F. In certain embodiments, the rhodium alloy does not comprise Alloy G.

The enhanced physical and mechanical properties of the rhodium alloys of the present invention make them suitable for use in high temperature or load bearing applications. As the alloys of the present invention demonstrate good resistance to erosion, the alloys may be used in ignition applications, e.g. as components in spark-plugs. The alloys may also be suitable for use as electrodes and some biomedical applications such as a stent. The alloys may also be suitable as pinning wire and lead-ins for sensors. The foregoing examples merely serve to illustrate the many potential uses of the present alloys and, as such, are not intended to be limiting in any way.

In another aspect, the invention provides the use of a rhodium alloy in an electrode or spark plug, wherein the rhodium alloy comprises:

i) rhodium; and

ii) nickel;

wherein the alloy comprises a greater quantity of rhodium as compared to any other individual element of the alloy.

The rhodium alloys are as generally described above.

In one embodiment, the rhodium alloy may be used in an electrode. In another embodiment, the rhodium alloy may be used in a spark plug.

In another aspect, the invention provides a rhodium alloy comprising:

i) rhodium;

ii) nickel; and

iii) one or more elements selected from the group consisting of yttrium, zirconium and samarium;

wherein the alloy comprises a greater quantity of rhodium as compared to any other individual element of the alloy.

The rhodium alloys are as generally described above.

The rhodium alloys may be manufactured by known methods and fabricated into any suitable form. Improvements in elongation to failure, or ductility, make the alloys particularly suitable for drawing into wires; however, the alloys may also be used to prepare tubes, sheets, grains, powders or other common forms. The alloys may also be used in spray coating applications.

Embodiments and/or optional features of the invention have been described above. Any aspect of the invention may be combined with any other aspect of the invention, unless the context demands otherwise. Any of the embodiments or optional features of any aspect may be combined, singly or in combination, with any aspect of the invention, unless the context demands otherwise.

The invention will now be described by way of the following non-limiting Examples and with reference to the following figures in which:

Figure 1 illustrates a cross-section through a wire of a rhodium ally (Alloy B) as manufactured.

Figure 2 illustrates a rhodium alloy (Alloy B) which has been annealed at 1100 °C for 15 minutes and then compressed in a die.

Examples

Example 1

Alloy Preparation

The rhodium alloys detailed in Table 1 below are prepared by argon arc melting. All values are given in weight percent (wt%) based on the total weight of the alloy.

Table 1:

Alloy	Rh (wt%)	Ir (wt%)	Ru (wt%)	Ni (wt%)	Mo (wt%)	Cr (wt%)	Ti (wt%)	Al (wt%)	W (wt%)	Zr (wt%)	Y (wt%)
A	80	0	0	19.86	0	0	0	0	0.1	0.04	0
B	55	2.86	0	42	0	0	0	0	0.1	0.04	0
C	74	0.86	0	25	0	0	0	0	0.1	0.04	0
D	75	1.86	7.5	15.5	0	0	0	0	0.1	0.04	0
E	65	9.86	0	25	0	0	0	0	0.1	0.04	0
F	50	0	19.86	30	0	0	0	0	0.1	0.04	0
G	60	0	29.86	10	0	0	0	0	0.1	0.04	0
H	72.4	0	0	20	2.5	5	0	0	0	0	0.1
I	75	20	0	5	0	0	0	0	0	0	0
J	50	5	0	45	0	0	0	0	0	0	0
K	57.5	12.5	0	30	0	0	0	0	0	0	0
L	54.5	3	0	41.5	0	0	1	0	0	0	0
M	55	3	0	42	0	0	0	0	0	0	0
N	63.1	0	0	30.5	0	3.4	0	3	0	0	0

Each alloy is subsequently processed to produce wire having a 1mm or 2mm diameter.

Example 2

Formability Testing

1. Wire at 1 – 2 mm diameter of Alloy B is cut into 50 mm lengths; actual diameter is noted. Figure 1 illustrates a cross-section through the wire.
2. Wire samples are evaluated in the as-drawn and annealed condition to check whether formability is condition dependent. The wire samples are annealed at 1100 ^{o}C in air for 15 minutes.
3. Evaluation uses a bespoke die set encompassing rectangular cavities held in a fly press.
4. The wire samples are placed in the appropriate cavity and the press closed to force the sample into the cavity. The press is manually operated.
5. Following pressing the wire samples are examined visually, by microscope and ultimately by cross sectioning and metallographic preparation to allow measurement, determine the degree of deformation and check whether the integrity of the samples are preserved.
6. Assessment of the alloy's formability is based on the presence of any cracks, the relative size (length/width) of the cracks and the degree of deformation as calculated by the relative thickness of the deformed wire in comparison to the original diameter.

Figures 1 and 2 illustrate that the alloy demonstrates a high degree of deformability and remains substantially crack free.

Example 3

Electrode Studies

The rhodium alloys of the present invention, an iridium standard and a rhodium standard are cut into electrode wire having 1 mm diameter. The wires are fixed into a four station test cell together with matching 3 mm diameter Ir earth electrodes and the gap between them adjusted and set with a vernier calliper. The test electrodes are set at negative polarity and the earth electrode as positive to concentrate erosion on the appropriate electrodes.

Testing commences with a 10 kV electric pulse driven by an automotive ignition coil being applied to each pair of electrodes at 200 Hz. This initiates a continuous series of rapid spark discharges between the electrodes as generated in a typical automotive engine. The test cell is visually checked at intervals to confirm functionality and after approximately 250 hr. the discharge is stopped and the electrode gap re-measured. A counter initiated at test commencement is used to measure elapsed time from which the number of spark discharges can be calculated.

The electrodes are reset in the test cell and discharge re-initiated. After a further approximately 250 hr. (approx. 500 hrs discharge time in total) the test is stopped and the same procedure of gap measurement and electrode inspection completed.

Test Duration

The test duration and approximate number of sparks were calculated. Therefore, for a 20 day test:

- 20 days x 24 hrs/day = 480 hrs

- 480 hrs x 3600 seconds/hr = 1,728,000 seconds
- 1,728,000 seconds x 200 sparks/second = 345,600,000 sparks (per test point)

Measurements of Gaps

Test gap – negative electrode	Startpoint Gap (mm)	Midpoint Gap (mm)	Endpoint Gap (mm)	Gap Growth (mm)
100% Ir (comparative)	8.2	8.6	8.9	0.7
100% Rh (comparative)	8.1	8.2	8.4	0.3
Alloy A	8.1	8.2	8.3	0.2
Alloy B	8.1	8.1	8.2	0.1
Alloy H	8.1	8.0	8.3	0.2
Alloy I	7.9	7.9	8.0	0.1
Alloy J	8.0	8.1	8.2	0.2
Alloy K	8.0	8.1	8.2	0.2
Alloy L	8.0	8.1	8.2	0.3
Alloy M	7.9	8.1	8.2	0.3

The 100% Ir electrode exhibits the worst (most) erosion, the gap measurement changing by 0.7 mm +/- 0.1 mm over the test duration.

The 100% Rh, and Alloy A, B and H-M electrodes exhibit less erosion than the 100% Ir electrode. The Alloy L and M electrodes exhibit comparable erosion resistance to the 100% Rh electrode over the test duration. The Alloy A, H, J and K electrodes exhibit better erosion resistance than the 100% Rh electrode as the gap measurements change by 0.2 mm +/- 0.1 mm in comparison to 0.3 mm +/- 0.1 mm for the 100% rhodium electrode over the test duration. Alloys B and I also exhibit better erosion resistance than the 100% Rh electrode as the gap measurements change by 0.1 mm +/- 0.1 mm in comparison to 0.3 mm +/- 0.1 mm for the 100% rhodium electrode over the test duration.

Claims

1. An electrode comprising a rhodium alloy, wherein the rhodium alloy comprises:
   i) rhodium; and
   ii) nickel;

   wherein the alloy comprises a greater quantity of rhodium as compared to any other individual element of the alloy.

2. An electrode according to claim 1, wherein the rhodium alloy further comprises:
   iii) one or more elements selected from the group consisting of yttrium, zirconium and samarium.

3. An electrode according to claim 1, wherein the rhodium alloy comprises:
   a) about 50 wt% or more of rhodium;
   b) up to about 49.99 wt% each of any one or more elements selected from the group consisting of iridium, platinum and palladium;
   c) up to about 35 wt% of ruthenium;
   d) about 0.01 to about 49.99 wt% of nickel;
   e) up to about 5 wt% each of any one of more elements selected from the group consisting of niobium, tantalum, titanium, chromium, molybdenum, cobalt, rhenium, vanadium, aluminium, hafnium and tungsten; and
   f) optionally about 0.01 to about 1.00 wt% each of any one or more elements selected from the group consisting of yttrium, zirconium and samarium; and

   wherein the total wt% of the rhodium alloy adds up to 100 wt%.

4. An electrode according to claim 1, wherein the rhodium alloy comprises:
   a) about 75 wt% or more of rhodium;
   b) 0 wt% each of any one or more elements selected from the group consisting of iridium, platinum and palladium;
   c) 0 wt% of ruthenium;
   d) about 0.01 to about 25 wt% of nickel;
   e) up to about 5 wt% each of any one of more elements selected from the group consisting of niobium, tantalum, titanium, chromium, molybdenum, cobalt, rhenium, vanadium, aluminium, hafnium and tungsten; and
   f) optionally about 0.01 to about 1.00 wt% each of any one or more elements selected from the group consisting of yttrium, zirconium and samarium; and

   wherein the total wt% of the rhodium alloy adds up to 100 wt%.

5. An electrode according to claim 1, wherein the rhodium alloy comprises:
   a) about 50 to about 95 wt% or more of rhodium;

b) up to about 25 wt% each of any one or more elements selected from the group consisting of iridium, platinum and palladium;

c) up to about 35 wt% of ruthenium;

d) about 0.01 to about 49.99 wt% of nickel;

e) up to about 5 wt% each of any one of more elements selected from the group consisting of niobium, tantalum, titanium, chromium, molybdenum, cobalt, rhenium, vanadium, aluminium, hafnium and tungsten; and

f) optionally about 0.01 to about 0.50 wt% each of any one or more elements selected from the group consisting of yttrium, zirconium and samarium;

wherein the rhodium alloy comprises at least one of iridium, platinum, palladium or ruthenium; and

wherein the total wt% of the rhodium alloy adds up to 100 wt%.

6. An electrode according to claim 1, wherein the rhodium alloy is selected from the group consisting of:

Alloy	Rh (wt%)	Ir (wt%)	Ru (wt%)	Ni (wt%)	Mo (wt%)	Cr (wt%)	Ti (wt%)	Al (wt%)	W (wt%)	Zr (wt%)	Y (wt%)
A	80	0	0	19.86	0	0	0	0	0.1	0.04	0
B	55	2.86	0	42	0	0	0	0	0.1	0.04	0
C	74	0.86	0	25	0	0	0	0	0.1	0.04	0
D	75	1.86	7.5	15.5	0	0	0	0	0.1	0.04	0
E	65	9.86	0	25	0	0	0	0	0.1	0.04	0
F	50	0	19.86	30	0	0	0	0	0.1	0.04	0
G	60	0	29.86	10	0	0	0	0	0.1	0.04	0
H	72.4	0	0	20	2.5	5	0	0	0	0	0.1
I	75	20	0	5	0	0	0	0	0	0	0
J	50	5	0	45	0	0	0	0	0	0	0
K	57.5	12.5	0	30	0	0	0	0	0	0	0
L	54.5	3	0	41.5	0	0	1	0	0	0	0
M	55	3	0	42	0	0	0	0	0	0	0
N	63.1	0	0	30.5	0	3.4	0	3	0	0	0

7. A spark plug comprising an electrode according to any one of claims 1 to 6.

8. The use of a rhodium alloy in an electrode or a spark plug, wherein the rhodium alloy comprises:

i) rhodium; and

ii) nickel;

wherein the alloy comprises a greater quantity of rhodium as compared to any other individual element of the alloy.

9. The use according to claim 8, wherein the rhodium alloy further comprises:
iii) one or more elements selected from the group consisting of yttrium, zirconium and samarium.

10. The use according to claim 8, wherein the rhodium alloy comprises:
a) about 50 wt% or more of rhodium;
b) up to about 49.99 wt% each of any one or more elements selected from the group consisting of iridium, platinum and palladium;
c) up to about 35 wt% of ruthenium;
d) about 0.01 to about 49.99 wt% of nickel;
e) up to about 5 wt% each of any one of more elements selected from the group consisting of niobium, tantalum, titanium, chromium, molybdenum, cobalt, rhenium, vanadium, aluminium, hafnium and tungsten; and
f) optionally about 0.01 to about 1.00 wt% each of any one or more elements selected from the group consisting of yttrium, zirconium and samarium; and
wherein the total wt% of the rhodium alloy adds up to 100 wt%.

11. The use according to claim 8, wherein the rhodium alloy comprises:
a) about 75 wt% or more of rhodium;
b) 0 wt% each of any one or more elements selected from the group consisting of iridium, platinum and palladium;
c) 0 wt% of ruthenium;
d) about 0.01 to about 25 wt% of nickel;
e) up to about 5 wt% each of any one of more elements selected from the group consisting of niobium, tantalum, titanium, chromium, molybdenum, cobalt, rhenium, vanadium, aluminium, hafnium and tungsten; and
f) optionally about 0.01 to about 1.00 wt% each of any one or more elements selected from the group consisting of yttrium, zirconium and samarium; and
wherein the total wt% of the rhodium alloy adds up to 100 wt%.

12. The use according to claim 8, wherein the rhodium alloy comprises:
a) about 50 to about 95 wt% or more of rhodium;
b) up to about 25 wt% each of any one or more elements selected from the group consisting of iridium, platinum and palladium;
c) up to about 35 wt% of ruthenium;
d) about 0.01 to about 49.99 wt% of nickel;

e) up to about 5 wt% each of any one of more elements selected from the group consisting of niobium, tantalum, titanium, chromium, molybdenum, cobalt, rhenium, vanadium, aluminium, hafnium and tungsten; and

f) optionally about 0.01 to about 0.50 wt% each of any one or more elements selected from the group consisting of yttrium, zirconium and samarium;

wherein the rhodium alloy comprises at least one of iridium, platinum, palladium or ruthenium; and

wherein the total wt% of the rhodium alloy adds up to 100 wt%.

13. The use according to claim 8, wherein the rhodium alloy is selected from the group consisting of:

Alloy	Rh (wt%)	Ir (wt%)	Ru (wt%)	Ni (wt%)	Mo (wt%)	Cr (wt%)	Ti (wt%)	Al (wt%)	W (wt%)	Zr (wt%)	Y (wt%)
A	80	0	0	19.86	0	0	0	0	0.1	0.04	0
B	55	2.86	0	42	0	0	0	0	0.1	0.04	0
C	74	0.86	0	25	0	0	0	0	0.1	0.04	0
D	75	1.86	7.5	15.5	0	0	0	0	0.1	0.04	0
E	65	9.86	0	25	0	0	0	0	0.1	0.04	0
F	50	0	19.86	30	0	0	0	0	0.1	0.04	0
G	60	0	29.86	10	0	0	0	0	0.1	0.04	0
H	72.4	0	0	20	2.5	5	0	0	0	0	0.1
I	75	20	0	5	0	0	0	0	0	0	0
J	50	5	0	45	0	0	0	0	0	0	0
K	57.5	12.5	0	30	0	0	0	0	0	0	0
L	54.5	3	0	41.5	0	0	1	0	0	0	0
M	55	3	0	42	0	0	0	0	0	0	0
N	63.1	0	0	30.5	0	3.4	0	3	0	0	0

14. A rhodium alloy comprising:

i) rhodium;

ii) nickel; and

iii) one or more elements selected from the group consisting of yttrium, zirconium and samarium;

wherein the alloy comprises a greater quantity of rhodium as compared to any other individual element of the alloy.

15. A rhodium alloy according to claim 14, wherein the alloy comprises:

a) about 50 wt% or more of rhodium;

b) up to about 49.99 wt% each of any one or more elements selected from the group consisting of iridium, platinum and palladium;
c) up to about 35 wt% of ruthenium;
d) about 0.01 to about 49.99 wt% of nickel;
e) up to about 5 wt% each of any one of more elements selected from the group consisting of niobium, tantalum, titanium, chromium, molybdenum, cobalt, rhenium, vanadium, aluminium, hafnium and tungsten; and
f) about 0.01 to about 1.00 wt% each of any one or more elements selected from the group consisting of yttrium, zirconium and samarium; and

wherein the total wt% of the rhodium alloy adds up to 100 wt%.

16. A rhodium alloy according to claim 14, wherein the alloy comprises:
a) about 75 wt% or more of rhodium;
b) 0 wt% each of any one or more elements selected from the group consisting of iridium, platinum and palladium;
c) 0 wt% of ruthenium;
d) about 0.01 to about 25 wt% of nickel;
e) up to about 5 wt% each of any one of more elements selected from the group consisting of niobium, tantalum, titanium, chromium, molybdenum, cobalt, rhenium, vanadium, aluminium, hafnium and tungsten; and
f) about 0.01 to about 1.00 wt% each of any one or more elements selected from the group consisting of yttrium, zirconium and samarium; and

wherein the total wt% of the rhodium alloy adds up to 100 wt%.

17. A rhodium alloy according to claim 14, wherein the alloy comprises:
a) about 50 to about 95 wt% or more of rhodium;
b) up to about 25 wt% each of any one or more elements selected from the group consisting of iridium, platinum and palladium;
c) up to about 35 wt% of ruthenium;
d) about 0.01 to about 49.99 wt% of nickel;
e) up to about 5 wt% each of any one of more elements selected from the group consisting of niobium, tantalum, titanium, chromium, molybdenum, cobalt, rhenium, vanadium, aluminium, hafnium and tungsten; and
f) about 0.01 to about 0.50 wt% each of any one or more elements selected from the group consisting of yttrium, zirconium and samarium;

wherein the rhodium alloy comprises at least one of iridium, platinum, palladium or ruthenium; and

wherein the total wt% of the rhodium alloy adds up to 100 wt%.

18. A rhodium alloy according to claim 14, wherein the alloy is selected from the group consisting of:

Alloy	Rh (wt%)	Ir (wt%)	Ru (wt%)	Ni (wt%)	Mo (wt%)	Cr (wt%)	Ti (wt%)	Al (wt%)	W (wt%)	Zr (wt%)	Y (wt%)
A	80	0	0	19.86	0	0	0	0	0.1	0.04	0
B	55	2.86	0	42	0	0	0	0	0.1	0.04	0
C	74	0.86	0	25	0	0	0	0	0.1	0.04	0
D	75	1.86	7.5	15.5	0	0	0	0	0.1	0.04	0
E	65	9.86	0	25	0	0	0	0	0.1	0.04	0
F	50	0	19.86	30	0	0	0	0	0.1	0.04	0
G	60	0	29.86	10	0	0	0	0	0.1	0.04	0
H	72.4	0	0	20	2.5	5	0	0	0	0	0.1
I	75	20	0	5	0	0	0	0	0	0	0
J	50	5	0	45	0	0	0	0	0	0	0
K	57.5	12.5	0	30	0	0	0	0	0	0	0
L	54.5	3	0	41.5	0	0	1	0	0	0	0
M	55	3	0	42	0	0	0	0	0	0	0
N	63.1	0	0	30.5	0	3.4	0	3	0	0	0

As Drawn

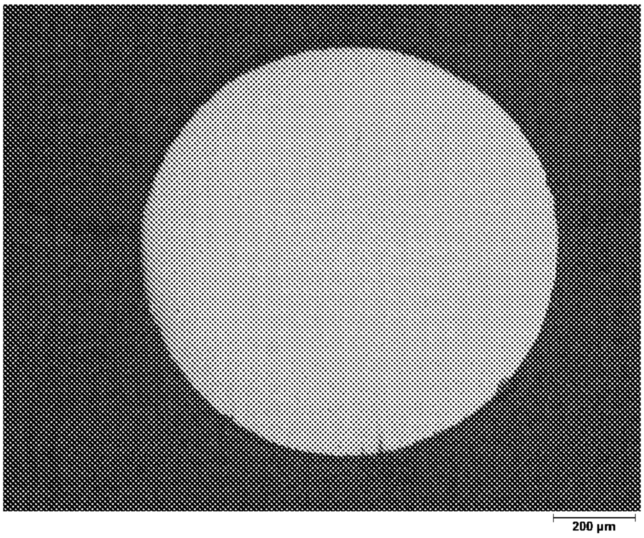

FIGURE 1

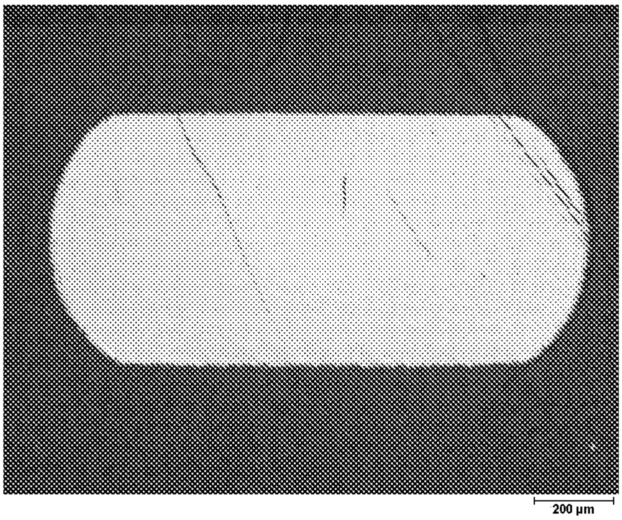

FIGURE 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2015/052236

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01T13/39
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01T

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2006/043856 A1 (MATSUTANI WATARU [JP] ET AL) 2 March 2006 (2006-03-02) abstract; claim 1; figures 1-4 -----	1-13
X	US 3 958 144 A (FRANKS HARRY E) 18 May 1976 (1976-05-18) column 1, line 44 - line 64; figure 1 -----	1,7,8
X	JP 2006 210325 A (NGK SPARK PLUG CO) 10 August 2006 (2006-08-10) claim 1; figures 1,2; table 1 -----	1,7,8

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 September 2015	07/12/2015

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Ruppert, Christopher

2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB2015/052236

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-13

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-13

   Electrode comprising Rh-Ni alloy and use of Rh-Ni alloy in an electrode

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2. claims: 14-18

   Rh-Ni alloy comprising at least one of Y, Zr, Sm

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2015/052236

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2006043856 A1	02-03-2006	NONE	
US 3958144 A	18-05-1976	NONE	
JP 2006210325 A	10-08-2006	JP 4944433 B2	30-05-2012
		JP 2006210325 A	10-08-2006