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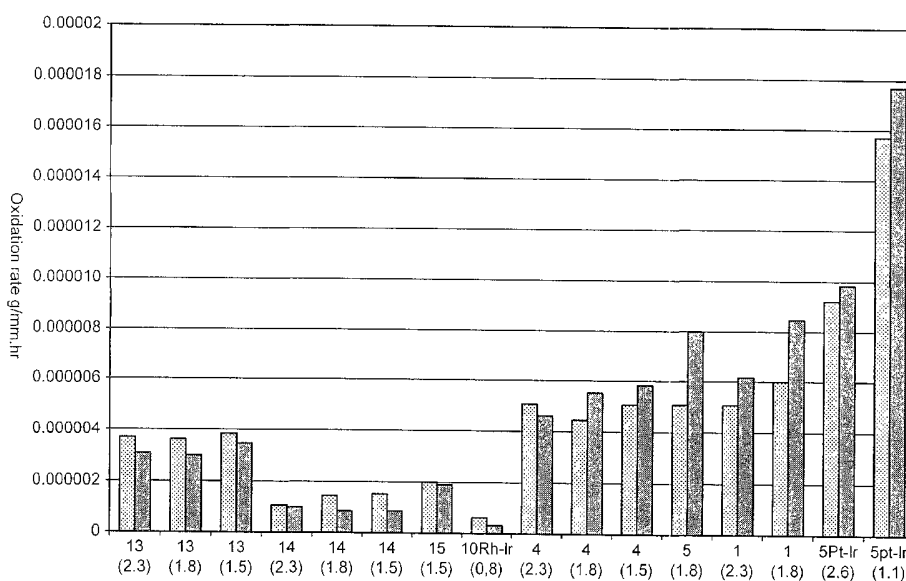
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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(75) Inventors/Applicants (for US only): COUPLAND,

(54) Title: ALLOY



(57) Abstract: An iridium alloy consists essentially of iridium and at least one of W and Zr, and optionally Rh. When present, W comprises between 0.01 and 5 wt % of the alloy; when present in combination with W, Zr comprises between 0.01 and 0.5 wt % of the alloy; when present alone or in combination with Rh only, Zr comprises between 0.01 and 0.09 wt % of the alloy; and when present, Rh comprises between 0.1 and 5 wt % of the alloy. The alloys may be modified by the addition of platinum and other platinum group metals and base metals. The alloys demonstrate enhanced physical and chemical properties and are suitable for use as electrode materials in spark plugs and other high temperature applications.

WO 2004/007782 A1

ALLOY

This invention relates to alloys of iridium, in particular to alloys of iridium with
5 low amounts of alloying elements and uses thereof.

Iridium is a member of the platinum group of metals and has a variety of applications including automobile catalysts, electrodes for industrial electrolysis, crucibles for crystal growth, thermocouples, rocket motor parts, glass making and spark
10 plugs. It has several attractive properties including a very high shear modulus at room temperature and elevated temperature strength second only to tungsten among the refractory metals. It is also thought to be the most corrosion resistant of all metals.

However, despite these benefits there are some disadvantages. Its mechanical
15 properties are sensitive to certain low level impurities and strain rate and it also exhibits a ductile-brittle transition. Due to the rarity of its occurrence in nature its price per gram is of the same order as platinum and furthermore its density is the second highest of all elements. Finally, although compared to the refractory metals its resistance to oxidation is excellent, it nevertheless does exhibit a significant weight loss at elevated temperature
20 under oxidising conditions.

As a result of its scarcity and difficulty in maintaining metal purity during manufacture, the metallurgy of iridium is poorly understood. Indeed little work, relative to that done on alloying of platinum for instance, has been carried out to investigate the
25 effect of alloying on properties. However, the alloying with some elements has been investigated by different workers. Oak Ridge National Laboratories in the USA have been responsible for developing one alloy, DOP-26 based on Ir-0.3W +Th, for radioisotope thermoelectric generator casings used to supply power to spacecraft. Tungsten has been shown to increase the alloy re-crystallisation temperature of iridium
30 by 400°C at >2wt% addition, which makes control of microstructure during hot working, much simpler. Thorium has been shown to promote ductility below the normal ductile/brittle transition zone, although its radioactivity is a major disadvantage when considering this alloy for normal commercial applications. Certain Rare Earth elements, Ce, Y and Lu have also been investigated, and Ce has been found promote similar

properties to Th, although less pronounced. ORNL have developed a new alloy range based on Ir-0.3W with low levels of Ce + Th.

US 3,918,965 describes a binary alloy of iridium with 0.3 to 1 wt% hafnium.

5 Improvements in physical properties are claimed.

Work has been limited in respect of alloying iridium with platinum group metals (PGM). Rhodium additions, up to a maximum of ca. 10wt%, have been shown to improve oxidation resistance, ductility and formability. Application of 40%Rh-Ir to novel rocket nozzles was reported in the early 1990's. Ternary alloys have also been long considered for pen nibs, and electrodes. The advent of long life spark plugs has re-invigorated interest in the potential of iridium alloys. Rhodium additions have been found to be beneficial, with 40wt% being best for oxidation resistance. Additions of 10wt% of both platinum and palladium also improve the oxidation resistance of iridium, although not as effectively as rhodium. Al, Si, Cr, Mo and W were found to be ineffective.

EP0866530 A1 discloses ternary and quaternary alloys of iridium, rhodium and at least one of rhenium and ruthenium. Low levels of Re and Ru, either singly or combined, significantly reduce the oxidation loss of an alloy at 1100°C for 30hours, compared to pure iridium. The presence of rhodium is essential, as Re and Ru have little or no effect when combined with iridium alone.

JP 2000290739 A discloses an alloy for the formation of crucibles which can be used at high temperatures without significant deformation or oxidation. The alloy is a binary or ternary alloy of iridium with 0.5-40wt% of Rh and/or Pt.

JP 10259435 A discloses a heat resistant iridium alloy which comprises a base of iridium to which 0.1 to 50wt% of one or more secondary elements is added. Platinum, palladium, rhodium, niobium, tantalum, hafnium, titanium, zirconium, yttrium and lanthanum are suggested as secondary elements however actual examples of only some of these are given, none of which contain secondary elements at less than 1wt%.

US 3,070,450 discloses alloys formed from a base of pure iridium or iridium-0.3wt%W, to which small amounts each of aluminium, iron, nickel, rhodium and thorium are added. The alloys are useful for the encapsulation of radioactive sources so the use of thorium can be tolerated. Thorium containing alloys are not usually suitable
5 for general application.

US 3,293,031 discloses a ductile ternary iridium alloy containing up to 0.5wt% of both titanium and zirconium.

10 Although prior attempts to improve the physical and mechanical properties of iridium by alloying have met with some success, there remains a need for further improvements.

In accordance with the present invention, an iridium alloy consists essentially of
15 iridium, at least one of W and Zr and optionally Rh; wherein when present, W comprises between 0.01 and 5 wt% of the alloy; wherein when present in combination with W, Zr comprises between 0.01 and 0.5 wt% of the alloy; wherein when present alone or in combination with Rh only, Zr comprises between 0.01 and 0.09 wt% of the alloy; and wherein when present, Rh comprises between 0.1 and 5 wt% of the alloy.

20 Preferably, when present, W comprises between 0.01 and 0.5 wt% of the alloy; when present in combination with W, Zr comprises between 0.01 and 0.5 wt% of the alloy; and when present alone or in combination with Rh only, Zr comprises between 0.02 and 0.07 wt% of the alloy.

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

30 The alloys of the present invention show enhanced physical and mechanical properties over pure iridium.

The alloy of the present invention may be modified by the addition of Pt in an amount of between 0.1 and 5 wt% of the alloy.

5 Additionally or alternatively, the alloy of the present invention may be modified by the addition of one or more of Ta, Nb, Mo, Cr, Ce, Sc, Lu, Co, Ni, Hf, Y, Ti, Ru and Pd individually in an amount of between 0.01 and 10 wt% of the alloy.

10 Preferably, when present, Ta, Nb, Mo, Cr, Ce, Sc, Lu, Co, Ni, Hf, Y and Ti individually comprise between 0.01 and 0.5 wt% of the alloy; and when present, Ru and Pd individually comprise between 0.1 and 5 wt% of the alloy.

In a preferred embodiment, the alloy consists essentially of iridium, W and Zr.

15 In a further preferred embodiment, the alloy consists essentially of iridium and W.

In a yet further preferred embodiment, the alloy consists essentially of iridium and Zr.

20 In measurements of stress rupture times at elevated temperatures, these alloys may outperform pure iridium by a factor of twenty or more. Creep rates at high temperature are also significantly reduced. Furthermore, W and Zr may also retard grain growth at high temperature, with small additions of both W and Zr being found to reduce the rate of grain growth at high temperature by a factor of two compared to pure iridium.

25 In a yet further preferred embodiment, the alloy consists essentially of iridium, Rh, W, and Zr.

30 In a yet further preferred embodiment, the alloy consists essentially of iridium, Pt, Rh, W and Zr.

Significant reduction in weight loss under high temperature oxidising conditions is found for these alloys, when compared to pure iridium.

In a yet further preferred embodiment, the alloy consists essentially of iridium,
5 Rh and W.

In a yet further preferred embodiment, the alloy consists essentially of iridium,
Rh and Zr.

10 In a yet further preferred embodiment, the alloy consists essentially of iridium,
Pt, Rh and W.

In a yet further preferred embodiment, the alloy consists essentially of iridium, Pt
and W. In tensile tests, these alloys demonstrate a considerable increase in elongation to
15 failure compared to pure iridium. In some cases, elongation to failure is increased
two-fold and more.

The enhanced physical and mechanical properties of the alloys of the present
invention make them suitable for use in many high temperature or load bearing
20 applications. For example, they may be used in ignition applications i.e. as components
in spark-plugs or as crucibles, e.g. for crystal growing or other equipment in chemical
and glass applications where high strength, low creep rate and good oxidation resistance
are required. Other applications include electrodes, heat shields and rocket nozzles.
The foregoing examples merely serve to illustrate the many potential uses of the present
25 alloys, and as such, are not intended to be limiting in any way.

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

The invention will now be described by way of example only and with reference to the following drawings in which;

Figure 1 is a bar chart comparing the mean elongation at room temperature of an alloy according to the present invention with pure iridium;

Figure 2 is a bar chart comparing the stress rupture time at elevated temperature of four alloys according to the present invention with pure iridium;

Figure 3 is a bar chart comparing the rate of grain growth at elevated temperature of four alloys according to the present invention with pure iridium;

Figure 4 is a graph comparing the measured weight loss of two alloys according to the present invention with pure iridium, and;

Figure 5 is a bar chart comparing the oxidation rate at two temperatures of several alloys according to the present invention with commercial iridium alloys.

EXAMPLE 1

Alloy Preparation

The alloys detailed in table 1 below were prepared by argon arc melting. All values are given in weight percent based on the total weight of the alloy. Balance in all cases is iridium.

Table 1.

Alloy	W	Zr	Rh	Pt	Other
1	0.3	-	-	0.2	-
2	-	0.07	-	-	-
3	0.3	0.02	-	-	-
4	0.05	-	-	-	-
5	0.02	0.02	-	-	-
6	0.3	0.07	2.5	-	-
7	0.3	0.07	2.5	2.5	-
8	0.3	-	2.5	2.5	-
9	0.5	-	1.0	-	-
10	0.3	-	1.0	1.0	-
11	0.3	-	1.0	5.0	-
12	1.0	-	1.0	-	-
13	2.0	-	2.5	-	-
14	0.5	-	2.5	-	-
15	-	0.07	2.5	-	-
16	0.3	-	-	-	-
17	-	-	2.5	-	Ta (0.5)
18	-	-	2.5	-	Nb (0.25)
19	-	-	2.5	-	Mo (0.25)
20	-	-	2.5	-	Cr (0.15)
21	-	-	2.5	-	Pd (0.3)
22	0.05	-	-	5.0	-
23	0.05	-	0.5	5.0	-
24	0.3	-	5.0	1.0	-

EXAMPLE 2**Elongation to Failure**

Alloy 1 was hot drawn into wires of 1.8mm diameter, and subjected to tensile testing with a gauge length of 51mm and a cross head speed of 5mm/minute. The result is shown in Fig. 1. Addition of Pt and W at the ppm level significantly improved the room temperature mechanical properties of the alloy. Although ultimate tensile strength was found to only be improved marginally, elongation to failure increased by 117% relative to similar wires of pure iridium.

10

EXAMPLE 3.**Stress Rupture**

Alloys 2-5 were hot rolled into sheets and tensile sample blanks formed by spark erosion machining. These were then surface ground to a thickness of nominally 1.8mm. The gauge length of each sample blanks was 30mm. Stress rupture times were measured at a temperature of 1400°C and stress of 75MPa. Results are shown in Fig. 2. Significant improvements in stress rupture times were found for all alloys compared to pure iridium, with ppm levels of Zr (alloy 2) or Zr and W (alloy 5) being most effective. Although not shown in Fig.2, creep rates at elevated temperature were also reduced, in some cases by as much as a factor of 16 compared to pure iridium.

15
20**EXAMPLE 4.****Grain Growth Retardation.**

Alloys 2-5 as detailed in table 1 above, were hot rolled into sheet of nominally 3.5mm thickness . The alloys were held at 1550°C for 400 hours and grain size measurements made. This was done using an optical microscope. The number of grains intersecting a line traversing the polished and etched section were counted and averaged over the cross sectional thickness. Results are shown in Fig. 3. Grain growth was reduced for all alloys compared to pure iridium, with ppm levels of Zr and W (alloy 5) showing a halving of grain size.

25
30

EXAMPLE 5.**Oxidation Weight Loss**

Alloys 6 and 7, as detailed in table 1 above, were hot drawn into wires of
5 between 0.6 and 1.2mm and their weights monitored while being held at 1000°C for
200 hours. Results are shown in Fig. 4. The weight loss of both alloys was
approximately 4 times less than that for pure iridium, over the duration of the test, and
approached that which was found for a commercial 10wt%Rh-Ir alloy.

10 Further oxidation weight loss experiments were carried out using wires of
different thicknesses formed from alloys according to the present invention. Fig. 5 shows
the weight loss rates of alloys 1, 4, 5, 13, 14 and 15. The heavily shaded bars in Fig. 5
represent experiments carried out at 1000°C and the lighter shaded bars represent
experiments carried out at 1100°C. The figure in brackets refers to the thickness of the
15 wire in mm. Oxidation rate is expressed in g/mm.hour. All alloys showed a significant
reduction in oxidation rate compared to a 5%Pt-Ir alloy.

EXAMPLE 6.**Engine Tests**

20 Alloys 6 and 7, as detailed in table 1 above, were formed into spark plug
electrodes. During testing in a high performance car engine over a period of 175 hours,
the electrodes were found to erode at a similar rate to commercial 10wt%Rh-Ir alloy
25 electrodes, and at a much reduced rate compared to pure iridium electrodes.

CLAIMS

1. An iridium alloy, the alloy consisting essentially of iridium, at least one of W and Zr and optionally Rh; wherein when present, W comprises between 0.01 and 5 wt% of the alloy; wherein when present in combination with W, Zr comprises between 0.01 and 0.5 wt% of the alloy; wherein when present alone or in combination with Rh only, Zr comprises between 0.01 and 0.09 wt% of the alloy; and wherein when present, Rh comprises between 0.1 and 5 wt% of the alloy.
2. An alloy according to claim 1, wherein when present, W comprises between 0.01 and 0.5 wt% of the alloy; wherein when present in combination with W, Zr comprises between 0.01 and 0.5 wt% of the alloy; wherein when present alone or in combination with Rh only, Zr comprises between 0.02 and 0.07 wt% of the alloy; and wherein when present, Rh comprises between 0.1 and 5 wt% of the alloy.
3. An iridium alloy, the alloy consisting essentially of an alloy according to claim 1 or claim 2, modified by the addition of Pt in an amount of between 0.1 and 5 wt% of the alloy.
4. An iridium alloy, the alloy consisting essentially of an alloy according to any of claims 1 to 3, modified by the addition of one or more of Ta, Nb, Mo, Cr, Ce, Sc, Lu, Co, Ni, Hf, Y, Ti, Ru and Pd individually in an amount of between 0.01 and 10 wt% of the alloy.
5. An alloy according to claim 4, wherein when present, Ta, Nb, Mo, Cr, Ce, Sc, Lu, Co, Ni, Hf, Y and Ti individually comprise between 0.01 and 0.5 wt% of the alloy; and wherein when present, Ru and Pd individually comprise between 0.1 and 5 wt% of the alloy.
6. An alloy according to claim 1 or claim 2, the alloy consisting essentially of iridium, W and Zr.

7. An alloy according to claim 1 or claim 2, the alloy consisting essentially of iridium and W.
8. An alloy according to claim 1 or claim 2, the alloy consisting essentially of
5 iridium and Zr.
9. An alloy according to claim 1 or claim 2, the alloy consisting essentially of iridium, Rh, W, and Zr.
- 10 10. An alloy according to claim 3, the alloy consisting essentially of iridium, Pt, Rh, W and Zr.
11. An alloy according to claim 1 or claim 2, the alloy consisting essentially of iridium, Rh and W.
15
12. An alloy according to claim 1 or claim 2, the alloy consisting essentially of iridium, Rh and Zr.
13. An alloy according to claim 3, the alloy consisting essentially of iridium, Pt, Rh
20 and W.
14. An alloy according to claim 3, the alloy consisting essentially of iridium, Pt and W.
- 25 15. An iridium alloy, the alloy consisting essentially of iridium, Rh and at least one of Ta, Nb, Mo, Cr and Pd; wherein Rh comprises between 0.1 and 5 wt% of the alloy; and wherein Ta, Nb, Mo, Cr and Pd individually comprise between 0.1 and 10 wt% of the alloy.
- 30 16. An electrode comprising an alloy according to any preceding claim.
17. A spark plug comprising an electrode according to claim 16.

18. The use of an alloy according to any of claims 1 to 15 in a high temperature application.

19. The use of an alloy according to any of claims 1 to 15 in a load bearing
5 application.

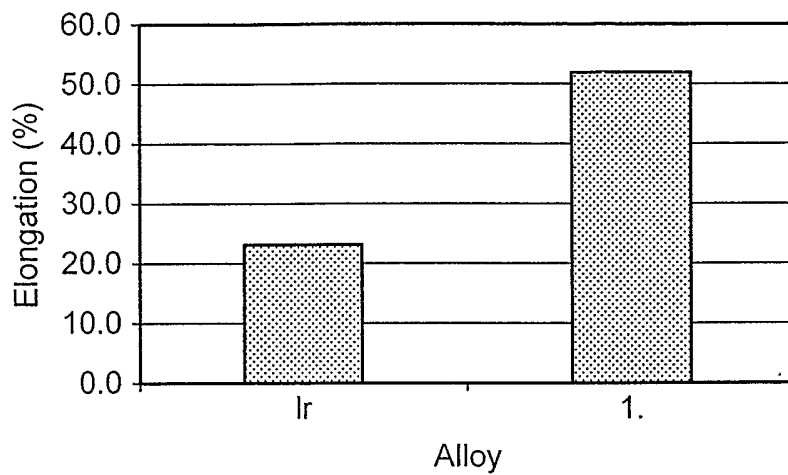


FIG. 1

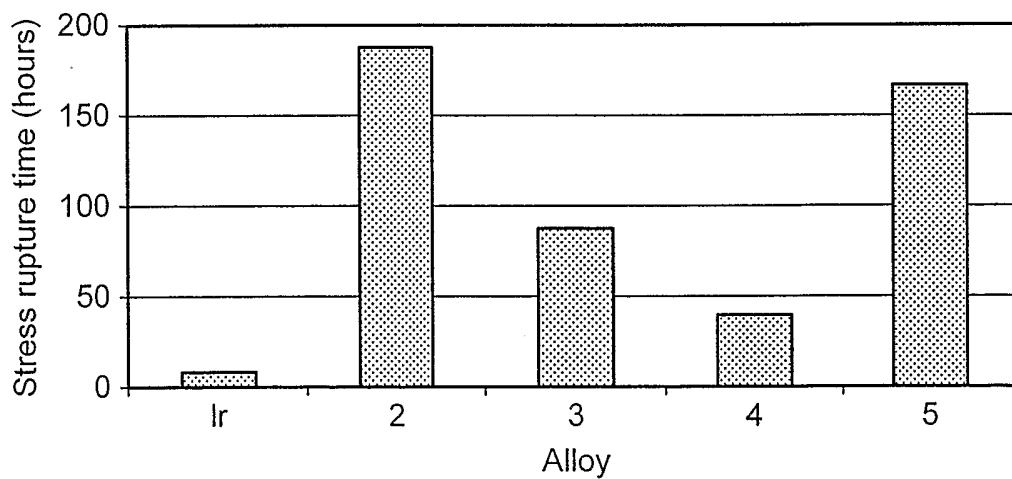


FIG. 2

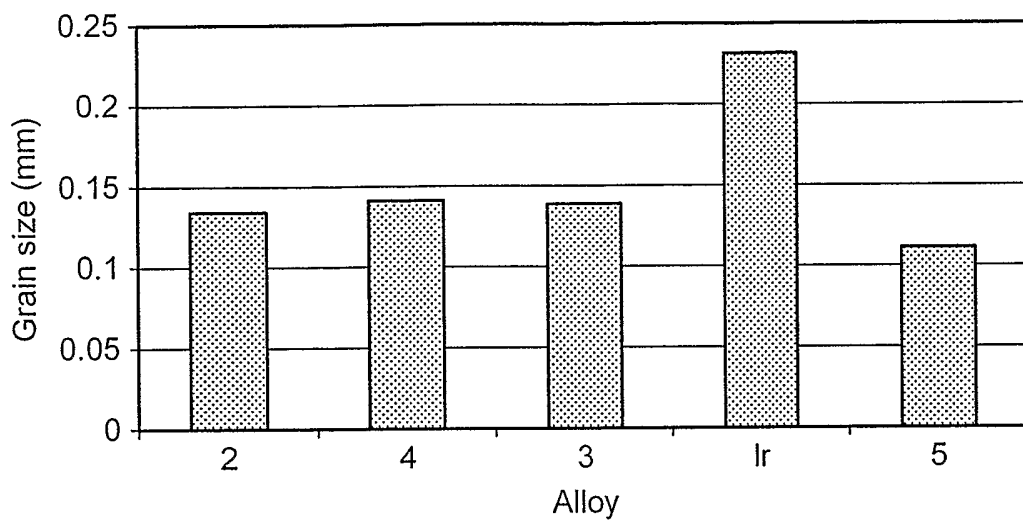


FIG. 3

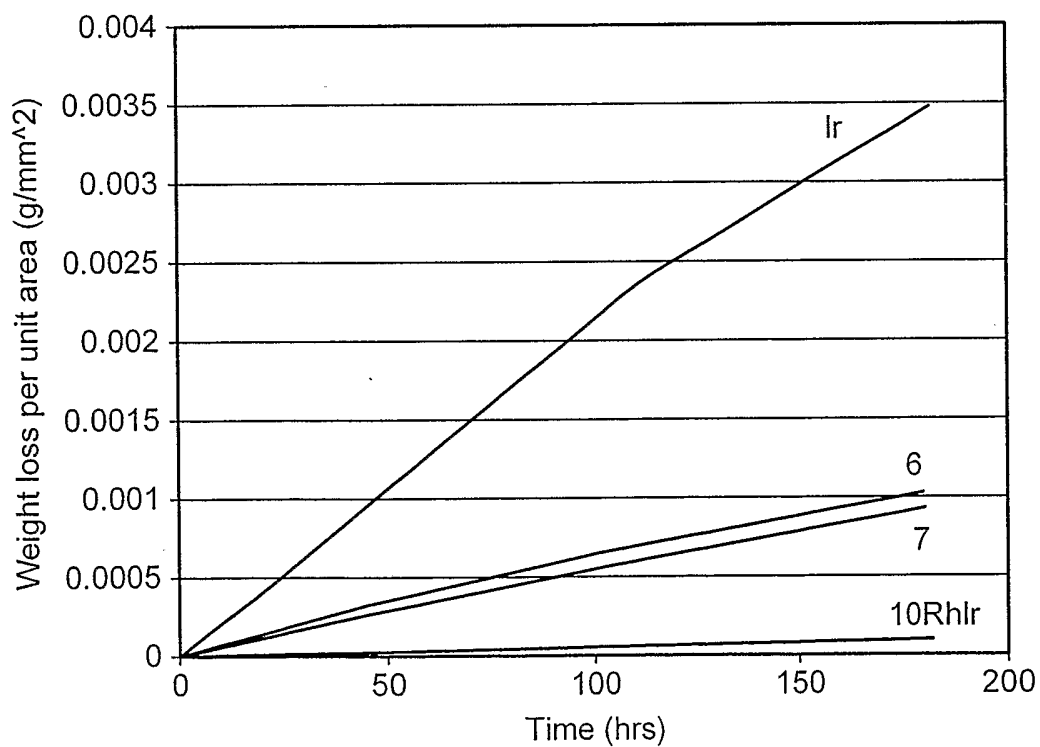


FIG. 4

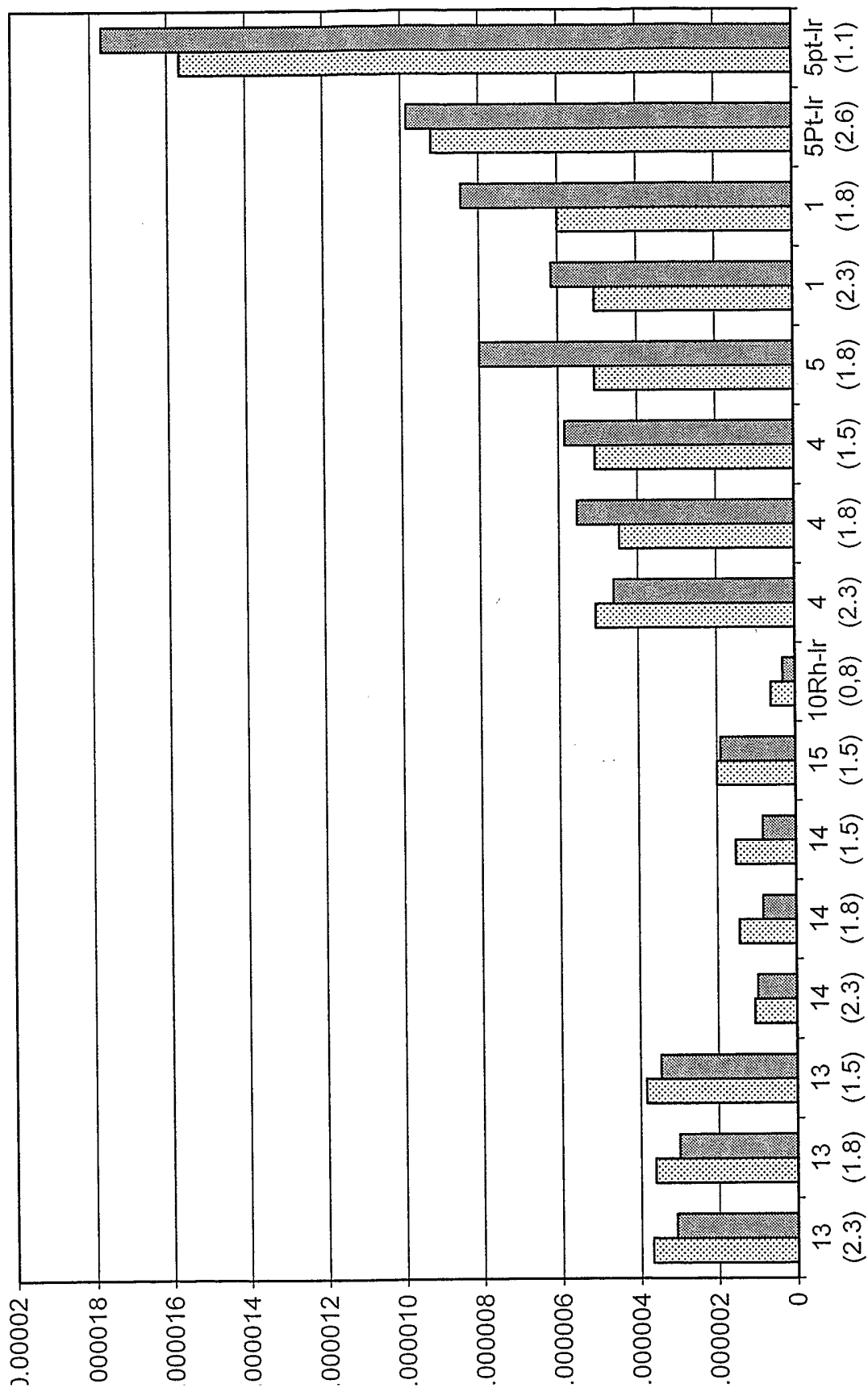


FIG. 5

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 03/03037

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C22C5/00 C22C5/04

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)

IPC 7 C22C

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 practical, search terms used)

EPO-Internal, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 262 779 A (DEZSO ROMHANYI LASZLO ET AL) 26 July 1966 (1966-07-26) claim 1 ---	1-19
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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 03/03037

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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