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(54) **Novel rhodium based amorphous metal alloys and use thereof as halogen electrodes.**

(57) Novel rhodium based amorphous metal alloys
having the formula Rh_rA_a where:

A is B, P, As and mixtures thereof;

r is from about 50 to 96 percent; and

a is from about 4 to 50 percent.

Novel rhodium based amorphous metal alloys are
also based on the formula $Rh_rB_bD_d$ where:

D is Ir, Pd, Ru, Ti, Zr, Nb, Ta, Y, Hf and mixtures
thereof;

r is from about 50 to 96 percent;

b is from about 4 to 50 percent; and

d is from about 0 to 60 percent; and

$$r + b + d = 100.$$

Novel process for the generation of halogens from
halide-containing solutions can be performed by em-
ploying the rhodium based metal alloys of the
present invention.

EP 0 209 264 A1

NOVEL RHODIUM BASED AMORPHOUS METAL ALLOYS AND USE THEREOF AS HALOGEN ELECTRODES

TECHNICAL FIELD

The present invention is directed toward novel amorphous metal alloys which can be considered metallic and are electrically conductive. Amorphous metal alloy materials have become of interest in recent years due to their unique combinations of mechanical, chemical and electrical properties which are specially well suited for newly emerging applications. Amorphous metal materials have compositionally variable properties, high hardness and strength, flexibility, soft magnetic and ferroelectric properties, very high resistance to corrosion and wear, unusual alloy compositions, and high resistance to radiation damage. These characteristics are desirable for applications such as low temperature welding alloys, magnetic bubble memories, high field superconducting devices and soft magnetic materials for power transformer cores.

Given their resistance to corrosion, the amorphous metal alloys of the present invention are particularly useful as electrodes in halogen evolution processes, as set forth in our copending application, U.S. Ser. No. 705,687. Other uses as electrodes include the production of fluorine, chlorate, perchlorate, and electrochemical fluorination of organic compounds. These alloys can also be employed as hydrogen permeable membranes.

BACKGROUND ART

The unique combination of properties possessed by amorphous metal alloy materials may be attributed to the disordered atomic structure of amorphous materials which ensures that the material is chemically homogeneous and free from the extended defects that are known to limit the performance of crystalline materials.

Generally, amorphous materials are formed by rapidly cooling the material from a molten state. Such cooling occurs at rates on the order of 10^6 °C/second. Processes that provide such cooling rates include sputtering, vacuum evaporation, plasma spraying and direct quenching from the liquid state. Direct quenching from the liquid state has found the greatest commercial success inasmuch as a variety of alloys are known that can be manufactured by this technique in various forms such as thin films, ribbons and wires.

U.S. Pat. No. 3,856,513 describes novel metal alloy compositions obtained by direct quenching from the melt and includes a general discussion of this process. The patent describes magnetic amorphous metal alloys formed by subjecting the alloy

composition to rapid cooling from a temperature above its melting temperature. A stream of the molten metal was directed into the nip of rotating double rolls maintained at room temperature. The quenched metal, obtained in the form of a ribbon, was substantially amorphous as indicated by X-ray diffraction measurements, was ductile, and had a tensile strength of about 350,000 psi (2415 MPa).

U.S. Pat. No. 4,036,638 describes binary amorphous alloys of iron or cobalt and boron. The claimed amorphous alloys were formed by a vacuum melt-casting process wherein molten alloy was ejected through an orifice and against a rotating cylinder in a partial vacuum of about 100 millitorr. Such amorphous alloys were obtained as continuous ribbons and all exhibited high mechanical hardness and ductility.

The amorphous metal alloys described hereinabove have not been suggested for usage as electrodes in electrolytic processes in distinction from the alloys utilized for practice of the present invention. With respect to processes for chlorine evolution from sodium chloride solutions, certain palladium-phosphorus based metal alloys have been prepared and described in U.S. Pat. No. 4,339,270 which discloses a variety of ternary amorphous metal alloys consisting of 10 to 40 atomic percent phosphorus and/or silicon and 90 to 60 atomic percent of two or more of palladium, rhodium and platinum. Additional elements that can be present include titanium, zirconium, niobium, tantalum and/or iridium. The alloys can be used as electrodes for electrolysis and the patent reports high corrosion resistance in the electrolysis of halide solutions.

The anodic characteristics of these alloys have been studied by three of the patentees, M. Hara, K. Hashimoto and T. Masumoto and reported in various journals. One such publication entitled "The Anodic Polarization Behavior of Amorphous Pd-Ti-P Alloys in NaCl Solution" *Electrochimica Acta*, **25**, pp. 1215-1220 (1980) describes the reaction of palladium chips and phosphorus at elevated temperatures to form palladium phosphide which is then melted with titanium. The resulting alloy was then formed into ribbons 10 to 30 microns in thickness by the rotating wheel method.

"Anodic Characteristics of Amorphous Ternary Palladium-Phosphorus Alloys Containing Ruthenium, Rhodium, Iridium, or Platinum in a Hot Concentrated Sodium Chloride Solution", reported in the *Journal of Applied Electrochemistry* **13**, pp. 295-306 (1983) describes the entitled alloys, again prepared by the rotating wheel method from the molten state. Palladium-silicon alloys were also

prepared and evaluated but were found to be unsatisfactory as anodes. The reported anode alloys were found to be more corrosion resistant and had a higher chlorine activity and lower oxygen activity than DSA.

Lastly, "Anodic Characteristics of Amorphous Palladium-Iridium-Phosphorus Alloys in a Hot Concentrated Sodium Chloride Solution" reported in Journal of Non-Crystalline Solids, 54, pp. 85-100 - (1983) describes such alloys also prepared by the rotating wheel method. Again, moderate corrosion resistance, high chlorine activity and low oxygen activity were reported.

The authors found that the electrocatalytic selectivity of these alloys was significantly higher than that of the known dimensionally stable anodes (DSA) consisting of an oxide mixture of ruthenium and titanium supported by metallic titanium. A disadvantage of DSA is that the electrolysis of sodium chloride is not entirely selective for chlorine and some oxygen is produced. The alloys reported were less active for oxygen evolution than DSA.

Dimensionally stable anodes are described in the following three early U.S. patents. U.S. Pat. No. 3,234,110 calls for an electrode comprising titanium or a titanium alloy core, coated at least partially with titanium oxide which coating is, in turn, provided with a noble metal coating such as platinum, rhodium, iridium and alloys thereof.

U.S. Pat. No. 3,236,756 discloses an electrode comprising a titanium core, a porous coating thereon of platinum and/or rhodium and a layer of titanium oxide on the core at the places where the coating is porous.

U.S. Pat. No. 3,771,385 is directed toward electrodes comprising a core of a film forming metal consisting of titanium, tantalum, zirconium, niobium and tungsten, carrying an outside layer of a metal oxide of at least one platinum metal from the group consisting of platinum, iridium, rhodium, palladium, ruthenium and osmium.

All three of these electrodes have utility in electrolytic processes although unlike the anodes of the present invention, none are amorphous. Thus, despite the state of the art in amorphous metal alloys, there has not been a teaching heretofore of the use of novel rhodium based amorphous metal alloys as anodes in halogen evolution processes. The specific alloys disclosed herein are extremely corrosion resistant and substantially 100 percent selective to chlorine.

SUMMARY OF THE INVENTION

The novel amorphous metal alloys of the present invention are based upon rhodium and have the following formulae:



where

A is B, P, As and mixtures thereof;

r is from about 50 to 96 percent;

a is from about 4 to 50 percent;



where

D is Ir, Pd, Ru, Ti, Zr, Nb, Ta, Y, Hf and mixtures thereof;

r is from about 50 to 96 percent;

b is from about 4 to 50 percent;

d is from about 0 to 60 percent;

and $r + b + d = 100$.

The foregoing novel amorphous metal alloys are employed as anodes in a process for the electrolysis of halide-containing electrolyte solutions. Such a process comprises the step of conducting electrolysis of the halide-containing solutions in an electrolytic cell having a rhodium based amorphous metal anode selected from the group consisting of Rh_rA_a and $\text{Rh}_r\text{B}_b\text{D}_d$ alloys

where A is B, P, As and mixtures thereof;

D is Ir, Pd, Ru, Ti, Zr, Nb, Ta, Y, Hf and mixtures thereof;

r is 50 to 96;

a is 4 to 50;

d is 0 to 60; and $r + b + d = 100$.

PREFERRED MODE FOR CARRYING OUT THE INVENTION

In accordance with the present invention, novel rhodium based amorphous metal alloys are provided having the formulae:



where

A is B, P, As and mixtures thereof;

r is from about 50 to 96 percent;

a is from about 4 to 50 percent;

$Rh_rB_bD_d$ II

where

D is Ir, Pd, Ru, Ti, Zr, Nb, Ta, Y, Hf and mixtures thereof;

r is from about 50 to 96 percent;

b is from about 4 to 50 percent;

e is from about 0 to 60 percent;

and $r + b + d = 100$.

The metal alloys can be binary or ternary, in the former instance certain ternary elements are optional. The use of the phrase "amorphous metal alloys" herein refers to amorphous metal-containing alloys that may also comprise one or more of the foregoing non-metallic elements. Amorphous metal alloys may thus include non-metallic elements such as boron, silicon, phosphorus, and carbon. Several preferred combinations of elements include Rh/P; Rh/B; Rh/As; Rh/P/B; Rh/B/Pd; Rh/B/Ru and Rh/B/Ti. The foregoing list is not to be construed as limiting but merely exemplary.

As part of this invention, it has been discovered that differences in the corrosion resistance and electro-chemical properties exist between the crystalline and amorphous phases of these alloys. For example, different overpotential characteristics for oxygen, chlorine and hydrogen evolution, differences in the underpotential electrochemical absorption of hydrogen and corrosion resistance under anodic bias, have all been observed and reported in the aforementioned copending applications.

Unlike existing amorphous metal alloys known in the art, the alloys of the present invention are not palladium based, although palladium can be present as a minor component. Moreover, being amorphous, the alloys are not restricted to a particular geometry, or to eutectic compositions.

The amorphous metal alloys of the present invention are novel in part because the relative amounts of the component elements are unique. Existing amorphous alloys have either not contained the identical elements or have not contained the same atomic percentages thereof. It is believed

that the electrochemical activity and corrosion resistance which characterize these alloys are attributable to the unique combination of elements and their respective amounts.

These alloys can be prepared by any of the standard techniques for fabricating amorphous metal alloys. Thus, any physical or chemical method, such as evaporation, chemical and/or physical decomposition, ion-cluster electron-beam or sputtering process can be utilized. The amorphous alloy can be either solid, powder or thin film form, either free standing or attached to a substrate. Trace impurities such as O, N, S, Se, Te and Ar are not expected to be seriously detrimental to the preparation and performance of the materials. The only restriction on the environment in which the materials are prepared or operated is that the temperature during both stages be lower than the crystallization temperature of the amorphous metal alloy.

The amorphous metal alloys of the present invention are particularly suitable as coatings on substrate metals which will ultimately be employed as anodes in various electrochemical processes for the generation of halogens. At least one preferred substrate for use as an electrode is titanium although other metals and various non-metals are also suitable depending upon intended uses. The substrate is useful primarily to provide support for the amorphous metal alloys and therefore can also be a non-conductor or semi-conductor material. The coating is readily deposited upon the substrate by sputtering, as is exemplified hereinbelow. Coating thicknesses are not crucial and may range broadly, for example, up to about 100 microns although other thicknesses are not necessarily precluded so long as they are practical for their intended use. A useful thickness, exemplified in the work hereinbelow, is 3000 Å.

As will be appreciated, the desired thickness is somewhat dependent upon the process of preparation of the electrode and somewhat upon the intended use. Thus, a free-standing or non-supported electrode, as prepared by liquid quenching, may have a thickness of approximately 100 microns. Or an amorphous alloy electrode can be prepared by pressing the amorphous alloy, in powder form, into a pre-determined shape and can also be thick enough to be free-standing. Where a sputtering process is employed, relatively thin layers can be deposited and these would be preferably supported by a suitable substrate, as noted hereinabove. Thus, it is to be understood that the actual electrode of the present invention is the amorphous metal alloy whether supported or unsupported. Where a very thin layer is employed, a support may be convenient or even necessary to provide integrity.

Irrespective of the use of the amorphous metal alloys, as a coating or a solid product, the alloys are substantially amorphous. The term "substantially" as used herein in reference to the amorphous metal alloy means that the metal alloys are at least fifty percent amorphous. Preferably the metal alloy is at least eighty percent amorphous and most preferably about one hundred percent amorphous, as indicated by X-ray diffraction analysis.

The present invention also provides a process for the generation of halogens from halide-containing solutions which employs the novel amorphous metal alloys described herein as anodes. One such process includes the step of conducting electrolysis of the halide-containing solutions in an electrolytic cell having a rhodium based amorphous metal anode selected from the group consisting of Rh_rA_a and $Rh_rB_bD_d$ alloys

where A is B, P, As and mixtures thereof;

D is Ir, Pd, Ru, Ti, Zr, Nb, Ta, Y, Hf and mixtures thereof;

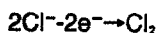
r is 50 to 96;

a is 4 to 50;

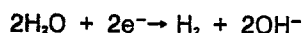
d is 0 to 60; and

$r + b + d = 100$.

A specific reaction that can occur at the anode in the process for chlorine evolution is as follows:



Similarly, at the cathode the corresponding reaction can be but is not necessarily limited to:



As stated hereinabove, the amorphous metal alloys employed herein are substantially 100 percent

selective to chlorine as compared to about 97 percent for DSA materials. This increased activity has two significant consequences. First, the chlorine evolution efficiency (per unit electrical energy input) is almost 100 percent, an improvement of about 3 percent or better. Second, separation steps may be obviated due to the negligible oxygen content.

As will be appreciated by those skilled in the art a wide variety of halide-containing solutions can be substituted for sodium chloride such as, for instance, potassium chloride, lithium chloride, cesium chloride, hydrogen chloride, iron chloride, zinc chloride, copper chloride and the like. Products in addition to chlorine can also include, for instance, chlorates, perchlorates and other chlorine oxides. Similarly, other halides can be present, in lieu of chlorides, and thus, other products generated. The present invention is, therefore, not limited by use in any specific halide-containing solution.

The process of electrolysis can be conducted at standard conditions known to those skilled in the art. These include temperatures between about 0° to 100° C with about 60° to 90° C being preferred; voltages in the range of from about 1.10 to 1.70 and, current densities of from about 10 to 1000 mA/cm². Electrolyte solutions (aqueous) are generally at a pH of 1 to 6 and molar concentrations of from about 0.5 to 4M. The cell configuration is not crucial to practice of the process and therefore is not a limitation of the present invention.

In the examples which follow, six rhodium based amorphous metal alloys were prepared via radio frequency sputtering in argon gas. A 2" Research S-Gun, manufactured by Sputtered Films, Inc. was employed. As is known, DC sputtering can also be employed. For each of the examples, a titanium substrate was positioned to receive the deposition of the sputtered amorphous alloy. The distance between the target and the substrate in each instance was approximately 10 cm. The composition of each alloy was verified by X-ray analysis and was amorphous thereto.

TABLE I
Amorphous Metal Alloy Halogen Electrodes

<u>Example No.</u>	<u>Alloy</u>
1	Rh ₇₅ B ₂₅
2	Rh ₇₀ B ₂₀ P ₁₀
3	Rh ₄₀ B ₂₀ Pd ₄₀
4	Rh ₃₅ B ₃₀ Pd ₃₅
5	Rh ₄₀ B ₃₀ Ru ₃₀
6	Rh ₆₀ B ₂₀ Ti ₂₀

The six alloys reported in Table I were each separately employed in a 4M NaCl solution for the evolution of chlorine when an anodic bias was applied in the solution. Voltages were recorded and corrosion rates for each alloy were determined and are presented in Table II, hereinbelow.

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TABLE II
Rhodium Based Electrodes for
the Generation of Chlorine

<u>Ex. No.</u>	<u>Voltage (SCE)</u> <u>at 200 mA/cm²</u>	<u>Corrosion Rate</u> <u>(μm/year)</u>
1	1.21	0.04
2	1.21	0.06
3	1.24	4.72
4	1.18	8.76
5	1.24	7.64
6	1.26	0.07

In order to demonstrate the superior corrosion resistance exhibited by the alloy anodes of the present invention, corrosion rates were determined for five different anodes for comparison. The anodes compared included: palladium; an amorphous Pd/Si alloy and an amorphous Pd/Ir/Rh/P alloy, both reported by Hara, et al, a DSA reported by

45

Novak, et al and an amorphous Pd/Ir/Ti/P alloy reported by Hara, et al but prepared by the manner set forth hereinabove. Respective corrosion rates of these anodes at 1000 A/m² in 4M NaCl at 80° C and pH 4 were measured and are presented in Table III, hereinbelow.

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Table III
Corrosion Rates

<u>Anode Material</u>	<u>Corrosion rate</u> <u>μm/year</u>
Pd	>100,000
a-Pd ₍₈₀₎ Si ₍₂₀₎ ^a	>100,000
a-Pd ₍₄₁₎ Ir ₍₃₀₎ Rh ₍₁₀₎ P ₍₁₉₎ ^b	4
DSA ^c	0.31
a-Pd ₍₄₀₎ Ir ₍₃₀₎ Ti ₍₁₀₎ P ₍₂₀₎ ^d	12.4

a) Hara, et al, Journal of Applied Electrochemistry, 13, p. 295 (1983).

b) Hara, et al, Journal of Non-Crystalline Solids, 54, pp. 85 (1983).

c) D. Novak, B. Tilak, B. Conway, Modern Aspects of Electrochemistry, Chapt. 4 (1983).

d) Sputtered 2000 Å film.

The data reported for the a-Pd₍₈₀₎Si₍₂₀₎ anode was estimated from polarization data given relative to Pd. The a-Pd₍₄₁₎Ir₍₃₀₎Rh₍₁₀₎P₍₁₉₎ anode was the most corrosion resistant material as reported in the Journal of Non-Crystalline Solids. As can be seen from Tables II and III, three of the amorphous metal alloy anodes of this invention were found to possess significantly better corrosion rates than any of the known anode materials.

Thus, the foregoing examples demonstrate the composition and use of novel rhodium based amorphous metal alloys. As noted hereinabove and demonstrated, the amorphous alloys of the present invention have utility as electrodes in various electrochemical processes. The superior resistance of other amorphous alloys to corrosion when so employed, has been demonstrated in aforementioned copending patent application, U.S. Ser. No. 705,687, the subject matter of which is incorporated herein by reference. From this it can be extrapolated that electrodes comprising amorphous alloys of the present invention will also be highly resistant to corrosion in electrolytic processes.

Although the alloys of this invention were prepared by a sputtering technique which is a useful means for depositing the alloy onto a metal substrate such as titanium, it is to be understood that neither the process of sputtering nor the coating of substrates are to be construed as limitations of the present invention, inasmuch as the alloys can be

prepared by other processes and have other forms. Similarly, the composition of the amorphous metal alloys of the present invention can be varied within the scope of the total specification disclosure and therefore neither the particular components nor the relative amounts thereof in the alloys exemplified herein shall be construed as limitations of the invention.

Furthermore, while one of the amorphous metal anodes exemplified herein have been utilized in conjunction with the evolution of chlorine gas from sodium chloride solutions such as brine and sea water, it will readily be appreciated by those skilled in the art that other chlorine containing compounds could also be produced via known electrolysis techniques by substituting the amorphous metal anodes of the present invention for the conventional DSA materials of other electrodes. Similarly, other halide-containing electrolyte solutions could be substituted for the sodium chloride reported herein with a variety of products being obtained. Moreover, these anodes could find utility in any other conventional electrolytic cell.

Thus, it is believed that any of the variables disclosed herein can readily be determined and controlled without departing from the spirit of the invention herein disclosed and described. Moreover, the scope of the invention shall include all modifications and variations that fall within the scope of the attached claims and is not to be

limited by the examples and related data set forth herein. These have been provided merely to demonstrate the preparation and amorphous nature of the alloys.

Claims

1. An anode comprising a substrate material and a rhodium based amorphous metal alloy coating on said substrate having the formula Rh_rA_a where:

A is B, P, As and mixtures thereof;

r is from about 50 to 96 percent; and

a is from about 4 to 50 percent; and

$r + a = 100$;

said anode having a corrosive rate of less than 10 microns per year.

2. An anode comprising a substrate material and a rhodium based amorphous metal alloy coating on said substrate having the formula $Rh_rB_bD_d$ where:

D is Ir, Pd, Ru, Ti, Zr, Nb, Ta, Y, Hf and mixtures thereof;

r is from about 50 to 96 percent;

b is from about 4 to 50 percent; and

d is from about 0 to 60 percent; and

$r + b + d = 100$;

said anode having a corrosion rate of less than 10 microns/year.

3. An anode as claimed in claim 1 or claim 2 characterised in that said amorphous metal alloy is about 100 percent amorphous.

4. An anode as claimed in any of claims 1 to 3 characterised in that said substrate is titanium.

5. An anode as claimed in any of claims 1 to 4 characterised in that the thickness of said amorphous metal alloy deposited on said substrate is about 3000 Å.

6. A process for the generation of halogens from halide-containing solutions comprising the step of: conducting electrolysis of said solutions in an electrolytic cell having a rhodium based amorphous metal anode selected from the group consisting of Rh_rA_a and $Rh_rB_bD_d$ alloys where:

A is B, P, As and mixtures thereof;

D is Ir, Pd, Ru, Ti, Zr, Nb, Ta, Y, Hf and mixtures thereof;

r is 50 to 96;

a is 4 to 50;

b is 4 to 50;

d is 0 to 60; and with the provisos that $r + a = 100$ and $r + b + d = 100$;

said anode having a corrosion rate of less than 10 microns/year.

7. A rhodium based amorphous metal alloy anode, as set forth in claim 6, wherein said amorphous metal alloy is about 100 percent amorphous.

8. A rhodium based amorphous metal alloy anode, as set forth in claim 6, wherein said halide is chloride.

9. A rhodium based amorphous metal alloy anode, as set forth in claim 8, which produces products selected from the group consisting of chlorine, chlorates, perchlorates and other chlorine oxides upon electrolysis of said chloride-containing solutions therewith.

10. A rhodium based amorphous metal alloy anode, as set forth in claim 6, wherein said halide-containing solution comprises sodium chloride solutions.

11. A rhodium based amorphous metal alloy anode, as set forth in claim 10, wherein chlorine is generated at said anode substantially free of oxygen.

12. Amorphous metal alloys as set forth in claim 9.

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DOCUMENTS CONSIDERED TO BE RELEVANT			EP 86304802.1
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	GB - A - 2 146 660 (DAIKI ENGINEERING) * Abstract *	1,2,6, 8,9,12	C 25 B 11/08 C 25 B 1/24 C 25 B 1/26 C 22 B 5/04
A	CHEMICAL ABSTRACTS, vol. 96, no. 12, March 22, 1982, Columbus, Ohio, USA TOYO SODA MFG. CO.: "Amorphous platinum metal alloys as electrodes for aqueous alkali chloride electrolysis" page 582, column 1, abstract-no. 94 052a & JP-A-81 150 148 (20-11-1981)	1,6,7, 8,9,10, 12	
D,A	US - A - 4 339 270 (HASHIMOTO et al.) * Column 1, line 45 - column 2, line 2 *	1,6,7, 8,10,12	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
D,A, P	US - A - 4 560 454 (HARRIS et al.) * Abstract *	1,6,7, 8,10,12	C 25 B C 22 B
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 29-09-1986	Examiner LUX
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			