

Micro-Nano Particle Manufacturing Processes

TECHNICAL AREA:

A metal alloy composite particle that reversibly react with gaseous hydrogen and/or its isotopes by absorption and desorption.

BACKGROUND:

A gas-loaded heat generator capable of producing a thermal energy by interaction between one or more isotopes of hydrogen and a plurality of metallic micro-structures is reported. The metallic micro-structure as a plurality of micro-nano particle could be a base for reversible reactions.

EXISTING TECHNOLOGIES:

Most of metallic materials that reversibly react with gaseous hydrogen and/or its isotopes are in alloys or intermetallic compounds, usually in a combination of metals with higher hydrogen affinity and with non-hydrogen affinity. These materials could be pulverized or filmed to maximize gas contact due to its increased surface area.

PROBLEMS WITH EXISTING TECHNOLOGIES:

The tailored metallic alloy or compounds absorb and desorb gaseous hydrogen and/or its isotopes into its lattice as a single atom and forms a beta phase hydride or deuteride therefore the whole bulk has a limited capacity of hydrogen and/or its isotopes.

SUMMARY OF THE PROPOSED SOLUTION AND THE ADVANTAGES THE PROPOSED SOLUTION IT PROVIDES:

The proposed method is to produce a composite material of alloys or intermetallic compounds as a form of micro-nano particle that provide not only a lattice substructure but also various types of defects including interstitial vacancies and dislocations where a multiplicity of hydrogen and/or its isotope

atoms could be formed as a dense cluster. These dense clusters could therefore increase the capacity for absorption and desorption. In order to create the interstitial vacancies a process of oxidation, cryogenic ball milling, and beta phase hydride formation is proposed.

DETAILED DESCRIPTIONS OF THE PROPOSED SOLUTION AND FIGURES:

1. Alloy preparation

In order to make the final product as a composite micro-nano particlematerial a single or multiple metals has to be chosen from a group of metal with hydrogen affinity additionally to it as a group of metal with or without hydrogen affinity for the purpose of cyclic absorption and desorption of hydrogen and/or its isotopes. This is alloyed with a second group of metals to be oxidized in the later part of process to form a matrix for the former metal group to be embedded.

The metals in group 1 to 5 in periodic table and the other metals and metalloids such as Al, Ga, In, Sc, Ti, Pb, Bi and B, Si, Ge, As, Sb, Te, Po and Pd and Ni are considered to be metals with hydrogen affinity and the metals in group 6 to 12 are metals without hydrogen affinity except Pd and Ni. The metals in the second group should form oxides that are more stable than those selected from the first group.

Once the choice of the metals are done for example Pd of 1 to 99 wt% as a hydrogen interaction element and Zr of 99 to 1 wt% as a matrix base for the Pd they are brought into the crucible and melted together using arc or induction heat heating. The materials are brought up to their melting point under inactive gas environment to prevent from the oxidation. In cases where the melting points of both metals have a considerable discrepancy: the metal with higher melting point has to be melted first. The other metal, with the with lower melting point, can be added to it in order to minimize the mass loss due to the evaporation of

the metal with lower melting point. The melted metal alloy or intermetallic compound has to be cooled under inert gas.

2. Pre-oxidation treatment

The products from the former process are assumed to be -metal ingots, rod, sponge, coarse powder, or other form factor of millimeter-scale or larger length scale. These must then be treated to acquire the extended surface area to provide maximized surface contact area with oxygen gas for the oxidation process. The following three standard methods can be applied for the purpose.

A. Inert gas atomization

The vacuum inert gas atomization *method* comprises a Vacuum Induction Melting furnace where the alloys are melted, refined and degassed. The refined melt is poured through a preheated tundish system into a gas nozzle where the melt stream is disintegrated by the kinetic energy of a high pressure inert gas stream. The *produced* metal powder produced solidifies in flight in the atomization tower located directly underneath the atomization nozzle. The powder gas mixture is transported via a conveying tube to the cyclone where the coarse and the fine powder fractions are separated from the atomization gas. The metal powder is collected in sealed containers which are located directly below the cyclones.

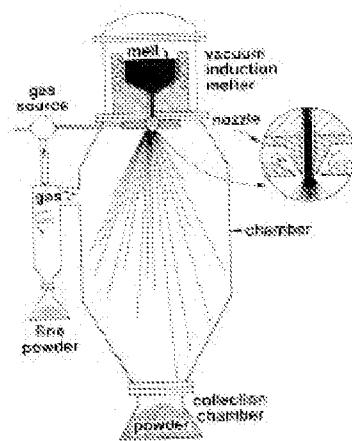


Fig 1. Gas atomization

B. Melt-spun ribbon manufacturing

A wheel is cooled internally, usually by water or *liquid nitrogen*, and rotated. A thin stream of *melted alloy* is then dripped onto the wheel and cooled, causing rapid solidification *which produces a metal ribbon*.

Originating with Robert Pond in a series of related patents from 1958-1961 (US Patent Nos. 2825108, 2910744, and 2976590), the current concept of the melt spinner was outlined by Pond and Maddin in 1969, though, at first, liquid was quenched on the inner surface of a drum. Liebermann and Graham further developed the process as a continuous casting technique by 1976, this time on the drum's outer surface. The process can continuously produce thin ribbons of material, with sheets several inches in width commercially available. This process has gained wide acceptance as a means of producing amorphous and nano-crystalline materials

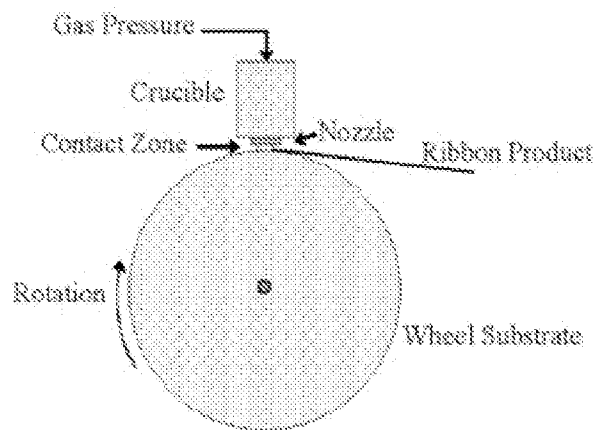


Fig 2. Schematic of melt spinning apparatus

C. Ball milling

A *high-energy ball milling*, a type of grinder, is a cylindrical device used in grinding (or mixing) materials like ores, chemicals, ceramic raw

materials and paints. Ball mills rotate around a horizontal axis, partially filled with the material to be ground plus the grinding medium (a sphere [ball] composed of a material of superior mechanical and tribological properties as compared to the milled material). A ball mill works on the principle of impact and attrition: size reduction is done by impact as the balls drop from near the top of the shell.

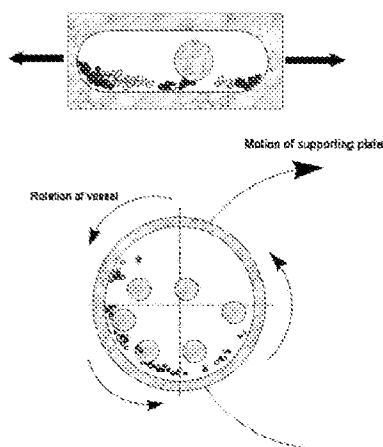


Fig 3. Ball milling schematic

3. Oxidation

Product from 2 should either be completely oxidized (both metals from 1 have shown full mass gain from oxidation) or they should be partially oxidized – only the second, more stable metal has been oxidized and the metal selected for hydrogen affinity remains unoxidized.

A. Full oxidation

Product from 2 will be heated under an atmosphere containing oxygen until a stable oxide is formed for both metal groups selected from 1.

B. Selective oxidation

Product from 2 will be heated under an atmosphere containing oxygen until a stable oxide is formed in the second group from 1 but leaves the first group from 1 (the group selected for hydrogen affinity) unoxidized and pristine. The processing conditions related to the level of thermal

energy input (heating) and oxygen partial pressure during the selective oxidation process is related to the Ellingham diagrams of metals as shown below.

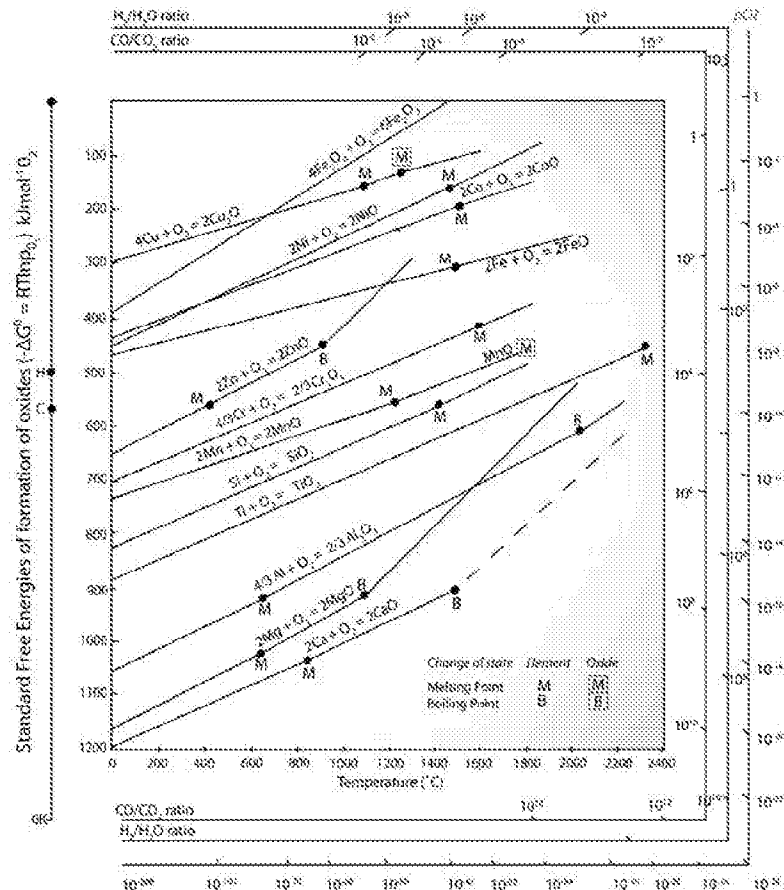


Fig 4. The Ellingham Diagram of various metal oxides

As an example of the selective oxidation, Pd and Zr are selected and for example when the PdZr alloy is heated (thermal energy input) at 553 K (280 °C) Zr part of the alloy only be oxidized to form ZrO_2 with the ambient of oxygen partial pressure less than 10^{-11} atm to higher than 10^{-93} atm as shown in Fig.5. This process produces the composite structure of Pd embedded on a ZrO_2 (zirconia) matrix.

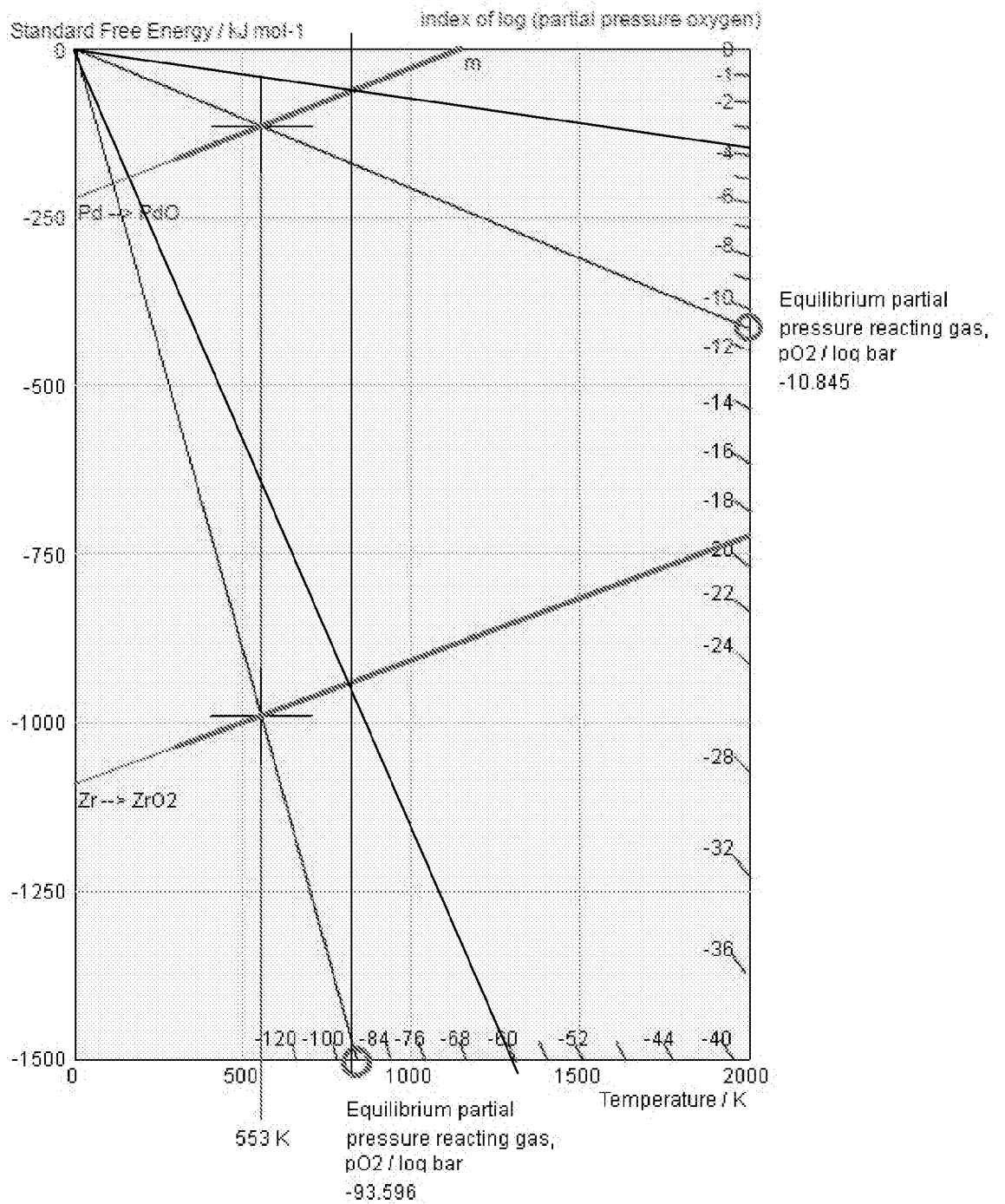


Fig 5. Ellingham and Richardson Diagram of Pd and Zr

4. Reduction for 3-A

The fully oxidized particle into a pressure chamber and exposed to an atmosphere of at least 24.7 psi. The stable metal oxides should remain

fully oxidized but the other less stable oxides are reduced and produce H_2O as a reduction byproduct. In case of the $PdOZrO_2$ the hydrogen pressurization causes a reduction in PdO to Pd and produces H_2O while ZrO_2 remains as a matrix material for the reduced Pd .

5. Pulverization

Product from 2B and any of 3 may be subsequently reduced in particle diameter by a process of ball milling similar to that shown in 2C.

Various stages of this process and feature length scales may be probed by both x-ray diffraction, scanning electron microscopy, and transmission electron microscopy. An example (Example 1) shown below starting as $Pd_{34.6}Zr_{65.4}$ was produced via $2B \rightarrow 3A \rightarrow 4$ and features a crystallite size measured to be 10 nm via powder x-ray diffractometry with transmission electron microscopy in agreement with that value. This would translate to a surface area $142 \text{ m}^2/\text{g}$ per g of Pd . Using the lattice constant of palladium as the depth of the surface (an upper estimate), this would translate to a grain boundary type defect volume of $5.07 \times 10^{-8} \text{ m}^3/\text{g}$. Additionally, dislocation defect density may be assessed by transmission electron microscopy.

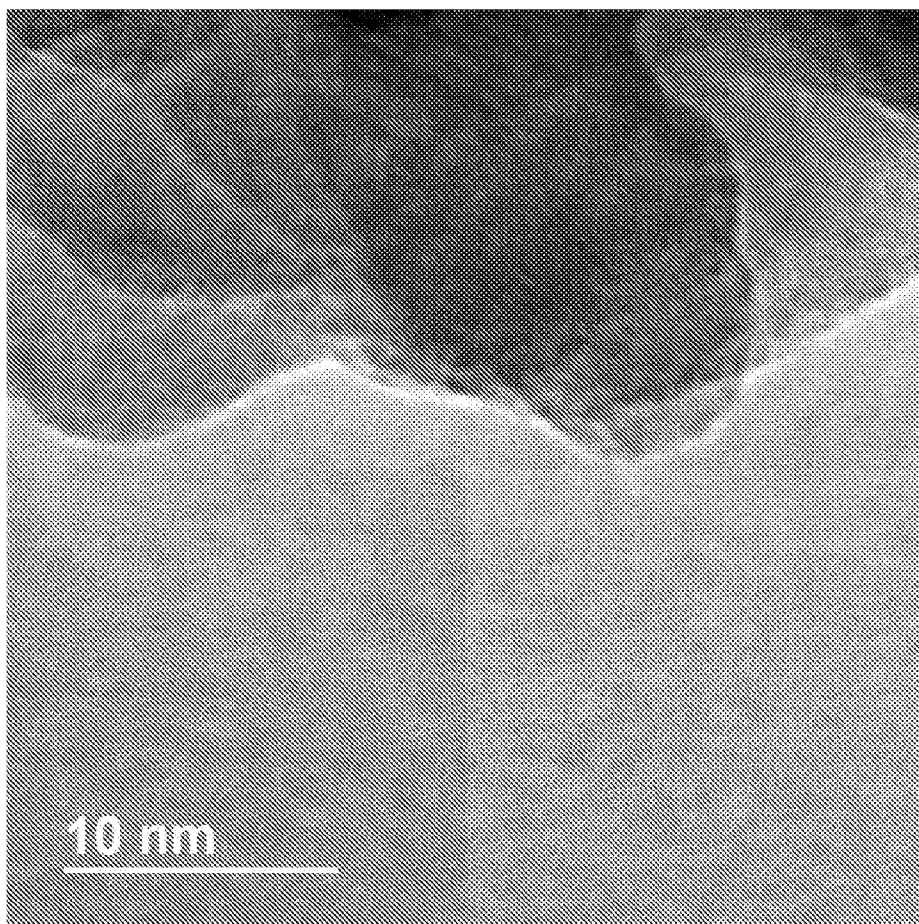


Fig. 6. Transmission electron microscopy of Example 1 material including grain boundaries and dislocation.

REFERENCES:

US 8603405 B2, Power Units Based On Dislocation Site Techniques.