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CA 2701843 A1 2009/04/16

(21) 2 701 843

(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION

(13) A1

(86) Date de dépôt PCT/PCT Filing Date: 2008/10/10
(87) Date publication PCT/PCT Publication Date: 2009/04/16
(85) Entrée phase nationale/National Entry: 2010/04/07
(86) N° demande PCT/PCT Application No.: EP 2008/008666
(87) N° publication PCT/PCT Publication No.: 2009/047011
(30) Priorité/Priority: 2007/10/11 (IT MI2007A001962)

(51) Cl.Int./Int.Cl. *C01B 3/00* (2006.01),
*C01B 6/04* (2006.01)

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(54) Titre : MATERIAU COMPOSITE POUR LE STOCKAGE D'HYDROGENE AVEC DES TAUX TRES ELEVES D'ABSORPTION ET DE DESORPTION ET PROCEDE DE FABRICATION DUDIT MATERIAU

(54) Title: COMPOSITE MATERIAL FOR HYDROGEN STORAGE WITH VERY HIGH RATES OF ABSORPTION AND DESORPTION AND METHOD OF PRODUCTION OF SAID MATERIAL

(57) Abrégé/Abstract:
Composite material, and associated method of production, used for hydrogen storage with very high rates of absorption and desorption, comprising a metal hydride, as matrix, and an alloy of zirconium and nickel at a zirconium/nickel weight ratio between 20/80 and 60/40, as particles and/or secondary phases, said metal hydride being in the form of particles of micrometric size and said alloy in the form of particles and/or as secondary phases with nanometric and/or micrometric dimensions.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
16 April 2009 (16.04.2009)

PCT

(10) International Publication Number
WO 2009/047011 A1

(51) International Patent Classification:
*C01B 3/00* (2006.01) *C01B 6/04* (2006.01)

(21) International Application Number:
PCT/EP2008/008666

(22) International Filing Date: 10 October 2008 (10.10.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
MI2007A001962 11 October 2007 (11.10.2007) IT

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**
— *with international search report*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

WO 2009/047011 A1

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# COMPOSITE MATERIAL FOR HYDROGEN STORAGE WITH VERY HIGH RATES OF ABSORPTION AND DESORPTION AND METHOD OF PRODUCTION OF SAID MATERIAL

The present invention relates to a composite material, and the associated method of production, for hydrogen storage with very high rates of absorption and desorption, in particular that can be used for applications in vehicles with hydrogen fuel cells or stations for storage of hydrogen as energy carrier for producing electricity during peak periods of consumption.

For the aforementioned uses, the hydrides of the magnesium hydride family ($MgH_2$), with a maximum theoretical storage capacity of 7.6 wt.% of hydrogen and desorption temperatures of approx. 300°C, which are necessary for a pressure of approx. 1 atmosphere for practical applications, are currently in competition with other materials such as the aluminium hydrides, with a storage capacity between 5.5% and 8.8% and desorption temperatures, in two stages, between 120 and 250°C, as well as with other families of hydrides with desorption temperature close to room temperature, based for example on elements such as lanthanum and nickel, with a storage capacity between 1 and 2 wt.%.

For example, for use in vehicles (motor cars), for the purpose of avoiding emission of carbon dioxide into the atmosphere, which occurs with fossil fuels (gas oil, gasoline, methane, LPG), a

storage capacity of 6 wt.% and autonomy of 500 km have been indicated as reasonable engineering objectives. Approx. 5 kg of hydrogen would be required for 500 km. With hydrides with desorption temperature close to room temperature this means a weight of 250-500 kg (i.e. 5-10 times the weight of a tank of fossil fuels: considered excessive).

With a tank containing magnesium-based hydrides and use of electric batteries for the preheating and heating of the hydrides the weight can be halved relative to that of the hydrides with desorption temperature close to room temperature. The magnesium-based hydrides could already be used today on light vehicles (motorcycles) as the autonomy required for these is less than for motor cars.

Apart from storage capacity, for practical purposes it is best to have a rate of absorption of hydrogen compatible with the times taken by the users of vehicles for filling up with fossil fuels and a rate of desorption compatible with the requirements of the vehicle (starting, acceleration).

The family of magnesium-based hydrides with various additives or catalytic phases is extensive as there are many different formulations of the additive, among which we may mention $Nb_2O_5$, $Cr_2O_3$, $Fe_2O_3$, Li-Pd, Zr, Pd, etc.

An additive having a catalytic effect has now been found, for adding to magnesium hydride, which provides a material that permits storage of hydrogen with very high rates of absorption and desorption, such as to permit applications compatible with the

practical requirements for a vehicle, connected with the fuel loading time, times for vehicle starting, acceleration, though with a slight reduction of the maximum storage value, a parameter connected in practical applications with the autonomy of the vehicle.

The composite material according to the present invention comprises a metal hydride, as matrix, and an alloy of zirconium (Zr) and nickel (Ni), at a zirconium/nickel weight ratio between 20/80 and 60/40, preferably between 40/60 and 55/45, as particles and/or secondary phases, said metal hydride being in the form of particles of micrometric size and said alloy in the form of particles and/or as secondary phases with nanometric and/or micrometric dimensions, preferably nanometric.

The preferred metal hydride is magnesium hydride ($MgH_2$).

The alloy of zirconium and nickel can preferably be selected from the alloys $Zr_{36}Ni_{64}$ and $Zr_{50}Ni_{50}$ (composition in atomic-%) and the intermetallic compounds $Zr_8Ni_{21}$, $Zr_7Ni_{10}$, $Zr_9Ni_{11}$ and ZrNi, from each alloy or compound separately, or combinations thereof.

If magnesium hydride is used, the weight ratio of magnesium hydride to alloy of zirconium and nickel is preferably between 98/2 and 80/20, more preferably between 92/8 and 88/12.

The composite material is preferably nanostructured.

Another object of the present invention is the method of preparation of an activated alloy of zirconium and nickel, preferably selected from the alloys $Zr_{36}Ni_{64}$ and $Zr_{50}Ni_{50}$ (composition in atomic-%) and the intermetallic compounds

$Zr_8Ni_{21}$, $Zr_7Ni_{10}$, $Zr_9Ni_{11}$ and ZrNi, from each alloy or compound separately, or combinations thereof, that comprises essentially the following stages:

- charging a furnace with the metals Zr and Ni, each with purity greater than or equal to 99.9 wt.%, at zirconium/nickel weight ratio between 20/80 and 60/40, and repeated melting, preferably between 4 and 6 times, under an inert atmosphere, followed by intermediate cooling and, optionally, by a final heat treatment at temperatures preferably between 900 and 1100°C for a time from several tens of hours to some days;
- activation of the alloy, to make it brittle, by means of cycles of absorption and desorption of hydrogen numbering between 2 and 6;
- cooling the embrittled alloy to room temperature;
- grinding of the cooled embrittled alloy to obtain particles with size between 100 and 300 micrometres.

The absorption of hydrogen can preferably be carried out at a pressure between 25 and 45 atm and at room temperature in a suitable volumetric system and the desorption of hydrogen can preferably be carried out in said suitable volumetric system by heating to a temperature between 285 and 315°C and under vacuum.

The furnace that is charged with the metals Zr and Ni is a furnace preferably selected from an electric arc furnace, for example with tungsten electrode, or an induction furnace.

The inert atmosphere is preferably of high-purity argon, more preferably greater than or equal to 99.998 wt.%.

A further object of the present invention is the method of production of the composite material described above that essentially comprises charging a suitable mill with the metal hydride and the activated alloy of zirconium and nickel, prepared as described above, and grinding said hydride and said alloy under an inert atmosphere for a time preferably between a few hours and some days, more preferably between 6 hours and 4 days.

The suitable mill can be a mill preferably selected from an attrition mill with container, vertical spindle with blades and balls, of hard steel or other hard materials, a horizontal-spindle mill, a hammer mill, a vibratory mill, or combinations thereof.

The mill selected is preferably modified so that it can operate with inert atmosphere thus avoiding safety problems for the operators owing to the flammability of the micrometric powder of magnesium and problems for the material through deterioration of storage properties through oxidation.

In the case of production of the composite material at the laboratory scale (at the scale of grams) the method differs from the process on an industrial scale in that mills of small dimensions and high energy are used, which reduce the times

taken for obtaining the composite and optimizing the hydrogen storage properties. Moreover, the reduced dimensions of the jars mean that very homogeneous conditions can be imposed for the grinding of the batch. The grinding process in these mills, which cannot be replicated with the dimensions required for industrial production, is in general different from the process taking place in an industrial mill of medium or large dimensions. It is for this reason, and not only because of the change of scale, that it is necessary for the hydrogen storage properties to be optimized again at the industrial scale, until those obtained at the laboratory scale are reached again, if possible.

At the laboratory scale, using a high-power mill for preparing the composite, and using various additives of the Zr-Ni system, it was possible to achieve, in the case of the additive $Zr_{36}Ni_{64}$, the highest rate of absorption (approx. 6 wt.% of hydrogen at a pressure of 10 atm and temperature of 250°C), the highest rate of desorption (at a pressure of 0.25 atm and temperature of 250°C) and the highest gradient or initial value of desorption.

Two examples will now be presented, the first of which is an application in accordance with the present invention, and the second is comparative.

Example 1

Industrial-scale production of the composite material comprising magnesium hydride $MgH_2$ and alloy $Zr_{36}Ni_{64}$, as catalytic additive.

Production of the alloy.

The alloy $Zr_{36}Ni_{64}$, 36-64 in atomic composition, and 47% of Zr and 53% of Ni as composition by weight, corresponds to the eutectic of the Zr-Ni constitution diagram, with a melting point of 1070°C.

Equipment:

1 arc furnace with tungsten electrode and with water-cooled copper crucible

1 volumetric system for the cycling of materials (absorption, desorption) in a hydrogen atmosphere, at various pressures or under vacuum and at room temperature or high temperature, equipped with a monitoring system with pressure, vacuum and temperature sensors for assurance of effectiveness of the cycles of hydrogenation and dehydrogenation

1 mortar

1 mill with hard steel balls

Operations:

Charging of the crucible with 47% of Zr and 53% of Ni as composition by weight, each with purity > 99.9%.

Melting of the charge in the arc furnace in an atmosphere of high-purity argon (> 99.998%).

Repeated melting, 6 times, to obtain homogeneity of composition of the alloy.

Activation of the additive

- embrittlement of the alloy, which exhibits a high value of hardness after melting, by means of 3 cycles of absorption and desorption of hydrogen
- absorption of hydrogen at a pressure p = 40 atmospheres at room temperature in the volumetric system
- desorption by heating in the volumetric system to a temperature T = 300°C and rotary pump vacuum
- grinding of the alloy to a particle size of 100-300 micrometres by means of the mortar and the mill.

Quality control:

Verification of particle size and morphology using a scanning electron microscope, SEM, using secondary electrons (SE) after activation and grinding.

The SEM micrographs in Fig. 1 and Fig. 2 show the particle size and morphology after cycling in a hydrogen atmosphere (activation) and grinding. The magnification is different in the two micrographs for observing the batch (Fig. 1) and the individual particles (Fig. 2).

Production of the composite.

Equipment:

1 standard attrition mill with container, vertical spindle with blades and balls, made of hard steel

Capacity of the container: 15 litres.

Modifications:

- pipes and circuit on the cover of the container, to provide a gas flow, so that grinding can be carried out under an inert atmosphere (argon).

- glove-bag for removing test samples under an inert atmosphere (argon)

- forced cooling of the bearing and sealing gasket of the rotating spindle for preventing escape of powder.

1 glove-box for carrying out manipulations relating to charging of the magnesium hydride ($MgH_2$), in the absence of air and moisture (slight nitrogen excess pressure)

Operations:

Charging of the container of the attrition mill with magnesium hydride (commercially available standard material, for example with a composition by weight of 95% $MgH_2$ and 5% Mg, in micrometric powder) and catalytic additive in weight ratio 90:10.

Weight ratio steel balls/weight of charge = 50:1

Grinding under an inert atmosphere of argon.

Rotary speed of the vertical spindle = 250 rev/min

Test samples taken every 24 hours in an argon atmosphere for control of the morphology of the powder and the storage requirements

Complete grinding of the batch under an inert atmosphere of argon (for 70 hours for a batch of 0.6 kg)

Discharge of the batch in an argon atmosphere.

Packaging of the batch in a plastic bottle with argon atmosphere.

Quality control:

Verification of particle size and morphology using a scanning electron microscope, SEM, using secondary electrons (SE) and back-scattered electrons (BSE). Fig. 3 shows the particles of magnesium hydride (1-4 micrometres) with particles corresponding to the catalytic additive (size less than 500 nanometres). Observing the same field by means of BSE electrons (Fig. 4) the particles corresponding to the additive can be seen in greater detail, as lighter zones revealed by the BSE electrons owing to the elements Zr and Ni, which have a higher atomic number than the atoms of the matrix (Mg and H), encapsulated inside the particles of magnesium hydride.

Verification of particle size using a Granulometer Laser:

Particle size: Diameter (v, 0.5) = 2.5 micrometres

Verification of properties as material on an industrial scale (kilograms) for hydrogen storage by means of a Sievert measuring instrument

(see Table 1).

Table 1

Characteristics of the magnesium-based hydride with catalytic additive $Zr_{36}Ni_{64}$ at the kilogram scale

| Maximum hydrogen storage | Time for absorption of the hydrogen, approx. 90% of the total (at p = 20 atmospheres and T = 300°C) | Time for desorption of hydrogen, approx. 90% of the total (at a test pressure p = 0.25 atmosphere and |
|---|---|---|

| | | |
|---|---|---|
| | | T = 300°C) |
| 5.4% by weight | 100 s | 300 s |

Example 2-Comparative

Production of a reference hydride: magnesium hydride containing as catalytic additive the oxide $Nb_2O_5$ on an industrial scale

This was manufactured at the kilogram scale with the same industrial method used for Example 1.

Equipment:

1 standard attrition mill, modified and improved as in Example 1.

1 glove-box as in Example 1.

Operations:

Charging of the container of the attrition mill with magnesium hydride $MgH_2$ (commercially available standard material, 95% $MgH_2$ and 5% Mg, in micrometric powder) and catalytic phase (oxide $Nb_2O_5$, commercially available standard material, in micrometric powder) in weight ratio 95:5

Weight ratio steel balls/weight of charge = 50:1

Grinding under an inert atmosphere of argon.

Rotary speed of the spindle = 300 rev/min

Test samples taken every 24 hours in an argon atmosphere for control of the morphology of the powder and the storage requirements

Complete grinding of the batch under an inert atmosphere of argon (for 72 hours for a batch of 0.5 kg)

Discharge of the batch in an argon atmosphere

Packaging of the batch in a plastic bottle with atmosphere of argon

Quality control:

Verification of particle size using a Granulometer Laser:

Particle size: Diameter (v, 0.5) = 4.6 micrometres

Verification of the properties as material on an industrial scale (kilograms) for hydrogen storage by means of Sievert measuring instrument (see Table 2)

Comparison of the times of absorption and desorption of hydrogen (approx. 90% of the total) in the case of the magnesium-based hydride with catalytic additive $Zr_{36}Ni_{64}$ according to the present invention (Table 1) and the corresponding times for a reference hydride, the magnesium-based hydride with catalytic phase $Nb_2O_5$ (Table 2), demonstrates that the kinetics of the hydride with catalytic additive $Zr_{36}Ni_{64}$ is higher.

A comparison with the more favourable characteristics obtained at the scale of grams for all the other hydrides of the family based on magnesium and with various additives indicates that the magnesium-based hydride with catalytic additive $Zr_{36}Ni_{64}$ according to the present invention displays, at the scale of grams as

well as at the scale of kilograms, the highest rates of absorption and desorption.

Table 2

Characteristics of the magnesium-based hydride with catalytic phase $Nb_2O_5$, at the kilogram scale

| Maximum storage of hydrogen | Time for absorption of hydrogen, approx. 90% of the total (at p = 20 atmospheres and at T = 300°C) | Time for desorption of hydrogen, approx. 90% of the total (at test pressure p = 0.25 atmosphere and at T = 300°C) |
|---|---|---|
| 6.2% by weight | 130 s | 600 s |

CLAIMS

1. Composite material comprising a metal hydride, as matrix, and an alloy of zirconium and nickel at zirconium/nickel weight ratio between 20/80 and 60/40, as particles and/or secondary phases, said metal hydride being in the form of particles of micrometre size and said alloy in the form of particles and/or as secondary phases with nanometric and/or micrometric dimensions.
2. Composite material according to Claim 1, characterized in that the metal hydride is magnesium hydride ($MgH_2$).
3. Composite material according to Claim 1, characterized in that the alloy of zirconium and nickel is selected from the alloys $Zr_{36}Ni_{64}$ and $Zr_{50}Ni_{50}$ (composition in atomic-%) and the intermetallic compounds $Zr_8Ni_{21}$, $Zr_7Ni_{10}$, $Zr_9Ni_{11}$ and ZrNi, from each alloy or compound separately, or combinations thereof.
4. Composite material according to Claim 2, characterized in that the weight ratio magnesium hydride/alloy of zirconium and nickel is between 98/2 and 80/20.
5. Composite material according to Claim 4, characterized in that the weight ratio magnesium hydride/alloy of zirconium and nickel is between 92/8 and 88/12.
6. Composite material according to Claim 1, characterized in that the alloy of zirconium and nickel is in the form of particles and/or as secondary phases with nanometric dimensions.

7. Composite material according to at least one of Claims 1 to 6, characterized in that said composite material is nanostructured.

8. Method of preparation of an activated alloy of zirconium and nickel, selected from the alloys $Zr_{36}Ni_{64}$ and $Zr_{50}Ni_{50}$ (composition in atomic-%) and the intermetallic compounds $Zr_8Ni_{21}$, $Zr_7Ni_{10}$, $Zr_9Ni_{11}$ and ZrNi, from each alloy or compound separately, or combinations thereof, comprising essentially the following stages:
   - charging a furnace with the metals Zr and Ni, each with purity greater than or equal to 99.9 wt.%, at zirconium/nickel weight ratio between 20/80 and 60/40, and repeated melting, under an inert atmosphere, followed by intermediate cooling and, optionally, by a final heat treatment;
   - activation of the alloy to make it brittle, by means of cycles of absorption and desorption of hydrogen numbering between 2 and 6;
   - cooling of the embrittled alloy to room temperature;
   - grinding of the cooled embrittled alloy to obtain particles with size between 100 and 300 micrometres.

9. Method according to Claim 8, characterized in that the absorption of hydrogen is carried out at a pressure between 25 and 45 atm and at room temperature in a suitable volumetric system and the desorption of hydrogen is carried out in said

suitable volumetric system by heating to a temperature between 285 and 315°C and under vacuum.

10. Method according to Claim 8, characterized in that the number of repeated melting operations is between 4 and 6.

11. Method according to Claim 8, characterized in that the furnace that is charged with the metals Zr and Ni is a furnace selected from an electric arc furnace or an induction furnace.

12. Method according to Claim 8, characterized in that the inert atmosphere is of argon of high purity greater than or equal to 99.998 wt.%.

13. Method of production of the composite material according to at least one of Claims 1 to 7, essentially comprising charging a suitable mill with the metal hydride and the activated alloy of zirconium and nickel, prepared according to at least one of Claims 8 to 12, and grinding said hydride and said alloy under an inert atmosphere for a time between a few hours and some days.

14. Method according to Claim 13, characterized in that the suitable mill is a mill selected from an attrition mill with container, vertical spindle with blades and balls made of steel, a horizontal-spindle mill, a hammer mill, a vibratory mill, or combinations of these methods of grinding.

15. Method according to Claim 13, characterized in that the grinding time is between 6 hours and 4 days.

16. Use of the composite material according to at least one of Claims 1 to 7 for hydrogen storage with very high rates of absorption and desorption.

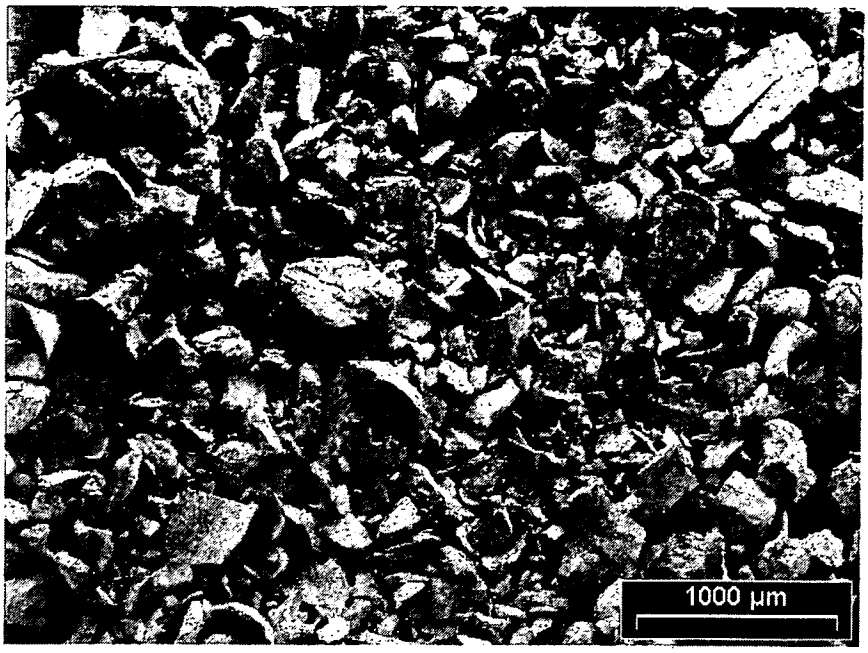


Fig. 1 Catalytic additive $Zr_{36}Ni_{64}$ after cycling in hydrogen atmosphere (activation) and grinding. SEM micrograph (SE).

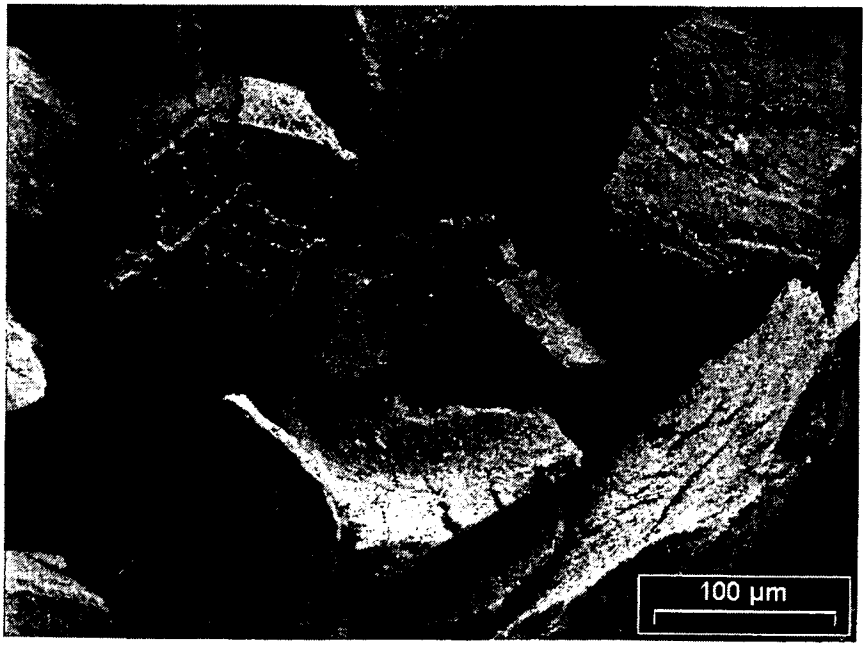


Fig. 2 Catalytic additive $Zr_{36}Ni_{64}$ after cycling in hydrogen atmosphere (activation) and grinding. SEM micrograph (SE).

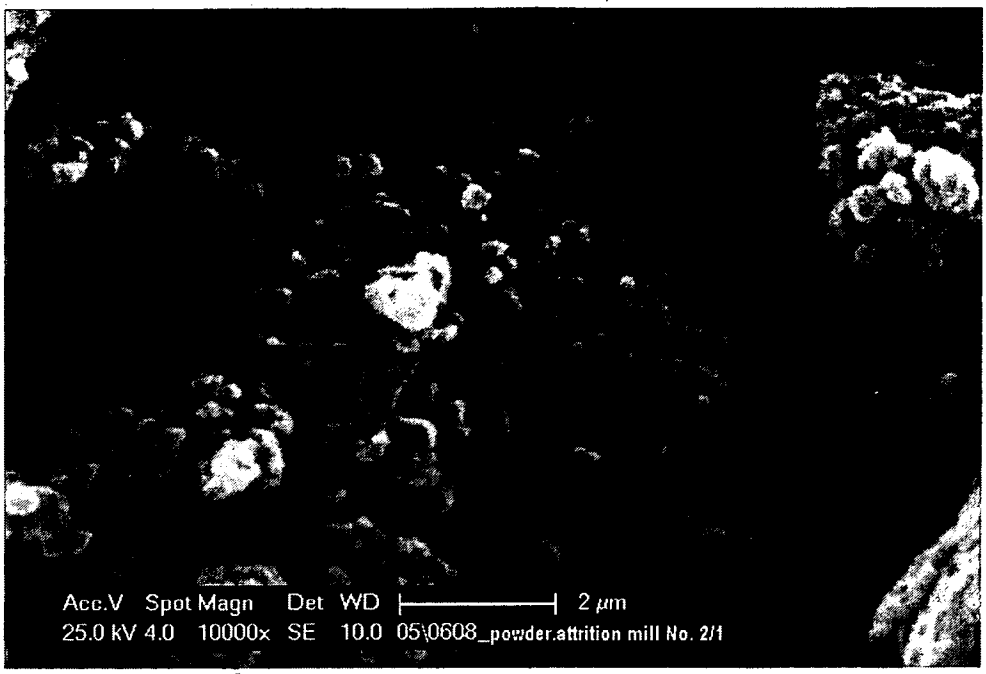


Fig. 3 Magnesium-based hydride, $MgH_2$, with catalytic additive $Zr_{36}Ni_{64}$, kilogram scale. SEM micrograph (SE).

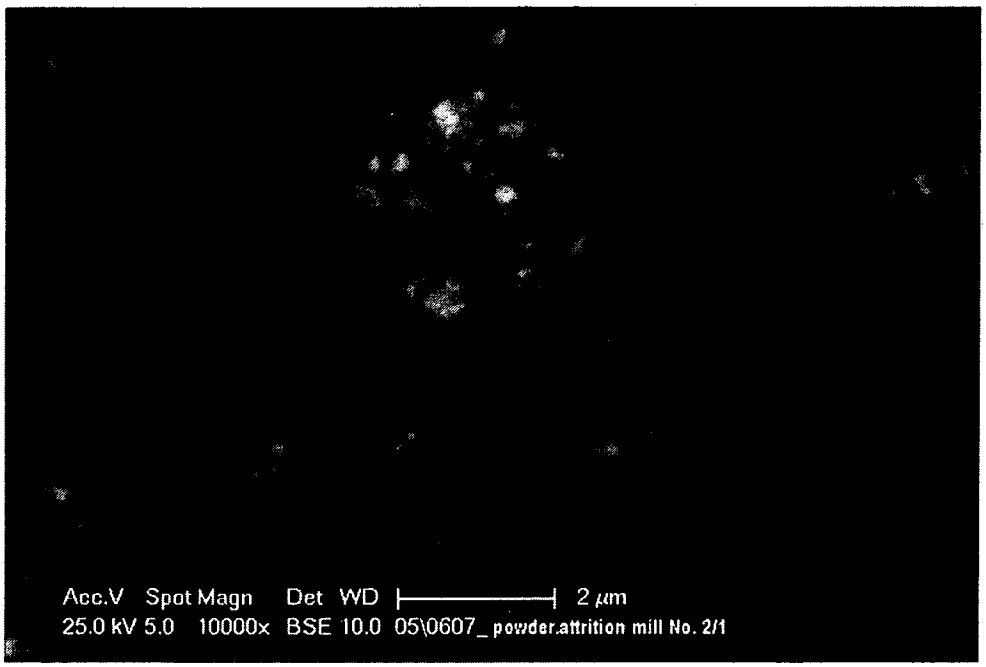


Fig. 4 Magnesium-based hydride, $MgH_2$, with catalytic additive $Zr_{36}Ni_{64}$, kilogram scale. SE