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(54) Title: A METHOD FOR THE MECHANICAL ACTIVATION OF POWDERS BY MEANS OF BALLS

(57) Abstract: The present invention relates to a method for the mechanical activation by means of balls of metal, semi-metal and/or non-metal powders (metal oxides, semimetal oxides, carbides, carbon and polymers) comprising: a) Providing a resonant acoustic mixer with vertical, horizontal or combined action; b) Providing an activation vessel, where the inner volume of said vessel is between 8 and 160 ml, preferably between 8 and 80 ml; c) Selecting balls and loading them in said vessel until obtaining a value of AVSF (Apparent Volumetric Sphere Filling) between 10% and 90%, preferably between 40% and 70%; d) Loading the powder (s) in said vessel; e) Optionally, adding a process controller (PCA) in said vessel; f) Optionally, bringing said vessel to volume with one or more gases; g) Closing said vessel and bringing said mixer to an acceleration above 50 G, preferably between 70 and 100 G, for a total process time between 5 and 480 min, preferably between 10 and 90 minutes.



"A method for the mechanical activation of powders by means of balls"

The present invention relates to a method for the mechanical activation by means of balls of metal, semi-metal and/or non-metal powders (metal oxides, semimetal oxides, carbides, carbon and polymers) comprising:

- a) Providing a resonant acoustic mixer with vertical, horizontal or combined action;
- b) Providing an activation vessel, where the inner volume of said vessel is between 8 and 160 ml, preferably between 8 and 80 ml;
- c) Selecting balls and loading them in said vessel until obtaining a value of AVSF (Apparent Volumetric Sphere Filling) between 10% and 90%, preferably between 40% and 70%;
- d) Loading the powder(s) in said vessel;
- e) Optionally, adding a process controller (PCA) in said vessel;
- f) Optionally, bringing said vessel to volume with one or more gases;
- g) Closing said vessel and bringing said mixer to an acceleration above 50 G, preferably between 70 and 100 G, for a total process time between 5 and 480 min, preferably between 10 and 90 minutes.

## Background Art

The resonant acoustic mixer is a machine which promotes the mixing of substances through small oscillations with close frequency to the resonant frequency of the system (mixing vessel + substances to be mixed). Acoustic resonant mixers have recently found wide application at the laboratory and industrial level for the production of cosmetics, pharmaceuticals, mixes of powders and energetic materials (propellants, explosives, etc.).

Ball milling is a process in which one or more materials are milled by balls of suitable material set in motion by appropriate systems, generally called mills. During the process, the motion of the balls causes the material or materials to be treated to be subjected to

severe mechanical stresses caused by the impact and friction actions generated by the balls. This type of process can be used to obtain different effects including reducing the size of a powder, changing the shape, the structure and even the composition of the initial material. If, during the treatment, no changes occur from the chemical viewpoint, for example the formation of new substances in considerable quantities or the passage from a crystalline to an amorphous phase, there is a "mechanical activation"; otherwise, the process is defined as "mechano-chemical activation". Mechanical activation, as well as mechano-chemical activation, is an extremely complex process comprising the correct selection / definition of a long series of parameters such as process time, the rotating speed of the mill (or the intensity of the vibration), the quantity of virgin material to be treated, the size, the shape and the material of the milling vessel, the size and the material of the grinding balls, the mass ratio between the grinding balls and the material being processed (ball-to-powder mass ratio - BPR), the temperature at which the compound should be, the quantity and the type of the process controller (PCA), etc.

**US3389105** describes methods for producing activated powders coated with fluoropolymers in which a low energy mill is used.

**US6334583** describes a planetary mill with two motors which mainly exploits centrifugal force to produce nanometric powders.

**US2983454** describes a vertical apparatus for mechanical activation based on ball milling. A vibratory mill is used, where a motor moves a vessel upwards and downwards, possibly also around its axis, promoting the motion of the balls positioned therein. In the system there is no resonance and the motion of the balls is rather orderly, leading to localized impacts, not distributed homogeneously inside the vessel.

**US3021082** also describes a vibratory mill, in which four activation vessels, arranged horizontally, are present.

Among high-energy mills, a typical apparatus where the impact action of the grinding balls is preponderant has been proposed in **US3458144**,

where the motion of the balls is induced by a series of blades set in rotation by an electric motor.

**CN2706231-Y** and **CN104209173-A** describe two-mass oscillatory mills, which do not allow the attainment of high acceleration levels.

5 There is a strongly felt need for methods allowing to obtain a change of specific surface area of the treated materials and/or of their composition, with the objective of increasing their reactivity. There is also a strongly felt need to have available a method for the mechanical or mechano-chemical activation of metal and non-metal  
10 powders by means of balls ("ball milling") which reduces production times and costs, boosting the effectiveness of the machining and activating processes with respect to the prior art and which can potentially be scaled up to industrial level.

#### Description of the invention

15 Described herein is a method for the activation of powders which uses a resonant acoustic mixer with vertical, horizontal or combined action with the ability to reach high accelerations (system with three or more masses). The specific selection of the parameters made herein allows a homogeneous distribution of the balls in the mixing  
20 vessel and the attainment of resonance, with the obtainment of activated powders with higher quality and greater operating efficiency.

In particular, the method according to the present invention allows to obtain powders the shape, surface area, specific surface area  
25 and/or composition of which are modified so as to increase their reactivity. By way of example, if the powders used are aluminum powders it is possible:

- to obtain a large increase in reactivity in air or another oxidizing atmosphere at high temperature ( $> 660^{\circ}\text{C}$ ),  
30 concurrently maintaining a low value of the specific surface area (flake particles with high metal content and ignition temperature above  $600^{\circ}\text{C}$ );
- to obtain a large increase in reactivity in air or another oxidizing atmosphere already at low temperature, increasing  
35 the specific surface area of the powder (particles with rough

surface, relatively low metal content and ignition temperature far lower than 600°C, until spontaneous ignition in air).

If the powders used are composite aluminum powders it is possible:

- to increase the reactivity of the powders in air or other oxidizing atmosphere both at low and high temperature;
- to increase the reactivity of the powders in pure water for the efficient generation of hydrogen.

Furthermore, it has been surprisingly observed that the method according to the present invention, applied to a blend of different powders, allows to combine materials together, with no need to use alloys and without generating new chemical compounds (for example, intermetallics). Therefore, the presence and the proportions of the virgin materials selected are assured, maximizing their desired effect.

Description of the figures:

Figure 1: Arrangement of the balls inside a vessel which is a) cylindrical; b) spherical.

Figure 2: sequence of photograms indicating the movement of the balls inside a cylindrical vessel.

Figure 3: sequence of photograms indicating the movement of the balls inside a cylindrical vessel, according to an additional embodiment.

Figure 4: (A) reference powder; (B) Act-Al\_EP\_CP\_R(TP0360) sample activated by ball milling.

Figure 5: DTA example 1

Figure 6: TG example 1

Figure 7: XRD example 1

Figure 8: (A) reference powder; (B) Act-Al\_S\_R(TP0360) sample activated by ball milling.

Figure 9: DTA example 2.

Figure 10: TG example 2.

Figure 11: XRD example 2.

Figure 12: (A) Mg reference powder; (B) nAl reference powder; (C) activated sample example 3.

Figure 13: EDX maps according to example 3. (A) original image; (B) Mg distribution; (C) Al distribution.

Figure 14: XRD example 3.

Figure 15: (A) reference powder; (B) Act-AlMg\_EP\_R12 activated sample.

Figure 16: DTA example 4.

5 Figure 17: TG example 4.

Figure 18: XRD example 4.

Figure 19: (A) reference powder; (B) Act-AlMg\_EP\_R13 activated sample.

Figure 20: TG example 5.

10 Figure 21: DT example 5.

Figure 22: TG example 5.

Figure 23: XRD example 5.

Figure 24: (A) reference powder; (B) Act-AlPTFE\_S\_R(TP60) activated sample.

15 Figure 25: EDX maps according to example 6. (A) original image; (B) Al distribution; (C) F distribution.

Figure 26: DT example 6.

Figure 27: TG example 6.

Figure 28: XRD example 6.

20 Figure 29: (A) reference powder; (B) Act-AlVC\_S\_R(TP0360) activated sample.

Figure 30: EDX maps according to example 7. (A) original image; (B) Al distribution; (C) V distribution.

Figure 31: DT example 7.

25 Figure 32: TG example 7.

Figure 33: XRD example 7.

Figure 34: (A) Al reference powder; (B) Fe<sub>2</sub>O<sub>3</sub> reference powder; (C) Act-T\_S\_R07 activated sample.

Figure 35: DT example 8.

30 Figure 36: TG example 8.

Figure 37: XRD example 8.

Figure 38: Granulometry of the powders obtained from can recycling; each track on the chart represents different process parameters.

Figure 39: SEM of the powders obtained in example 9.

35 Figure 40: Hydrogen evolution of the powders obtained in example 9.

Figure 41: % of evolved hydrogen relative to the maximum obtainable, e.g. 10.

Figure 42: (A) Effect of the AVSF on the quantity of hydrogen generated per kg of powder ( $T = 20^{\circ}\text{C}$ ); (B) Effect of the AVSF on the yield of hydrogen generated ( $T = 20^{\circ}\text{C}$ ). The dashed line is for comparison purposes.

Figure 43: (A) Effect of the milling time with BPR equal to 20:1 on the quantity of hydrogen generated per kg of powder ( $T = 20^{\circ}\text{C}$ ). (B) Effect of the milling time with BPR equal to 20:1 on the yield of hydrogen generated ( $T = 20^{\circ}\text{C}$ ).

Detailed description of the invention:

The present invention relates to a method for the mechanical activation by means of balls of metal, semi-metal and/or non-metal powders (metal oxides, semimetal oxides, carbides, carbon and polymers) comprising the following steps:

- i) Providing a resonant acoustic mixer with vertical, horizontal or combined action;
- ii) Providing an activation vessel, where the inner volume of said vessel is between 8 and 160 ml, preferably between 8 and 80 ml;
- iii) Selecting balls and loading them in said vessel until obtaining a value of AVSF (Apparent Volumetric Sphere Filling) between 10% and 90%, preferably between 40% and 70%;
- iv) Loading the powder(s) in said vessel;
- v) Optionally, adding a process controller (PCA) in said vessel;
- vi) Optionally, bringing said vessel to volume with one or more gases;
- vii) Closing said vessel and bringing said mixer to an acceleration above 50 G, preferably between 70 and 100 G, for a total process time between 5 and 480 min, preferably between 10 and 90 minutes.

The authors of the present invention have demonstrated that the parameters defined in the process described herein allow, surprisingly, to maximize the result obtained, both in terms of quality of the finished product and of process efficiency.

For the purposes of the present invention, the term "activation of the powders" means that the powders undergo a modification of the specific surface area, of the shape, and/or of the composition such as to change its reactivity.

5 In a preferred embodiment, the resonant acoustic mixer is a 3-mass mixer, where the three masses consist of: motor, plate, structure of the mixer itself.

The activation vessel has the indicated volumes. Preferably, said vessel is cylindrical, with non-chamfered edges and without  
10 interference elements.

The material whereof said vessel is made is selected on the basis of the type of substance to be activated (hardness), of the specific effect desired (change of the shape, of the specific surface area, etc.) and of the maximum level of contamination allowed. It is  
15 advisable to use a vessel of the same material as the powder to be activated or, alternatively, built with a substance having higher hardness than that of the powder to be activated. In one embodiment, said vessel is made of steel.

With regard to the balls, the parameter indicating the loading volume  
20 has been found to be essential.

Additional characteristics taken into consideration in the selection are:

a. the distribution of the balls which may be unimodal, bimodal, or multimodal, where it has been observed that the presence of balls  
25 of large size increases the activation effectiveness of the smaller balls going to increase the overall effectiveness of the activation process. In case of multimodal distribution, the ratio between the mass of the larger balls and that of the smaller balls is calculated (Large-to-Small ball mass Ratio LSR). In case of tri- or quadri-  
30 modal distribution, the LSR value is calculated dividing the balls in two groups based on the number average diameter. In an embodiment, said balls have a diameter between 1 and 20 mm, preferably between 2 and 10 mm, and preferably balls of two mutually different diameters are loaded. In one embodiment, LSR vessel is 1:2.1 or 4:1.



b. the Ball-to-Powder mass Ratio (BPR), which contributes to determine the quantity of energy which can be transferred to the powder in a unit of time. The BPR is between 40:1 and 2:1, preferably between 20:1 and 5:1.

5 c. The material of the ball. This parameter is selected on the basis of the type of substance to be activated (hardness), of the effect desired (change of the shape, milling, etc.) and of the maximum level of contamination allowed. To optimize both parameters and avoid the abrasion of the balls, the process needs to be carried out with balls  
10 having hardness which is equal to or higher than that of the powder to be activated. The material is preferably selected from the group comprising metals, metal alloys, "hard metals" and polymers, for example steel, titanium, tungsten carbide, plastic materials, Teflon.

15 The PCA, when reached, is preferably selected in the group which comprises cyclopentane, hexane, cyclohexane, toluene, acetone, paraffin.

The absence or the use of a liquid PCA with 100% filling of the activation vessel promotes dispersal of the powders. The possibility  
20 of inclusion between particles is also influenced by the quantity of PCA and by the granulometry of the powders. The presence of a high quantity of PCA greatly reduces the maximum temperature reached by the system during ball milling. The temperature reduction promoted by the liquid PCA with 100% filling of the vessel depends on the  
25 values of AVSF and BPR as well as on the nature and on the chemical-physical characteristics of the selected PCA. It should also be noted that the absence of a PCA causes, in addition to the temperature increase, also an aggravation of the phenomenon of cold welding between particles, inducing a process of progressive growth of the  
30 size of the materials. The quantity of PCA can be reduced to values below 100% of filling. In this case, the temperature reduction effect declines severely because of the impacts between balls and walls of the vessel not wet (or only partially wet) by the PCA. On the other hand, the proximity between particles to be activated is increased  
35 with the related increase of the inclusive effects. The quantity of

PCA can be optimized to obtain slurries on the basis of the specific surface area of the powders to be activated. In an embodiment, where the volume of the vessel is 80 ml the volume of PCA is between 5 ml and 7.25 ml. In an additional embodiment, where the volume of the vessel is 12 ml, the volume of PCA is between 1 ml and 8 ml.

In the absence of PCA, or with a global volumetric filling of the vessel below 100%, the free volume can be filled with an inert gas, for example argon, alone or mixed, in order to reduce the probability of ignition of the powder or processes which can reduce the purity of the material(s) because of the presence of oxygen. In an embodiment, this global volumetric filling is between 6.4 and 100%. The process duration was found to be essential for the achievement of the desired effects.

Additional process parameters considered for the resonant acoustic mixer are:

Number and duration of the pauses. Above all for high values of AVSF and in the absence of external cooling, one or more pauses should be provided, to allow the cooling of the vessel and of the powder. The number of the pauses, as well as their duration, depends on the type of powder to be activated, on the value of AVSF and on the type of activation. Purely by way of indication, for AVSF equal to or higher than 75% and in the absence of any type of external cooling, pause periods with a duration of 15 minutes are defined every 10 minutes of activation. Alternatively, if the vessel allows it, it is possible to provide for external, internal or combined cooling by means of an appropriate circuit in order to maintain the temperature at the levels required by the specific procedure, for example low temperature for reducing the granulometry of the starting materials, relatively high temperatures for alloy processes.

Intensity of the activation. The higher the intensity, the greater the acceleration of the milling system with consequent increase of the energy transferred to the powder system.

The following examples show particularly advantageous embodiments according to the present invention; the examples should be deemed indicative and not limiting the invention.

Example 1: Production of micrometric aluminum with high reactivity and low specific surface area through mechanical activation, ball milling, without the addition of additives.

Objectives: To increase the reactivity of micrometric aluminum maintaining a low value of specific surface area and a high metal content and particles of micrometric size.

Table 1. Formulation of the powder produced.

Ingredients	d, $\mu\text{m}$	Mass fraction
Al	30.0	100%

Table 2. Other information about the virgin material used for mechanical activation.

Info	Value
Specific surface area of powder, $\text{m}^2/\text{g}$	<0.1
Nominal shape of the Al particles	Spherical

Table 3. Characteristics of the activation vessel.

Properties of the Activation Vessel	
Material	AISI 304 steel
Shape of cavity	Cylindrical with non-chamfered edges
Presence of interference elements	No
Internal volume, ml	80

Table 4. Characteristics of the grinding balls.

Properties of the Balls	
Material	AISI 304 steel
Diameter(s)	6 mm / 3 mm
LSR	1:2 1

Table 5. Characteristics of the process controller (PCA).

PCA (Process Controller).	
Substance	Distilled cyclopentane
Presence of oxygen in the molecule	No
Additives	-
Type of liquid	Nonpolar
PH	Av. No.

Table 6. List of the selected activation parameters.

Activation Parameters	
POWDERS AND BALLS	
Powder Mass, g	2.5
Mass of Balls, g	50

BPR (ball to powder mass ratio)	20:1
Premixing of powders	Av. No.
PCA	
AVSF (apparent volume sphere filling)	12.8%
Volume of PCA, ml	72.5
Filling	100% (Full PCA)
Use of inert gas	No
RESONANT ACOUSTIC MIXER	
Acceleration	80 G
Total process time	60 min
Number of pauses	0
Duration of pauses	Av. No.
Cooling	Yes (air)
POST PROCESS TREATMENT	
Washing	No
Drying	Yes*
Temperature °C	60
Time, h	24

\* Recovery of the excess solvent

#### Results:

The activated powder (Act-Al\_EP\_CP\_R(TP0360)) obtained according to the described process is characterized by particles having completely different (lamellar) structure from the reference structure (consisting of spherical granules, or at most oblong ones). Figure 4 shows an image of the reference powder (A) and of the sample (Act-Al\_EP\_CP\_R(TP0360)) of the example. The outer surface of the particles is relatively smooth and essentially lacking bodies of small dimensions.

Table 7 contains the data about the specific surface area of the aluminum powder before and after the activation process. Therefore, the ball milling procedure does not entail a significant increase of the specific surface which remains below 1.00 m<sup>2</sup>/g.

Table 7. Specific surface of the sample Act-Al\_EP\_CP\_R(TP0360): comparison with the reference powder.

Powder	Specific surface area, m <sup>2</sup> /g
Reference powder	0.07*
Activated powder (code Act-Al_EP_CP_R(TP0360))	< 1.00

\* Value calculated assuming spherical particles

The increase in reactivity of the activated powder is shown by the DT analysis (differential thermal analysis), carried out in the following conditions: air, RT-1100°C, 10°C/min) provided in Figure 5. After activation, the powder (grey line) is characterized by the

presence of a clear exothermic peak with onset located at about 950°C. This behavior is not observed in the virgin sample which, on the contrary, exhibits low reactivity (black line). Replacing cyclopentane with acetone (dashed line) does not lead to the same result, confirming the importance of the process controller.

The strong increase in reactivity of the powder processed with the proposed treatment is further highlighted by the thermogravimetric (TG) traces shown in Figure 6. The activated powder, in particular, shows a higher mass gain than the other comparison samples both at about 600°C, and at the end of the test. For this parameter, too, mechanical activation carried out with the same parameters, but using acetone instead of cyclopentane (dashed line), leads to worse results.

The XRD analysis (X-Ray Diffraction), illustrated in Figure 7, shows the absence of crystalline impurities (e.g. any fragments due to the erosion of the vessel and of the grinding balls). Table 8 shows the values of actual metal content of the powders being compared. It can be noted that, with respect to the activation process, the reduction in metal content with respect to the virgin material is relatively low, about 1%, whereas reactivity increased markedly. In spite of the higher reactivity, the cyclopentane-activated powder shows, statistically speaking, the same metal content as the sample processed in acetone.

Table 8. Metal content of the sample Act-Al\_EP\_CP\_R(TP0360) with respect to the virgin powder and to the sample processed in acetone.

Powder	Metal content, ‰
Reference powder	99.1 ±0.3
Act-Al_EP_CP_R(TP0360)	98.0 ±0.9
Act-Al_EP_R(TP0360)	98.4 ±0.3

Example 2: Production of micrometric aluminum with high reactivity and specific surface area through mechanical activation, ball milling, without the addition of additives.

Objectives: To increase the reactivity of micrometric aluminum and of its specific surface area maintaining a high metal content and particles of micrometric size.

Strategy: Increasing the reactivity of the basic particles changing their shape (from spherical to flat). Increasing the specific surface area increasing the surface roughness of the particles. Maintaining a "Slurry" configuration to promote both impact and rubbing actions.

5 Preserving a high metal content

Table 9. Formulation of the powder produced

Ingredients	d, $\mu\text{m}$	Mass fraction
Al	30.0	100%

Table 10. Other information about the virgin material used for mechanical activation.

Info
Specific surface area of powder, $\text{m}^2/\text{g}$
Nominal shape of the Al particles

10

Table 11. Characteristics of the activation vessel.

Properties of the Activation Vessel

Properties of the Activation Vessel	
Material	AISI 304 steel
Shape of cavity	Cylindrical with non-chamfered edges
Presence of interference elements	No
Internal volume, ml	80

Table 12. Characteristics of the Grinding balls.

Properties of the Balls	
Material	AISI 304 steel
Diameter(s)	6 mm/3 mm
LSR	1:2.1

15 Table 13. Characteristics of the process controller (PCA).

PCA (Process controller).	
Substance	Distilled acetone
Presence of oxygen in the molecule	Yes
Additives	-
Type of liquid	Polar
PH	Av. No.

Table 14. List of the selected activation parameters.

Activation Parameters	
POWDERS AND BALLS	
Powder Mass, g	2.5
Mass of Balls, g	50

BPR (ball to powder mass ratio)	20:1
Premixing of powders	Av. No.
PCA	
AVSF (apparent volume sphere filling)	12.8%
Volume of PCA, ml	5.0
Filling	12.8%
Use of inert gas	Yes (Ar)
RESONANT ACOUSTIC MIXER	
Acceleration	80 G
Total process time	60 min
Number of pauses	0
Entry of pauses	Av. No.
Cooling	Yes (air)
POST PROCESS TREATMENT	
Washing	No
Drying	Yes
Temperature °C	60
Time, h	24

#### Results:

With reference to Figure 8, the activated powder (Act-Al\_S\_R(TP0360)) (panel B) is characterized by particles having completely different (lamellar) shape from the reference powder, consisting of spherical granules, or at most oblong ones (Panel A). The outer surface of the activated particles is extremely irregular and characterized by high surface roughness also given by the presence of different "scales".

Table 15 contains the data about the specific surface area of the aluminum powder before and after the activation process. Therefore, the ball milling procedure does not entail a significant increase of the specific surface tied to the increase in the surface roughness of the particles and to the specific shape.

Table 15. Specific surface area of the sample Act-Al\_EP\_CP\_R(TP0360): comparison with the reference powder.

Powder	Specific surface area, m <sup>2</sup> /g
Reference powder	0.07*
Activated powder (code Act-Al_S_R(TP0360))	6.90 ± 0.10
*Value calculated assuming the powders to be spherical	

The increase in reactivity of the activated powder is shown by the DT analysis (test conditions: air, RT-1100°C, 10°C/min) provided in Figure 9. After activation, the powder shows two exothermic peaks (grey line). A first peak position before the melting of the aluminum

(onset at about 580°C) and a second one after the melting peak (onset at about 960°C). This behavior cannot be observed in any of the other samples used as comparison (virgin powder, black line and a sample activated in cyclopentane using the same procedures, dashed line).

The strong increase in reactivity of the powder processed with the proposed treatment is further highlighted by the traces shown in Figure 10. As in the previous example, the activated powder shows a higher mass gain than the samples used as comparisons both at about 600°C, and at the end of the test.

It should be noted that mechanical activation carried out with the same parameters, but using cyclopentane instead of acetone (red dashed line), leads to worse results, underlining the importance of the selection of PCA.

The XRD analysis illustrated in Figure 11 shows the absence of crystalline impurities (fragments due to the erosion of the vessel and of the grinding balls).

Table 16 shows the values of actual metal content of the three powders compared herein. As a result of the improvement of the activation effectiveness, tied to the selection of the "SLURRY" configuration which allows to prefer friction actions between balls and powder over impact actions, the metal content of the powder activated in acetone is significantly reduced with respect to the reference powder, while still remaining well above 90% (reference value for a 100 nm uncoated nanometric aluminum powder). The metal content is also lower than that of powder activated in cyclopentane. The reason is the lower activation effectiveness when cyclopentane is used, also highlighted by a lower reactivity of this sample than that activated with acetone, as shown in Figures 11 and 12.

Table 16. Metal content of the sample Act-Al\_S\_R(TP0360) with respect to the virgin powder and to a sample activated in cyclopentane (Act-Al\_S\_CP\_R(TP3360B)).

Powder	Metal content, %
Reference powder	99.1 ± 0.3
Act-Al_S_CP_R(TP3360B)	98.1 ± 0.6
Act-Al_S_R(TP0360)	95.0 ± 0.5



Example 3: Production of nano-structured magnesium with aluminum having high specific surface area through mechanical activation (ball milling).

- 5 Objectives: To increase the specific surface area of the powder maintaining micrometric dimensions. To obtain mixed Mg/Al particles. Strategy: Increasing the surface roughness of the particles through a "Slurry" process, where rubbing actions are preponderant. Adding nanometric aluminum to increase activation effectiveness and to  
10 promote the incorporation of Al in the Mg particles.

Table 17. Details on the formulation of the powder produced.

Ingredients	d. $\mu\text{m}$	Mass fraction
Mg	44.0	95%
Al	0.1	5%

Table 18. Other information about the virgin materials used for mechanical activation.

Info	Value
Specific surface area of powder (nAl+Mg), $\text{m}^2/\text{g}$	1.2*
Nominal shape of the Al particles	Spherical
Nominal shape of the Mg particles	Flakes

\*Value calculated assuming spherical particles

15

Table 19. Characteristics of the activation vessel.

Properties of the Activation Vessel	
Material	AISI 304 steel
Shape of cavity	Cylindrical with non-chamfered edges
Presence of interference elements	No
Internal volume, ml	80

Table 20. Characteristics of the Grinding balls.

Properties of the Balls	
Material	AISI 316 steel
Diameter(s)	6 mm / 3 mm
LSR	4:1

20 Table 21. Characteristics of the process controller (PCA).

PCA (Process Controller)	
Substance	Distilled acetone
Presence of oxygen in the molecule	Yes
Additives	-
Type of liquid	Polar
PH	Av. No.

Table 22. List of the selected activation parameters.

Activation Parameters	
POWDERS AND BALLS	
Powder Mass, g	5
Mass of Balls, g	50
BPR (ball to powder mass ratio)	10:1
Premixing of powders	Yes
PCA	
AVSF (apparent volume sphere filling)	12.8%
Volume of PCA, ml	5.0
Filling	12.8% (SLURRY)
Use of inert gas	Yes (Ar)
RESONANT ACOUSTIC MIXER	
Acceleration	90 G
Total process time	120 min
Number of pauses	1 (after 60 min)
Duration of pauses	5 min
Cooling	Yes (air)
POST PROCESS TREATMENT	
Washing	No
Drying	Yes
Temperature °C	60
Time, h	24

## Results:

The shape changed obtained through the activation process is shown in Figure 12. The activated particles, panel C, are characterized by an extremely irregular shape. On the surface and in the interstices generated by the union of multiple particles, the presence is observed of porous structures compatible with the union of micro- and nano-powders. The comparison is with virgin powders of Mg, panel A, and of nAl, panel B.

The EDX (Energy Dispersive X-ray Analysis) maps shown in Figure 13 show an excellent homogenization of the final product with Al, panel C, uniformly distributed on the particles of Mg, panel B. Panel A shows the original image.

The specific surface area of the virgin blend and of the activated material are shown in Table 37. After the activation process, an increase of the specific surface area equal to 31 times the initial value is observed. In theoretical terms, considering a material with equal density to that of the virgin blend (1.770 g/cm<sup>3</sup>), the specific surface area obtained through mechanical activation would be

equivalent to that of a nanometric powder having spherical particles with diameter of about 90 nm. However, the powder obtained remains micrometric as is readily apparent in Figure 12, with significant advantages from the safety viewpoint.

5 Table 23. Specific surface area of the sample Act-Mg\_S\_R01: comparison with the reference powder.

Powder	Specific surface area, m <sup>2</sup> /g
Al/Mg blend	1.2*
Activated powder (code Act-Mg_S_R01)	38.4 ± 0.5

\*Value calculated assuming spherical particles

The XRD analysis carried out on the sample produced shows the absence of impurities due to the erosion of the vessel and/or of the balls  
10 used during the process (see Figure 14). On the other hand, traces of magnesium aluminate (MgAl<sub>2</sub>O<sub>4</sub>) are noted, the formation of which is probably due to the local conditions of temperature and pressure obtained during the milling process.

Example 4: Production of a micrometric composite material (Al/Mg)  
15 with high reactivity and low specific surface area through mechanical activation, ball milling.

Objectives: To increase the reactivity of micrometric aluminum maintaining a relatively low specific surface area and particles of micrometric size.

20 Strategy: Coupling aluminum with a strongly reactive substance (Mg) in order to increase the reactivity of the final powder. Increasing the reactivity of the Al/Mg blend approaching the two substances through the ball milling process. Increasing the reactivity of the basic particles changing their shape (from spherical to flakes or  
25 flat) preferring impact actions ("Full PCA" configuration).

Table 24. Details on the formulation of the powder produced.

Ingredients	D, $\mu$ m	Mass fraction
Al	15.0	80%
Mg	44.0	20%

Table 25. Other information about the virgin materials used for mechanical activation.

Info	Value
------	-------

Specific surface area of powder (Al+Mg), m <sup>2</sup> /g	0.13*
Nominal shape of the Al particles	Spherical
Nominal shape of the Mg particles	Flakes

\*Value calculated assuming spherical particles

Table 26. Characteristics of the activation vessel.

Properties of the Activation Vessel	
Material	AISI 304 steel
Shape of cavity	Cylindrical with non-chamfered edges
Presence of interference elements	No
Internal volume, ml	80

Table 27. Characteristics of the Grinding balls.

Properties of the balls	
Material	AISI 304 steel
Diameter	6 mm/3 mm
LSR	1:2.1

5

Table 28. Characteristics of the process controller (PCA).

PCA (Process Controller).	
Substance	Distilled acetone
Presence of oxygen in the molecule	Yes
Additives	-
Type of liquid	Polar
PH	

Table 29. List of the selected activation parameters.

Activation Parameters	
POWDERS AND BALLS	
Powder Mass, g	5.0
Mass of Balls, g	50
BPR (ball to powder mass ratio)	10:1
Premixing of powders	Yes
PCA	
AVSF (apparent volume sphere filling)	12.8%
Volume of PCA, ml	72.5
Filling	100% (Full PCA)
Use of inert gas	No
RESONANT ACOUSTIC MIXER	
Acceleration	90 G
Total process time	120 min
Number of pauses	1 (after 60 min)
Duration of pauses.	5 min
Cooling	Yes (air)

POST PROCESS TREATMENT	
Washing	No
Drying	Yes
Temperature °C	60
Time, h	24

#### Results:

In the embodiment of example 4, a strong transformation of the shape was obtained as attested by Figure 15, panel A control, panel B sample activated according to the example. In the blend containing the virgin powders, the particles of Al are distinguishable from particles of Mg because of the different shape. In the activated powder, instead, the presence of flattened particles is observed, the shape of which is similar to the geometric family of oblate disks or spheroids, without the possibility of distinguishing the two ingredients anymore. In general, all particles underwent the effects of activation without size distinctions

The specific surface area of the virgin blend and of the activated material are shown in Table 30 and they exhibit a small change caused essentially by the change in the shape of the particles.

Powder	Specific Surface Area, m <sup>2</sup> /g
Al/Mg blend	0.13*
Activated powder (code Act-AlMg EP R12)	1.66 ±0.03

\*Value calculated assuming spherical particles

The increase in reactivity of the activated powder is attested by the DT analysis (test conditions: air, RT-1100°C, 10°C/min) provided in Figure 16. The ACT-AMg\_EP\_R12 powder shows that the first exothermic peak is clearly earlier than for the reference blend (from 595°C to about 530°C) as well as the presence of a second reaction peak just before the melting of the aluminum. The increase in reactivity is further confirmed by the results of the TG tests shown in Figure 17, where a higher final mass gain is shown for the activated powder with respect to the reference counterparty.

The XRD analysis shown in Figure 18 attests only the presence of aluminum and magnesium in crystalline form, thus excluding significant quantities of crystalline impurities.

Example 5: Production of a micrometric composite material (Al/Mg) with high reactivity and specific surface area through mechanical activation, ball milling.

Objectives: To increase the reactivity of micrometric aluminum maintaining the powder micrometric.

Strategy: Coupling aluminum with a strongly reactive substance (Mg) in order to increase the reactivity of the final powder. Increasing the reactivity of the Al/Mg blend approaching the two substances through the ball milling process. Increasing the reactivity of the basic particles changing their shape from spherical or in flakes to flat and wrinkling their outer surface preferring rubbing actions to impact actions (configuration with high AVSF).

Table 31. Details on the formulation of the powder produced.

Ingredients	d, $\mu\text{m}$	Mass fraction
Al	15.0	80%
Mg	44.0	20%

Table 32. Other information about the virgin materials used for mechanical activation.

Info	Value
Specific surface area of powder (Al+Mg), $\text{m}^2/\text{g}$	0.13*
Nominal shape of the Al particles	Spherical
Nominal shape of the Mg particles	Flakes

\*Value calculated assuming spherical particles

Table 33. Characteristics of the activation vessel.

Properties of the Activation Vessel	
Material	AISI 304 steel
Shape of cavity	Cylindrical with non-chamfered edges
Presence of interference elements	No
Internal volume, ml	30

Table 34. Characteristics of the Grinding balls.

Properties of the Balls	
Material	AISI 316L steel
Diameter(s)	2 mm
LSR	Av. No.

Table 35. Characteristics of the process controller (PCA).

PCA (Process controller).	
Substance	Distilled acetone
Presence of oxygen in the molecule	Yes
Additives	-
Type of liquid	Polar
PH	Av. No.

Table 36. List of the selected activation parameters.

Activation Parameters	
POWDERS AND BALLS	
Powder Mass, g	5.0
Mass of Balls, g	50
BRR (ball to powder mass ratio)	10:1
Premixing of powders	Yes
PCA	
AVSF (apparent volume sphere filling)	80.0%
Volume of PCA, ml	3
Filling	100%
Use of inert gas	No
RESONANT ACOUSTIC MIXER	
Acceleration	80 G
Total process time	60 min
Number of pauses	1 (after 30 min)
Duration of pauses.	3 min
Cooling	Yes (air)
POST PROCESS TREATMENT	
Washing	No
Drying	Yes
Temperature °C	60
Time, h	24

## Results:

5 After the ball milling process, the particles have an extremely irregular shape as attested by Figure 19. In the activated powder, panel B, the presence of flattened particles is observed, the shape of which is similar to the geometric family of oblate disks or spheroids, with a particularly irregular surface. The edges are also particularly jagged. Al and Mg are no longer clearly distinguishable at the morphological level. In this case, the presence of small-size particles is observed, as well as that of fragments the nature of which, probably oxides, is not known.

15 The activation process leads to a strong increase of the specific surface area (see Table 37). In theoretical terms, considering a material with equal density to that of the analyzed blend (2.432 g/cm<sup>3</sup>), the specific surface area obtained through mechanical activation would be equivalent to that of a nanometric powder having

spherical particles with diameter of 100 nm. However, the powder obtained remains micrometric as is readily apparent in Figure 19, with significant advantages from the safety viewpoint with respect to a nano-powder.

5 Table 37. Specific surface area of the sample Act-AlMg\_EP\_R13: comparison with the reference powder.

Powder	Specific Surface Area, m <sup>2</sup> /g
Al/Mg blend	<0.13*
Activated powder (code Act-AlMg_EP_R13)	24.0±0.2

\*Value calculated assuming spherical particles

#### DRYING TREATMENT

10 The activated powder according to the present invention is optionally subjected to an additional drying process in order to assure a smaller presence of residual solvent (, 0.5%) instead of the about 4.0% obtained by the basic process.

The treatment consists of bringing the powder, already dried in a furnace at 60°C, to a temperature of 320°C for a limited time (about 15 5 minutes), then bringing it back to ambient conditions. The entire process has a duration of less than 20 minutes. The treatment consists of reducing the residual quantity of solvent (impurities) trapped in the particles, but also of increasing the reactivity of the final material. The reference is to Figure 20, which shows the 20 related TGs (dashed curve). This process, appropriately adapted to the type of powder, is also applied to other materials obtained by mechanical activation.

The increase in reactivity of the activated powder is attested by the DT and TG analyses (test conditions: air, RT-1100°C, 10°C/min) 25 provided respectively in Figure 21 and Figure 22. After ball milling, the ACT-AlMg\_EP\_R13 powder (both in the original and in the "DRY" version) shows that the first exothermic peak is clearly earlier than for the Al/Mg blend (from 595°C to about 550°C). The single peak observed in the Al/Mg mechanical blend before the melting of 30 the Al, is divided in two peaks of lower intensity in the case of the activated powder. The TG analysis shows a strong increase in reactivity and the presence of an initial desorption if a dedicated drying treatment is not provided.



The XRD analysis shown in Figure 23 attests only the presence of aluminum and magnesium in crystalline form, thus excluding significant quantities of crystalline impurities.

Example 6: Production of a composite material (Al/PTFE) in the form of micrometric powder with high reactivity through mechanical activation, ball milling.

Objectives: Strong increase in the reactivity of the material maintaining the powder micrometric.

Strategy: Intimately blending Al and PTFE to reduce the distance between the two materials. Promoting the reaction of aluminum with the decomposition products of the PTFE, where the consequent release of energy leads to the partial destruction of the superficial layer of oxide of the remaining part of Al, promoting the normal oxidation of the metal with the environmental oxygen. Increasing the specific surface area of the material to promote the oxidation chemical reactions (increase of the friction action by means of "Slurry").

Table 38. Details on the formulation of the powder produced.

Ingredients	d, $\mu\text{m}$	Mass fraction
Al	30.0	70.0%
PTFE	1.0	30.0%

Table 39. Other information about the virgin materials used for mechanical activation.

Info	Value
Specific surface area of powder (Al+Fe <sub>2</sub> O <sub>3</sub> ), m <sup>2</sup> /g	0.9*
Nominal shape of the Al particles	Spherical
Nominal shape of the PTFE particles	Spherical

\*calculated, not measured specific surface area

Table 40. Characteristics of the activation vessel.

Properties of the Activation Vessel	
Material	AISI 304 steel
Shape of cavity	Cylindrical with non-chamfered edges
Presence of interference elements	No
Internal volume, ml	80

Table 41. Characteristics of the Grinding balls.

Properties of the Balls	
Material	AISI 304 steel
Diameter(s).	6 mm/3 mm
LSR	1:2.1

Table 42. Characteristics of the process controller (PCA).

PCA (Process Controller).	
Substance	Distilled acetone
Presence of oxygen in the molecule	Yes
Additives	-
Type of liquid	Polar
PH	Av. No.

Table 43. List of the selected activation parameters.

Activation Parameters	
POWDERS AND BALLS	
Powder Mass, g	2.5
Mass of Balls, g	50
BPR. (ball powder mass ratio)	20:1
Premixing of powders	No
PCA	
AVSF (apparent volume sphere filling)	12.8%
Volume of PCA, ml	5.0
Filling	12.8% (SLURRY)
Use of inert gas	Yes (argon)
RESONANT ACOUSTIC MIXER	
Acceleration	80 G
Total process time	60 min
Number of pauses	0
Duration of pauses.	0 min
Cooling	Yes (air)
POST PROCESS TREATMENT	
Washing	No
Drying	Yes
Temperature °C	60
Time,	24 h

5

## Results:

The activation process carried out produced a significant morphological change of the particles relative to the starting powder. In particular, the granules take the shape of scales which can join to form clusters of extremely complex shapes, as shown in panel B of Figure 24. The EDX maps shown in Figure 25 show an excellent degree of blending between PTFE and Al on the surface, thus assuring an efficient contact between the two materials.

In this case as well, the "slurry" process assures a strong increase of the specific surface area as already pointed out in the above cases. However, the use of a high quantity of PTFE, a relatively soft material (hardness equal to 934 on the Knoop scale), reduces

the activation effectiveness determining a relatively small increase in the specific surface area (see Example 1). In theoretical terms, considering a material with equal density to that of the analyzed blend (2.529 g/cm<sup>3</sup>), the specific surface area obtained would be equivalent to that of a nanometric powder having spherical particles with diameter of 275 nm.

Table 44. Specific surface area of the sample Act-AlPTFE\_S\_R(TP60): comparison with the reference powder.

Powder	Specific Surface Area, m <sup>2</sup> /g
Al/PTFE blend	0.9*
Activated powder (code Act-AlPTFE_S_R(TP60))	8.6±0.1

\*Value calculated theoretically assuming particles of spherical shape

The increase in reactivity of the activated powder is attested by the DT analysis (test conditions: air, RT-1100°C, 10°C/min) provided in Figure 26. The activated sample, in particular, shows an increase in reactivity not only with respect to the starting components (30 µm Al and 1 µm PTFE), but also with respect to the mechanical mix between Al/PTFE. In both cases, the decomposition of the PTFE (carbon- and fluorine-based compounds) is seen to be associated with reaction between C and O<sub>2</sub> present in the air. However, the reaction appears to be earlier than in the case of the activated powder with an onset located at 480°C with respect to 515°C of the mechanical mix. The increase in reactivity of the activated powder is also shown by the presence of an additional exothermic peak positioned before the aluminum melting peak, a behavior hindered by the aluminum melting process (thus poorly visible) in the case of the mechanical blend.

The increase in reactivity and the interaction between PTFE and Al is shown in Figure 27. In the absence of mechanical activation, the behavior of the Al/PTFE blend between RT and 600°C is similar to that of the pure PTFE (loss of mass respectively equal to about 27% and 30% due to the decomposition of the polymer). The only difference is an earlier onset equal to about 60°C for the Al/PTFE mechanical blend. When the activated powder is tested, on the contrary, the maximum loss of mass measured between RT and 600°C is usually equal

to 14.4%. This result can be explained with the formation of a certain quantity of aluminum fluoride ( $\text{AlF}_3$ ) due to the proximity of Al and PTFE. If all the F reacts with Al to generate  $\text{AlF}_3$ , the decline in mass tied only to the loss of C should be equal to 7.2%. In the presence of a decline in mass by 14.4%, it can be assumed that about 32% of the Fluorine contained in the PTFE is lost (decomposition of the PTFE with loss of the products), while the remaining 68% reacts with the Aluminum to form  $\text{AlF}_3$  and generate energy.

The analysis of the activated sample illustrated in Figure 28 shows a powder which is essentially free of crystalline impurities, only the peaks related to aluminum and to the PTFE being distinguishable. The metal content of the powder, which tends to be low because it is strongly charged with PTFE, exhibits a value deviating by about 4.7% relative to the ideal value. This variation is caused by the activation process and it is compatible with the information provided in Table 16 for the powder activated by means of the same methodology, but without additives (deviation equal to 4.1%).

Table 45. Metal content of the sample Act-AlPTFE\_S\_R(TP60) with respect to the virgin powder.

Powder	Metal content, %
Ideal metal content	69.4
Act-AIPTFE S R(TP60)	64.7 $\pm$ 0.6

Example 7: Production of an Al/vanadium carbide (VC) composite material in the form of micrometric powder characterized by high specific surface area and high irregularity of the particles.

Objectives: To increase the reactivity of micrometric aluminum and of its specific surface area (change of the shape and increase of surface roughness). Marked change in the shape of the powder.

Strategy: Increasing the reactivity and the specific surface area of the basic particles changing their shape from spherical to flat. Adding a substance with high hardness able to increase the reactivity of the final powder and to increase the action of the grinding balls (VC). Maintaining a "Slurry" configuration to prefer rubbing actions.

Table 46. Details on the formulation of the powder produced

Ingredients	d, $\mu\text{m}$	Mass fraction
Al	30.0	70%
VC	1.0	30%

Table 47. Other information about the virgin materials used for mechanical activation

Info	Value
Specific surface area, powder (blend). $\text{m}^2/\text{g}$	0.36*
Nominal shape of the Al particles	Spherical
Nominal shape of the VC particles	Spherical

\* value calculated assuming spherical particles

5 Table 48. Characteristics of the activation vessel.

Properties of the Activation Vessel	
Material	AISI 304 steel
Shape of cavity	Cylindrical with non-chamfered edges
Presence of interference elements	No
Internal volume, ml	80

Table 49. Characteristics of the Grinding balls.

Properties of the Balls	
Material	AISI 316L steel
Diameter/i	6 mm/ 3 mm
LSR	1:2.1

Table 50. Characteristics of the process controller (PCA).

PCA (Process controller).	
Substance	Distilled acetone
Presence of oxygen in the molecule	Yes
Additives	-
Type of liquid	Polar
PH	Av. No.

10

Table 51. List of the selected activation parameters.

Activation Parameters	
POWDERS AND BALLS	
Powder Mass, g	2.5
Mass of Balls, g	50
BPR (ball to powder mass ratio)	20:1
Premixing of powders	No
PCA	
AVSF (apparent volume sphere filling)	12.8%
Volume of PCA, ml	5.0
Filling	12.8%
Use of inert gas	Yes(Ar)
RESONANT ACOUSTIC MIXER	
Acceleration	80 G
Total process time	60 min
Number of pauses	0
Duration of pauses.	Av. No.

Cooling	Yes (air)
POST PROCESS TREATMENT	
Washing	No
Drying	Yes
Temperature °C	60
Time,	24 h

#### Results:

The activation process leads to a marked change in the shape of the powder generating particles which are extremely irregular and of small size with respect to those of the starting aluminum. The granules obtained have jagged edges and a greatly wrinkled surface, indicating high activation effectiveness. The reference is to Figure 29.

The EDX maps shown in Figure 30 show excellent homogenization (panel A) between aluminum (B) and vanadium carbide (C).

The values of specific surface area relating to the virgin blend and to the activated sample are shown in Table 52.

The activation process described herein causes a strong increase of the specific surface area. In purely theoretical terms, assuming spherical particle and a powder comprising a material with equal density to that of the analyzed blend ( $3.215 \text{ g/cm}^3$ ), the specific surface area obtained would be equivalent to that of a powder having granulometry of 81 nm. The marked increase in reactivity is tied both to the reduction of the size of the particles, and to the marked irregularities of the surface of the grains.

Table 52. Specific surface area of the sample Act-AlVC\_S\_R(TP0360): comparison with the reference powder.

Powder	Specific Surface Area, $\text{m}^2/\text{g}$
Reference powder	0.36*
Activated powder (code Act-AlVC S R(TP0360))	23.10±0.20

\* Value calculated assuming spherical powders

The presence of vanadium carbides markedly increases the reactivity of the activated as attested both by the DT and TG analysis (test conditions: air, RT-1100°C, 10°C/min) provided respectively in Figure 31 and Figure 32. After activation, the powder has several exothermic peaks of which the first (onset at about 465°C) is due

to the presence of VC (in particular to its decomposition in V and C and subsequent reaction of C with the oxygen present in the air). All the other peaks are probably due to the reaction of the aluminum and of the vanadium with the external oxidizing environment. Of particular interest is the strong exothermic peak located immediately after the melting of the aluminum.

The strong increase in reactivity of the activated powder is further highlighted by the traces shown in Figure 32. In this case, it is necessary to consider that part of the mass gain (which reaches its maximum amount around 850°C) is tied to the oxidation of the remaining vanadium after the loss of carbon. The XRD analysis illustrated in Figure 33 shows the absence of crystalline impurities (fragments due to the erosion of the vessel and of the grinding balls), but only the initial components.

The metal content of the powder shows a rather significant deviation from the ideal value and equal to 9.9% (see Table 53). The measured deviation is greater than that observed for activation with PTFE (see Table 45), indicating a greater activation effectiveness. Table 53. Metal content of the sample Act-AlVC\_S\_R(TP60) with respect to the virgin powder.

Powder	Metal content, %
Ideal metal content	69.4
Act-AlVC S R(TP60)	59.5 ±0.6

Example 8: Production of a micrometric thermite based on Al and Fe<sub>2</sub>O<sub>3</sub> characterized by high reactivity and specific surface area through mechanical activation, ball milling.

Objectives: Strong increase in the reactivity of the material.

Strategy: Internally mixing Al and iron oxide in order to reduce the distances between the two materials and promote the passage of oxygen from the oxide to the metal. Increasing the specific surface area of the material in order to maximize its reactivity. Maintaining a "Slurry" configuration to prefer rubbing actions.

Table 54. Details on the formulation of the powder produced.

Ingredients	d, μm	Mass fraction
Al	30.0	25.25%
Fe <sub>2</sub> O <sub>3</sub>	1.0	74.75%

Table 55. Other information about the virgin materials used for mechanical activation.

Info	Value
Specific surface area, powder (Al+ Fe <sub>2</sub> O <sub>3</sub> ), m <sup>2</sup> /g	0.8*
Nominal shape of the Al particles	Spherical
Nominal shape of the Fe <sub>2</sub> O <sub>3</sub> particles	Cluster of particles

\*Specific surface area calculated assuming particles of spherical shape

5 Table 56. Characteristics of the activation vessel.

Properties of the Activation Vessel	
Material	AISI 304 steel
Shape of cavity	Cylindrical with non-chamfered edges
Presence of interference elements	No
Internal volume, ml	30

Table 57. Characteristics of the Grinding balls.

Properties of the Balls	
Material	AISI 31L6 steel
Diameter(s)	8 mm/ 2 mm
LSR	4:1

Table 58. Characteristics of the process controller (PCA).

PCA (Process controller).	
Substance	Distilled acetone
Presence of oxygen in the molecule	Yes
Additives	-
Type of liquid	Polar
PH	Av. No.

10

Table 59. List of the selected activation parameters.

Activation Parameters	
POWDERS AND BALLS	
Powder Mass, g	2.3
Mass of Balls, g	18.6
BPR (ball to powder mass ratio)	8:1
Premixing of powders	Yes
PCA	
AVSF (apparent volume sphere filling)	26.5%
Volume of PCA, ml	2.8
Filling	26.5%(SLURRY)
Use of inert gas	Yes (argon)
RESONANT ACOUSTIC MIXER	
Acceleration	70 G
Total process time	30 min
Number of pauses	2 (after 10 min)
Duration of pauses.	3 min
Cooling	Yes (air)
POST PROCESS TREATMENT	
Washing	No
Drying	Yes



Temperature °C	60
Time, 24	h

## Results:

In the embodiment according to example 8, strong blending between the two powders is observed, associated with a significant variation in particle shape. The granules of  $\text{Fe}_2\text{O}_3$  are incorporated inside the powder causing an evident change in color with respect to the case of simple mechanical blending (from bright red to reddish purple). In the activated powder, the presence of irregular particles is observed, with a particularly wrinkled surfaces with "powdery" appearance (see Figure 34).

The activation process entails an increase of the specific surface area equal to 10 times that of the starting blend (see Table 60). In theoretical terms, considering a material with equal density to that of the analyzed blend ( $2.432 \text{ g/cm}^3$ ), the specific surface area obtained would be equivalent to that of a nanometric powder having spherical particles with diameter of about 100 nm. However, the powder obtained remains micrometric as is readily apparent in Figure 34.

Table 60. Specific surface area of the sample Act-T\_S\_R07: comparison with the reference powder.

Powder	Specific Surface Area, $\text{m}^2/\text{g}$
Al/ $\text{Fe}_2\text{O}_3$ blend	2.4*
Activated powder (code Act- T S R07)	26.0±0.2

\* Surface calculated assuming particles of spherical shape

The strong increase in reactivity of the activated powder is attested by the DT analysis shown in Figure 35 (test conditions: argon, RT-1100°C, 10°C/min). In the activated powder, the exothermic peak corresponding to the reaction between Al and iron oxide is earlier by about 635°C with respect to the standard powder. However, the freed energy is slightly lower, probably because of the loss of active metal due to the activation process itself.

The chart shown in Figure 36 comprises the possible presence of residues of PCA inside the powder, attested by a loss of mass of

about 3% between ambient temperature and 500°C. As is demonstrated for other materials, the problem can be solved with an appropriate drying process.

The XRD analysis of the activated sample illustrated in Figure 37 shows a powder which is essentially free of crystalline impurities, only the peaks related to aluminum and to iron oxide being distinguishable.

#### Example 9: recycling aluminum cans

Aluminum cans, optionally after washing, are broken up into small flakes of about 4 - 10 mm. Said flakes are inserted into a vessel with the characteristics per table 61. Optionally, in the same vessel is added acetone, in a quantity of about 2% p/p. The free volume of the vessel is filled with an inert gas, whereupon the vessel is closed and the mixer is started. The selected activation parameters are shown in table 62.

Table 61. Characteristics of the activation vessel.

Properties of the Activation Vessel	
Material	AISI 304 steel
Shape of cavity	Cylindrical with non-chamfered edges
Presence of interference elements	No
Internal volume, ml	12.3

Table 62. Activation Parameters.

Properties of the Balls	
Material	AISI 304 steel
	6 mm / 3 mm for the lateral part
Diameter(s)	8 mm / 3 mm for the upper part
	8 mm / 3 mm for the lower part
	1:2.1 for the lateral part
LSR	1:1 for the upper part
	1:1 for the lower part
Activation Parameters	
POWDERS AND BALLS	
Mass of Al Scrap, g	1.5
Mass of Balls, g	30
BPR (ball to powder mass ratio)	20:1

Premixing of powders	No
PCA	
AVSF (apparent volume sphere filling)	50.1%
Mass of PCA	Up to 2% by mass relative to the mass of powder
Filling	Av. No.
Use of inert gas	Yes (Ar)
RESONANT ACOUSTIC MIXER	
Acceleration	80 G
Total process time	60 min or 30 min
Number of pauses	0
Duration of pauses.	Av. No.
Cooling	Air

The table refers to different diameters in relation to upper part, lateral part, lower part because, in a preferred embodiment, the flakes obtained from the lateral part of the cans are kept separate from the flakes obtained from the upper and lower portions thereof. The method proved to be surprisingly effective in producing powders from each part of the can (lateral, base and upper part). The powders obtained are of the category of "activated powders" with consequent strong increase in reactivity. Therefore, changing the procedure, materials with different characteristics and performance can be obtained.

The powders are adequate to be used in the production of hydrogen having optimized granulometry and reactivity. The granulometry is shown in Figure 38. In the absence of PCA, samples ActCAN-m60-21-0\_A and ActCAN-m60-11-0-t\_A the average dimensions tend to be greater than when PCA is used. In general, granulometry is always below 200  $\mu\text{m}$  with partial inclusion of particles of larger dimensions which can be removed with a rapid sifting process. In case of use of PCA, the reactivity increases until reaching pyrophoricity (spontaneous ignition in air). What is shown in Figure 38 is confirmed by the SEM analyses grouped in Figure 39.

Powders thus obtained were tested for the capacity of leading to the evolution of hydrogen. Depending on the selected activation process,

the metal content of the powder changes between 76% and 95%, always maintaining a strong capacity of developing hydrogen. Figure 40 shows the quantities of hydrogen developed by the 4 different samples of powder. All powders with the exception of the lot ActCAN-m30-11-008-  
 5 b have the capacity to develop over 79% of available hydrogen in 60 minutes and to reach over 88% at 90 minutes. Table 63 shows the metal content and the evolution of hydrogen at 60 and 90 minutes for the powders considered. The powders are inserted in a 4% solution of water and sodium hydroxide at a temperature of 24°C.

10 Table 63:

<b>Powder</b>	<b>Content of Al metal content, %</b>	<b>Fraction of theoretical H<sub>2</sub> released in 60 minutes, %</b>	<b>Fraction of theoretical H<sub>2</sub> released in 90 minutes, %</b>
ActCAN-m60-11-0-t_A	91.3 %	79.3 %	88.5 %
ActCAN-m60-21-0_A	94.6 %	80.7 %	92.1 %
ActCAN-m30-11-02-b_A	76.5 %	98.6 %	100.0 %
ActCAN-m30-11-008-b_A	92.8%	69.6%	78.5 %

Example 10: Production of a composite activated powder able to effectively generate hydrogen.

The example demonstrates the extraordinary effectiveness of the  
 15 method according to the present invention in increasing the capacity of the powders to produce hydrogen in pure water as demonstrated by the trend of the yield of Figure 41, i.e. the percentage of hydrogen evolved relative to the maximum obtainable. Powders produced with standard methods (dashed line) yield just above 30%, while the method  
 20 of the patent assures values above 80% for equal formulation (solid line). The method proposed, moreover, has proved to be extraordinarily rapid and effective because it allows to obtain the powder activated in only 15 minutes and with a BPR of 20:1 versus 300 minutes and a BPR of 30:1 necessary for the standard method  
 25 present in the literature.

Table 64: Composition of the powder produced

Ingredients	d, $\mu\text{m}$	Mass fraction
Al	30.0	80%
Bi	44.0	10%
Sn	10.0	10%

Table 65: characteristics of the activation vessel.

Properties of the Activation Vessel	
Material	AISI 304 steel
Shape of cavity	Cylindrical with non-chamfered edges
Presence of interference elements	No
Internal volume, ml	12.3

Table 66: Characteristics of the activation balls

Properties of the Balls	
Material	AISI 304 steel
Diameter(s)	6 mm / 3 mm
LSR	1:2.1

Table 67: Activation parameters

Activation Parameters	
POWDERS AND BALLS	
Powder Mass, g	1.4
Mass of Balls, g	28
BPR (ball to powder mass ratio)	20:1
Premixing of powders	No
PCA	
AVSF (apparent volume sphere filling)	50.0%
Volume of PCA, ml	No PCA
Filling	Av. No.
Use of inert gas	Yes (Ar)
RESONANT ACOUSTIC MIXER	
Acceleration	80 G
Total process time	15 min
Number of pauses	0
Duration of pauses.	Av. No.
Cooling	Yes (air)

5 Example 11: Effect of the apparent filling volume of the vessel (AVSF)

Process parameters:

Powder: Al/Bi/Zn 90/5/5

BPR = 20:1

Acceleration = 80 G

5 Vessel = 12.3 ml (AISI 316 L)

AVSF = 12.5%; 30%; 50 %; 70%; 90%

D\_Balls = 6 mm / 3 mm

Balls material + Steel (AISI 316)

LSR = 1:2.1

10 PCA = None

Atmosphere = Ar

PCA Volume = 0 ml

Cooling: yes (air)

Milling time = 15 minutes

15 The results obtained are shown in Table 68 and in Figure 42, panel A and panel B.

The activation data apply only for the powders produced using the method according to the present invention. "BM STD", dashed line in Figure 42, panel B, refers to a comparative figure obtained with  
20 powders having the formulation shown in Table 64, but activated according to standard methodologies.

The apparent filling of the vessel is of fundamental importance for the end result. The parameters do not influence the metal content of the powder, which remains practically unchanged between 88% and  
25 90%, as indicated in Table 68. What changes is the evolution of hydrogen.

Table 68. Effect of the AVSF on the metal content of the samples.

AVSF, %	Metal content, %
12.5	88.1 ± 1.0
30.0	88.1 ± 1.0
50.0	90.1 ± 1.0
70.0	88.7 ± 1.0
90.0	89.9 ± 1.0

Passing from AVSF 30% to AVSF 50%, a substantial change is noted in the results, due to a change of the activation modes (from pure impact to friction + impact). Within the scope of the same activation mode ( $AVSF \leq 30\%$ ;  $AVSF \geq 50\%$ ), as the value of AVSF grows, a decrease is observed in the hydrogen developed and yield (see Figure 42, panel A and B). The mode of activation essentially by impact assures a more rapid development whereas the mixed or essentially friction mode leads to a more gradual development of hydrogen. The test was interrupted at 90 minutes, but as is readily apparent from the curve of Figure 42, panel B, the activated powder in accordance with the present invention would have continued to react in a longer time overcoming the yield of the reference material. Example 13: Effect of the process time

Process parameters:

15 BPR = 20:1

Powder: Al/Bi/Zn 90/5/5

BPR = 20:1

Acceleration = 80 G

Vessel = 12.3 ml (AISI 316 L)

20 AVSF = 50%

D\_Balls = 6 mm / 3 mm

Balls material + Steel (AISI 316)

LSR = 1:2.1

PCA = None

25 Atmosphere = He

PCA Volume = 0 ml

Cooling: yes (air)

Milling time = 5 min.; 10 min.; 15 min.

The milling time, operating in He atmosphere, does not influence the metal content of the powder, which remains unchanged and close to 90% (see Table 69).

Table 69. Effect of the milling time on the metal content of the samples ().

Time, min	Metal content, %
-----------	------------------

5	89.7
10	89.7
15	89.6

The activation time influences, instead, the rapidity of release of hydrogen as well as the quantity of hydrogen which can evolve (yield). Increasing the process time, there is a progressive increase in the hydrogen produced, in the production rate and in the yield, up to values close to 100% (test in water at 20°C) see Figure 43, panel A and panel B). In this case, too, it is possible to regulate the times so as to obtain the desired release speed.

#### Advantages:

The method described hitherto is easily scalable at the industrial level thanks to the availability of the market of acoustic resonant mixers able to treat large quantities of material. The possibility of using multiple vessels in series is also a valid approach to increase the treated volumes, maintaining the process parameters which have been demonstrated herein to be surprisingly advantageous. There are numerous fields in which it is possible to apply the method proposed, including the production of advanced materials with low environmental impact, aerospace and defense, energy, hydrogen production, pyrotechnics, construction, catalysis and powder metallurgy with possible positive effects also on the sectors connected therewith.

By way of example, the method according to the present invention finds application for the production of graphene, the production of metal powders, the production of materials with increased reactivity and reduced environmental impact with respect to nanoparticles, the production of nanostructured materials, the production of optimized powders in terms of morphology and chemical-physical properties.

The method proposed herein was successfully used for the activation of metals/semimetals (Al, Mg, Si, Steel, Bi, Sn), non-metal substances (Teflon, graphite, plastic materials, oxides), as well as for hybrid activation (two or more substances, also of different natures).



In particular, the activation of aluminum powders with the method according to the present invention allows to obtain ideal reactive powders for their use in hydrogen production.

In addition, the method according to the present invention is particularly useful to obtain composite metal materials, without  
5 needing to use metal alloys.

## CLAIMS

1. A method for the mechanical activation by means of balls of metal, semi-metal and/or non-metal powders (metal oxides, semimetal oxides, carbides, carbon and polymers) comprising:
  - a) Providing a resonant acoustic mixer with vertical, horizontal or combined action;
  - b) Providing an activation vessel, wherein the inner volume of said vessel is between 8 and 160 ml, preferably between 8 and 80 ml;
  - c) Selecting balls and loading them in said vessel until obtaining a value of AVSF (Apparent Volumetric Sphere Filling) between 10% and 90%, preferably between 40% and 70%;
  - d) Loading the powder(s) in said vessel;
  - e) Optionally, adding a process controller (PCA) in said vessel;
  - f) Optionally, bringing said vessel to volume with one or more gases;
  - g) Closing said vessel and bringing said mixer to an acceleration above 50 G, preferably between 70 and 100 G, for a total process time between 5 and 480 min, preferably between 10 and 90 minutes.
2. A method according to claim 1, wherein said vessel is a cylindrical vessel, with non-chamfered edges and without interference elements.
3. A method according to claim 1, wherein said balls have a diameter between 1 and 20 mm, preferably between 2 and 10 mm.
4. A method according to one of claims 1 to 3, wherein balls of two mutually different diameters are loaded, preferably 3 and 6 mm or 2 and 8 mm.
5. A method according to one of claims 1 to 4, wherein the Ball-to-Powder mass ratio (BPR) is between 40:1 and 2:1, preferably between 20:1 and 5:1.
6. A method according to one of claims 1 to 5, wherein said balls are made of one more materials selected from the group comprising metals, metal alloys, "hard metals" and polymers, by

way of example they are made of steel, titanium, tungsten carbide, plastic materials, Teflon.

7. A method according to one of claims 1 to 6, wherein said PCA is selected from cyclopentane, hexane, cyclohexane, toluene, acetone, paraffin.
8. A method according to one of claims 1 to 7, wherein said PCS is present in volume between 5 and 72.5 ml, wherein the volume of the vessel is 80 ml, or between 1 and 8 ml, wherein the volume of the vessel is 12 ml.
9. A method according to one of claims 1 to 8, wherein said gas is an inert gas, preferably argon and/or helium.
10. A method according to one of claims 1 to 9, wherein said mixer operates according to the following parameters:
  - acceleration: above 50 G, preferably from 70 to 100 G;
  - number of pauses: optional, up to 4;
  - duration of pauses (where present): between 1 and 15 min., preferably between 3 and 5 min.
11. A method according to one of claims 1 to 10, wherein said mixing takes place under cooling.
12. A method according to one of claims 1 to 11, wherein at the end of said mixing the product is exposed to drying.
13. A method according to one of claims 1 to 12, wherein said metal powder is an aluminum powder, optionally with the addition of PTFE, vanadium carbide, Bismuth, Tin, for example.
14. Powders obtained by a process according to claims from 1 to 13.
15. Powders according claim 14 which are aluminum powders for use in the production of hydrogen.

"A method for the mechanical activation of powders by means of balls"

Abstract

The present invention relates to a method for the mechanical activation by means of balls of metal, semi-metal and/or non-metal powders (metal oxides, semimetal oxides, carbides, carbon and polymers) comprising:

- a) Providing a resonant acoustic mixer with vertical, horizontal or combined action;
- b) Providing an activation vessel, where the inner volume of said vessel is between 8 and 160 ml, preferably between 8 and 80 ml;
- c) Selecting balls and loading them in said vessel until obtaining a value of AVSF (Apparent Volumetric Sphere Filling) between 10% and 90%, preferably between 40% and 70%;
- d) Loading the powder(s) in said vessel;
- e) Optionally, adding a process controller (PCA) in said vessel;
- f) Optionally, bringing said vessel to volume with one or more gases;
- g) Closing said vessel and bringing said mixer to an acceleration above 50 G, preferably between 70 and 100 G, for a total process time between 5 and 480 min, preferably between 10 and 90 minutes.

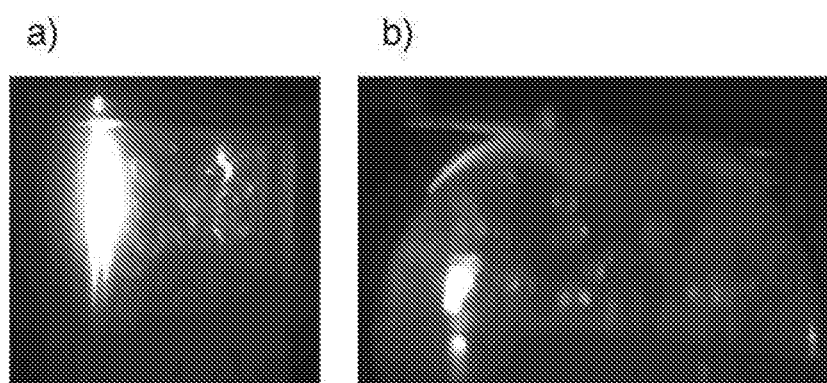


FIG. 1

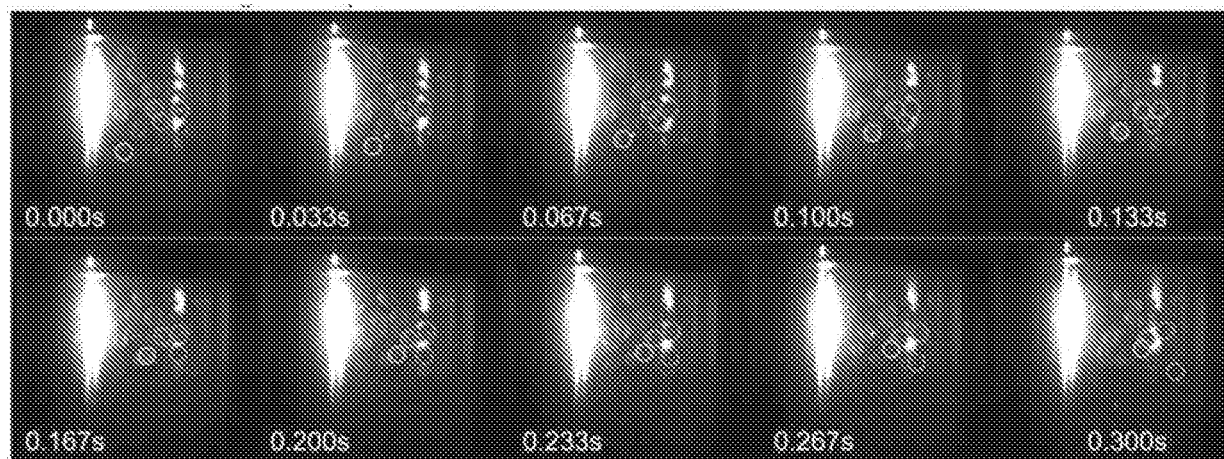


FIG. 2

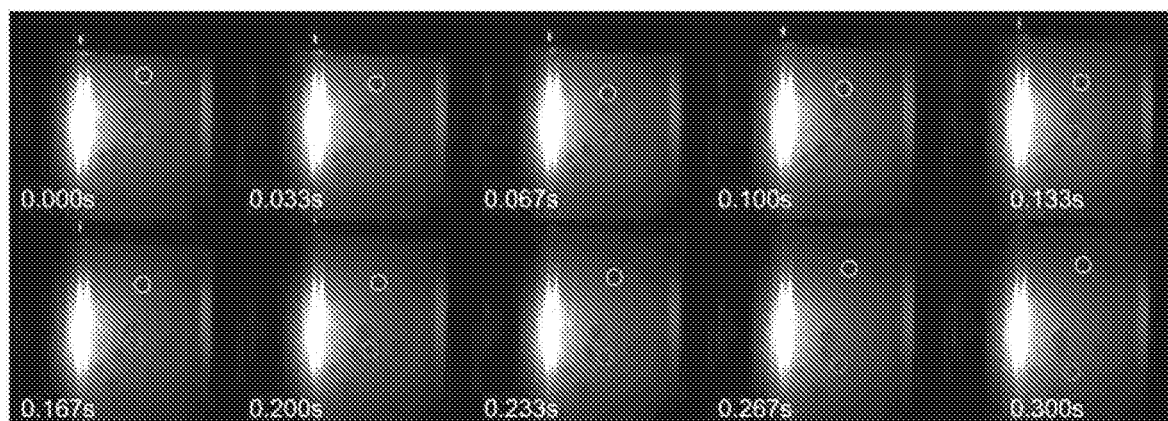


FIG. 3

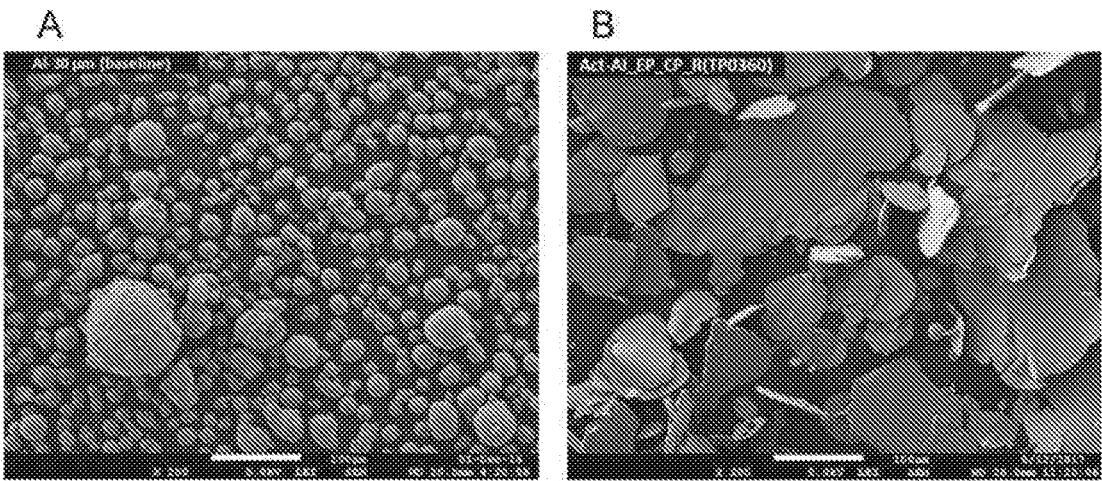


FIG. 4

FIG. 5

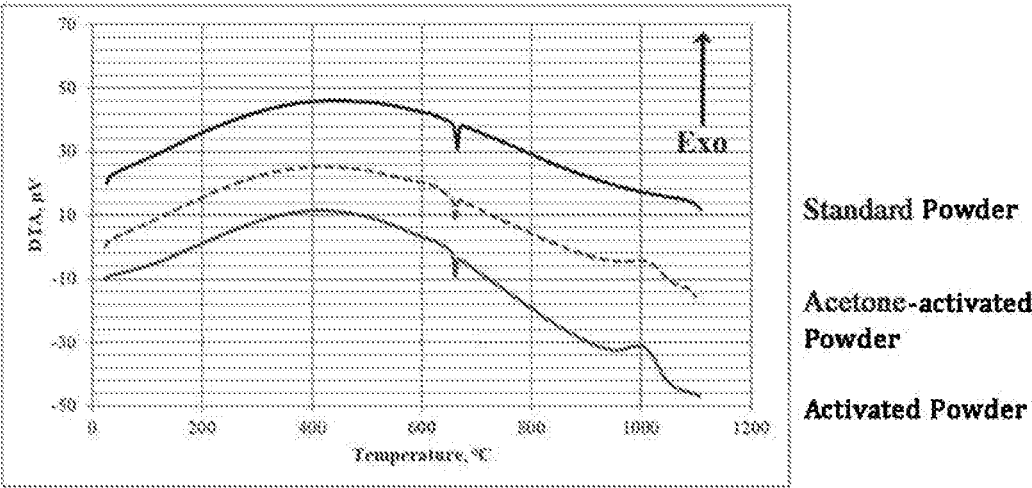
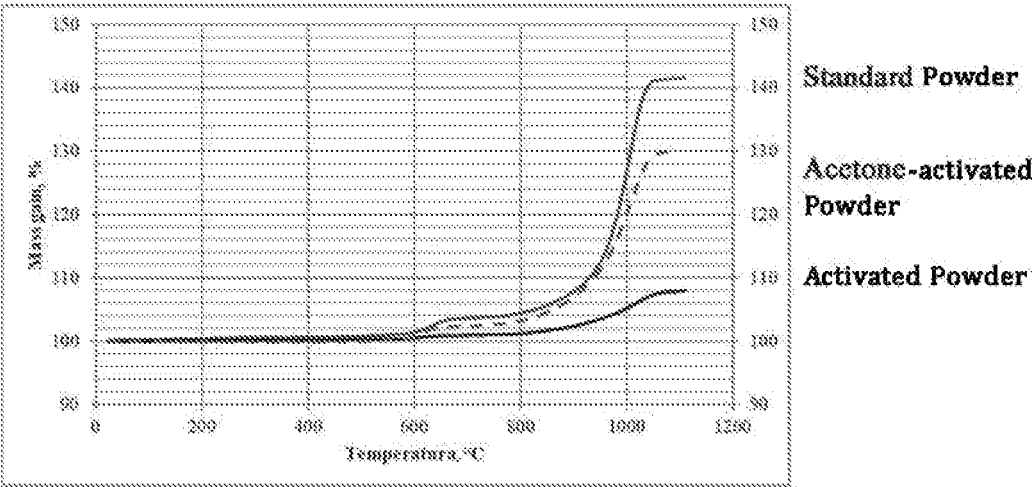


FIG. 6



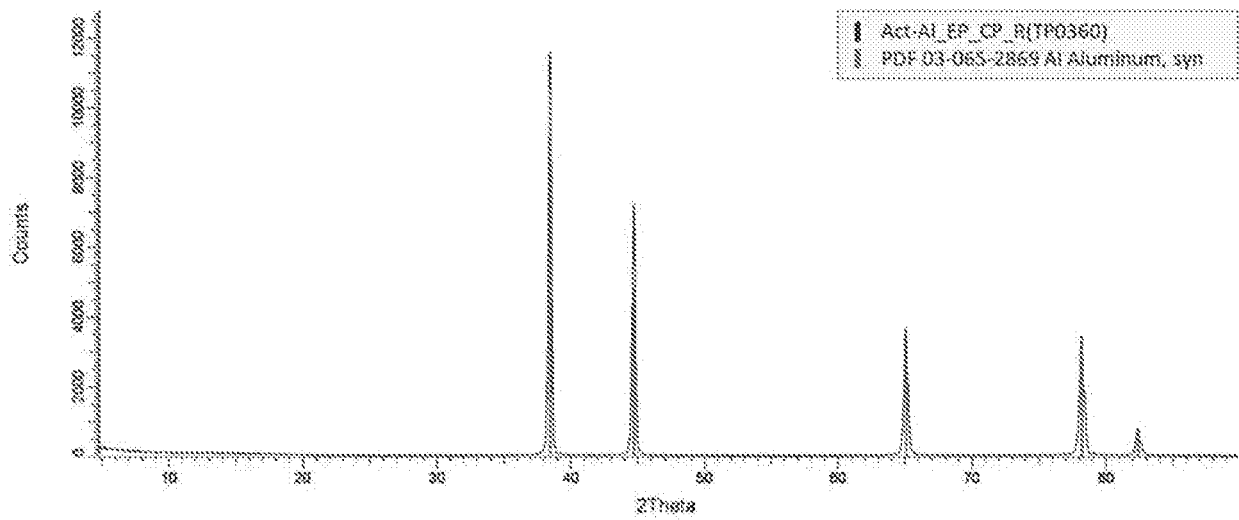


FIG. 7

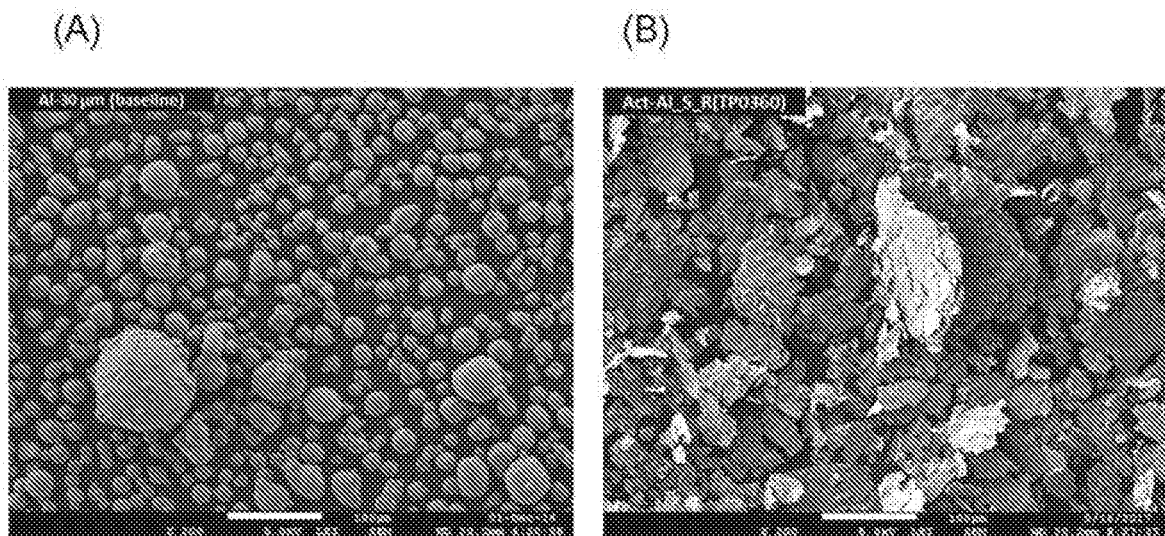


FIG. 8



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FIG. 9

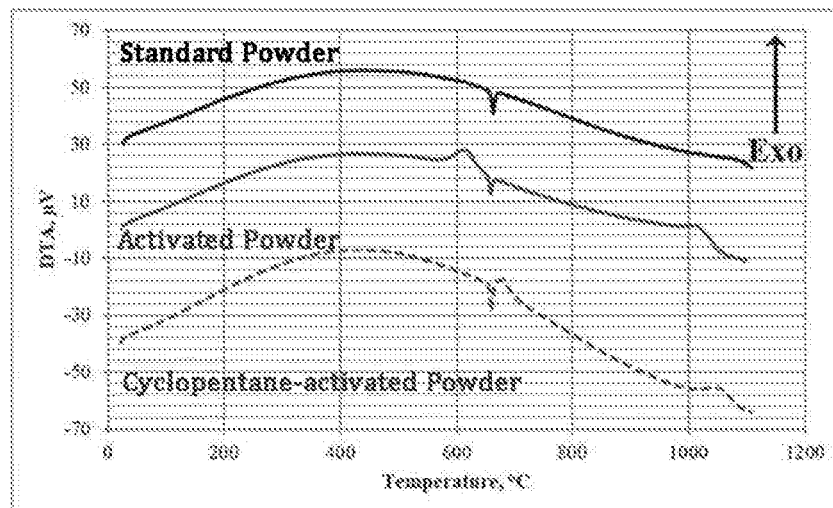


FIG. 10

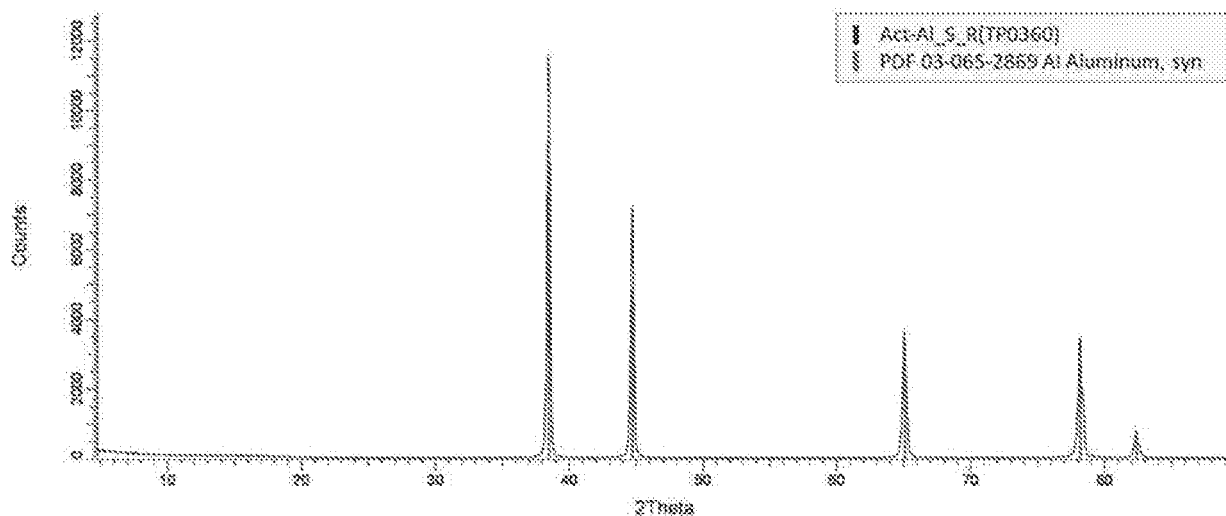
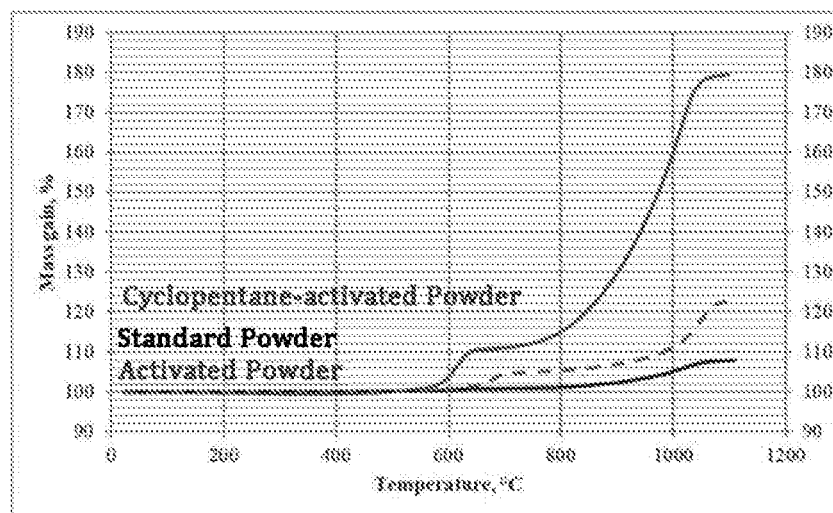


FIG. 11

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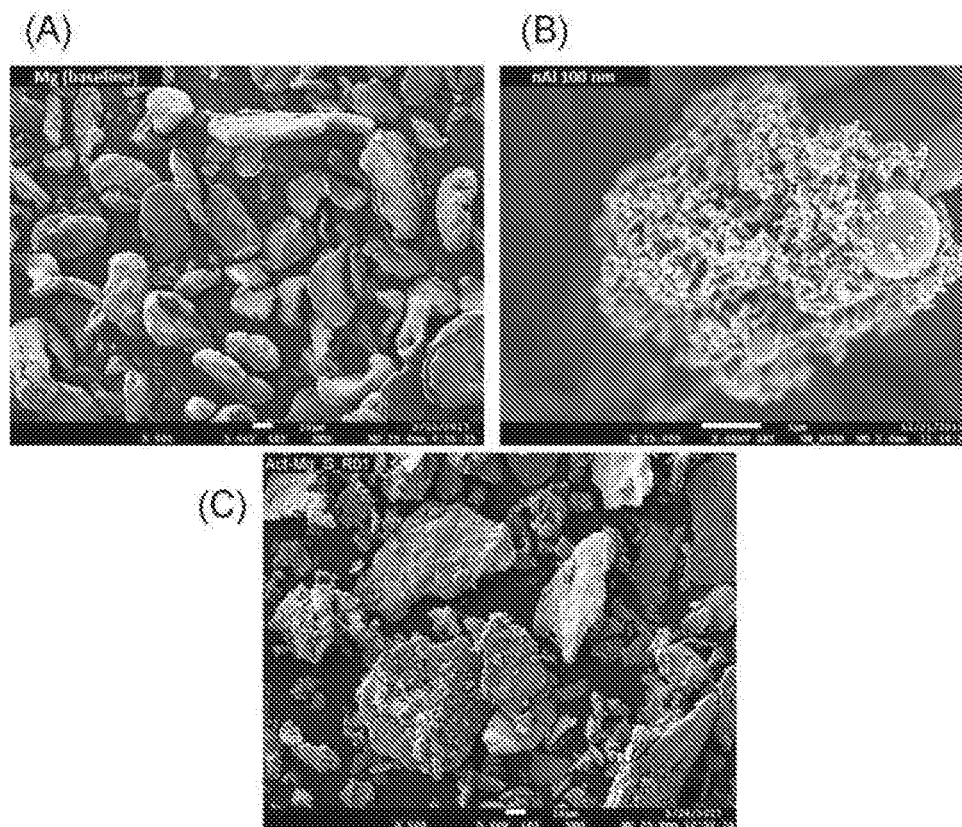


FIG. 12

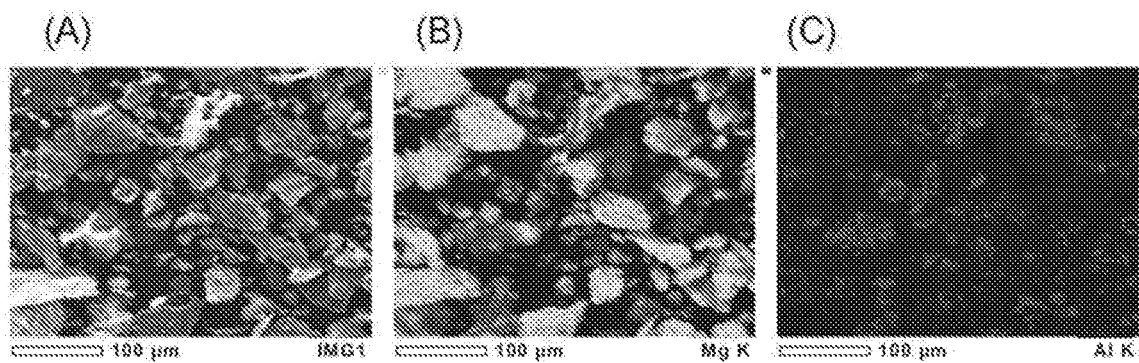


FIG. 13

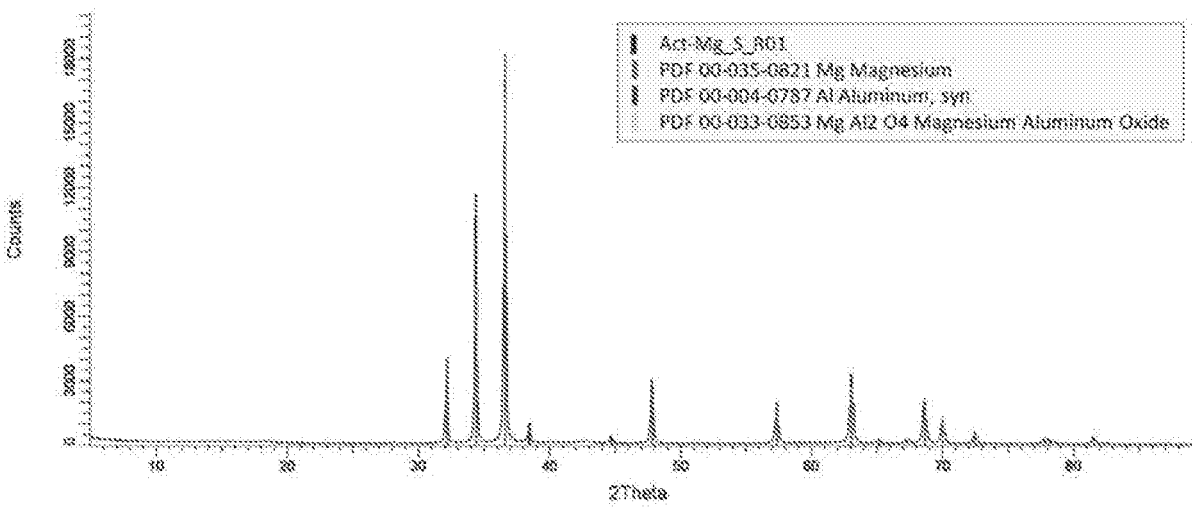


FIG. 14

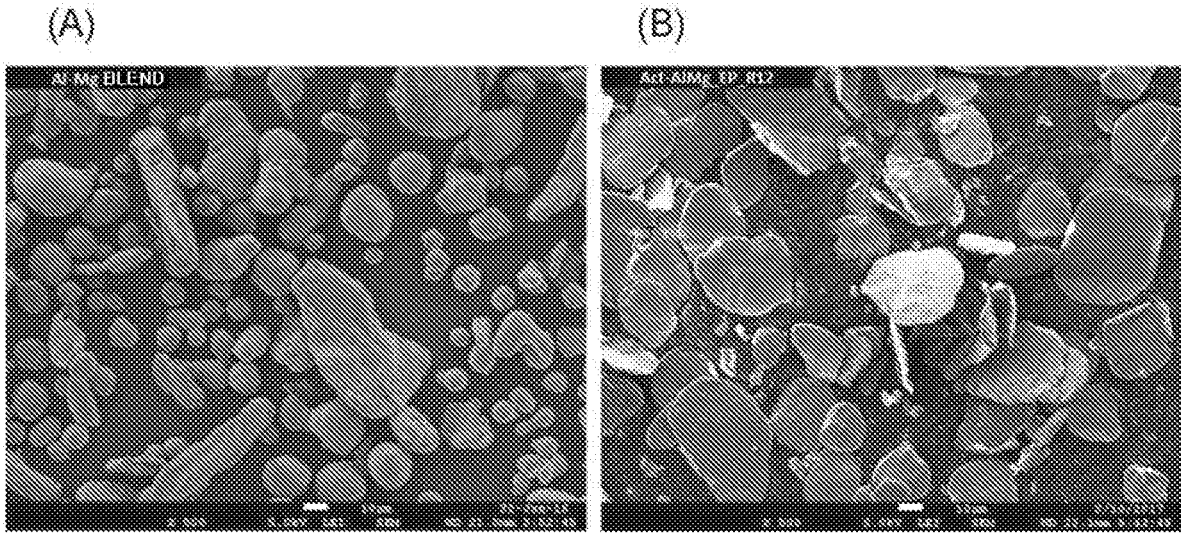


FIG. 15

FIG. 16

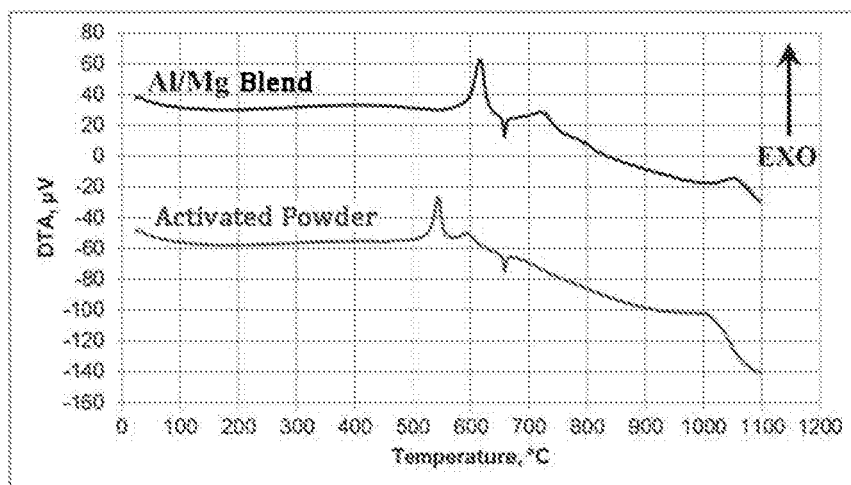


FIG. 17

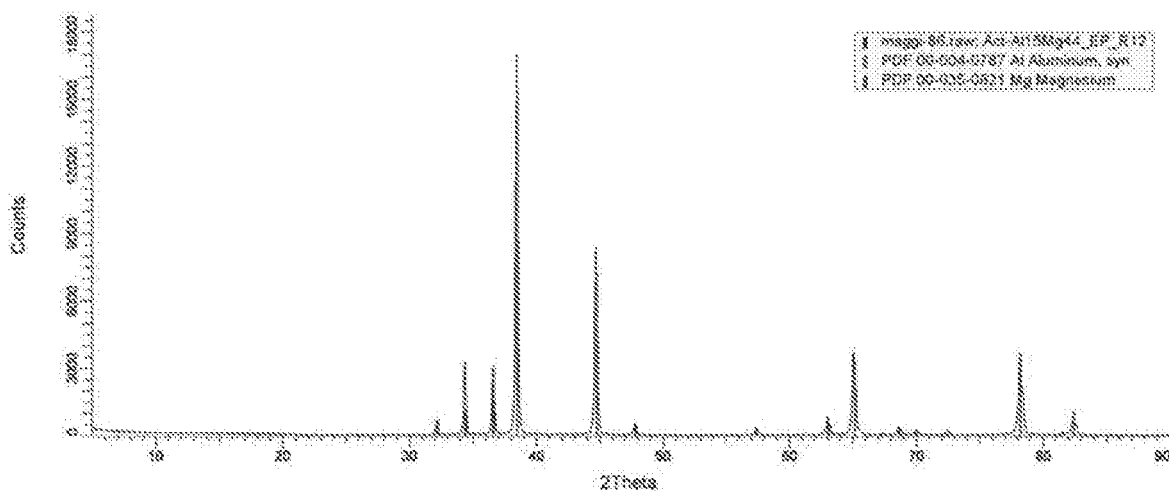
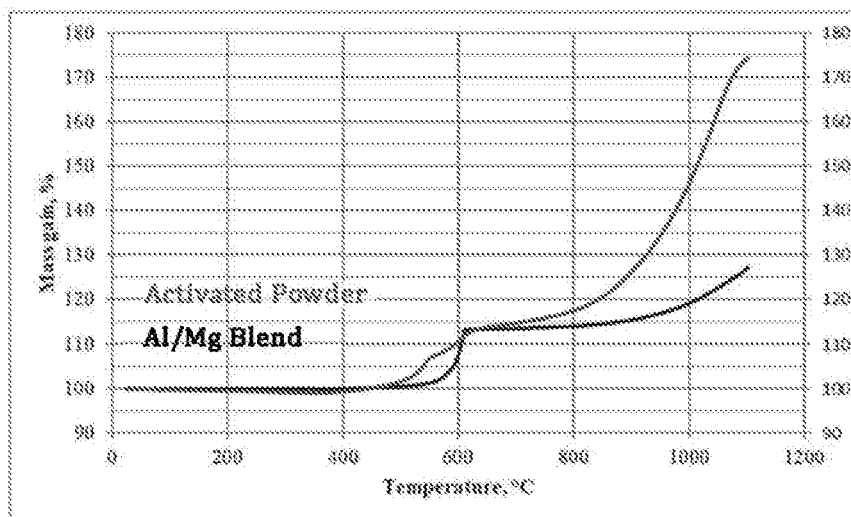


FIG. 18

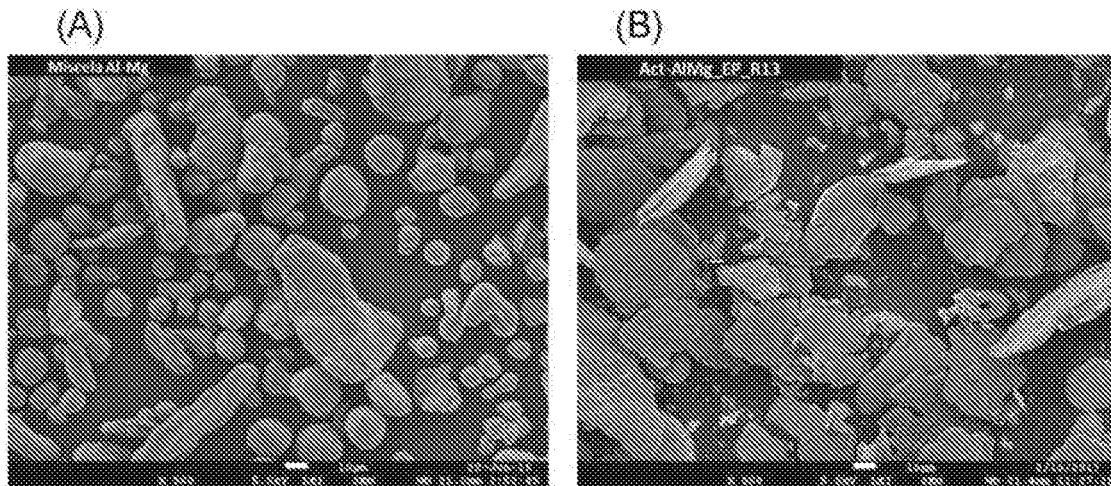


FIG.19

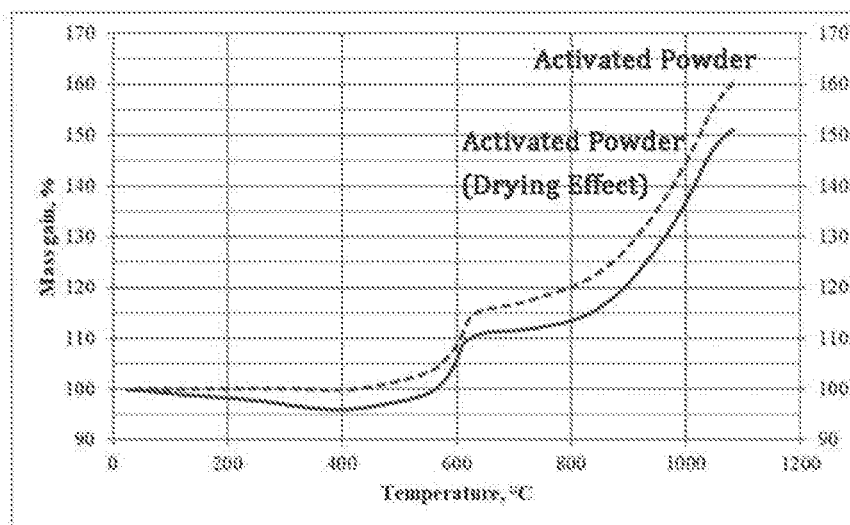


FIG. 20

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FIG. 21

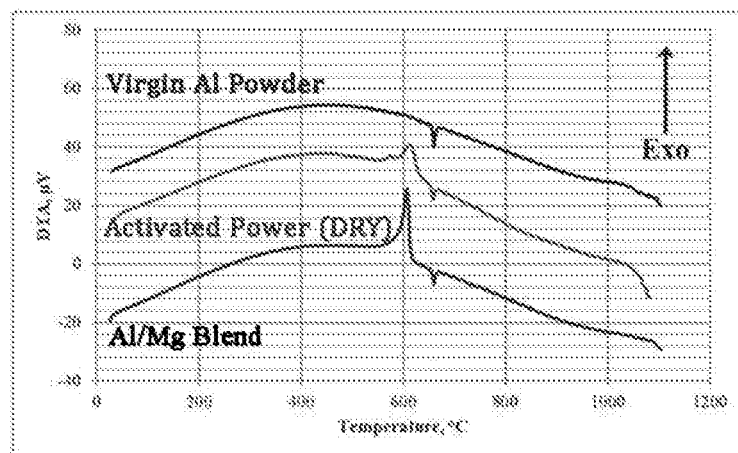


FIG. 22

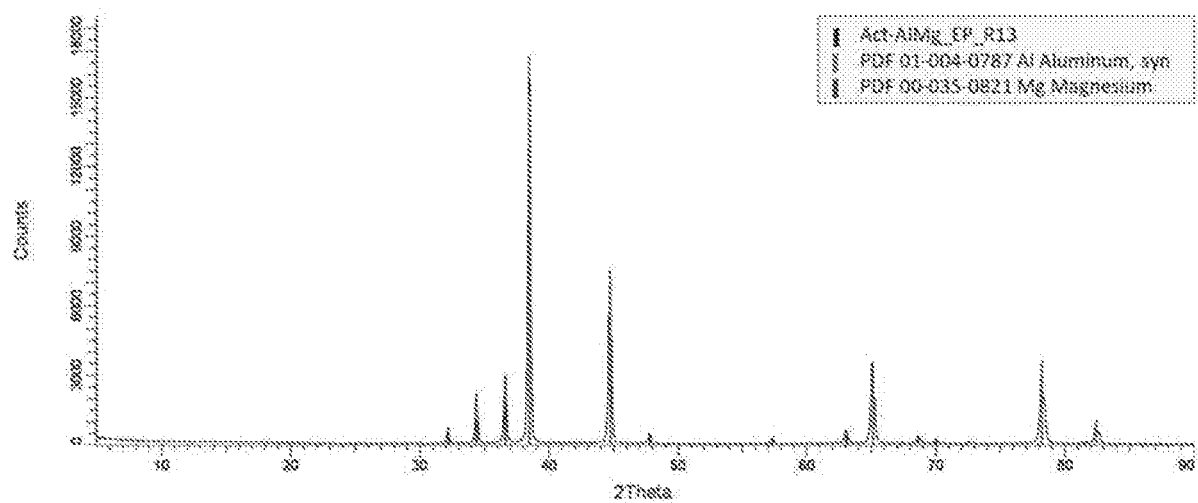
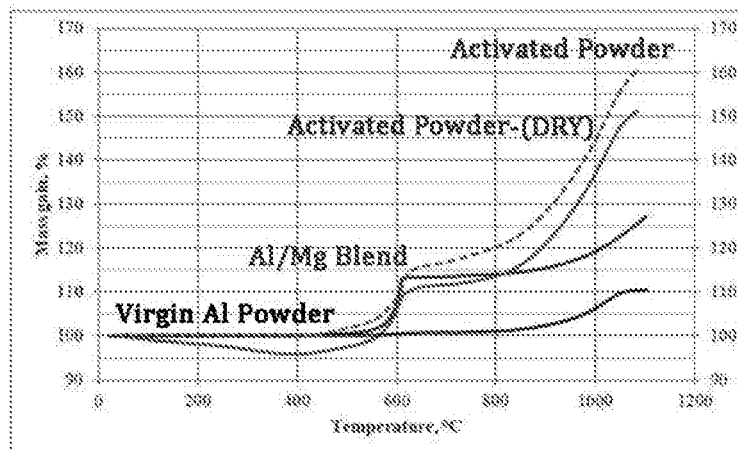


FIG. 23

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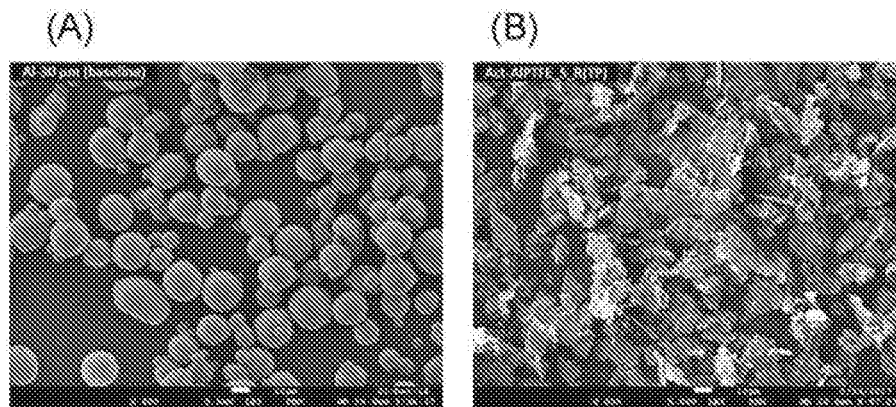


FIG. 24

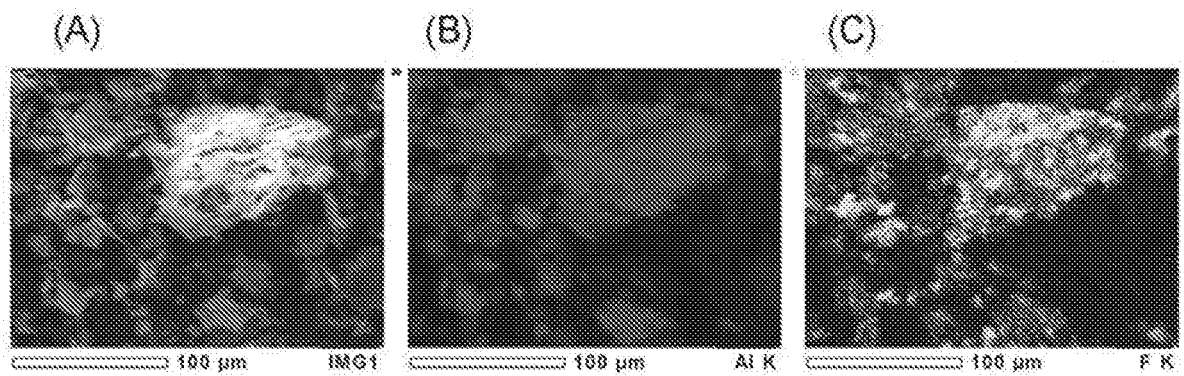


FIG. 25

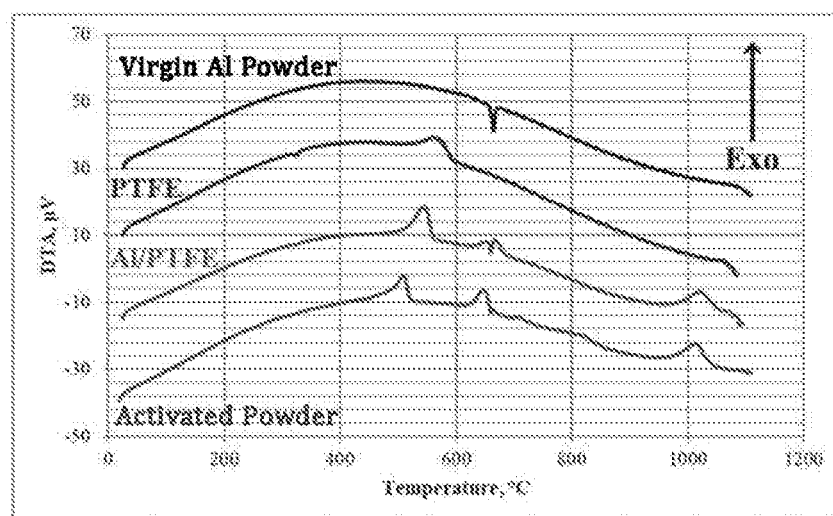


FIG. 26

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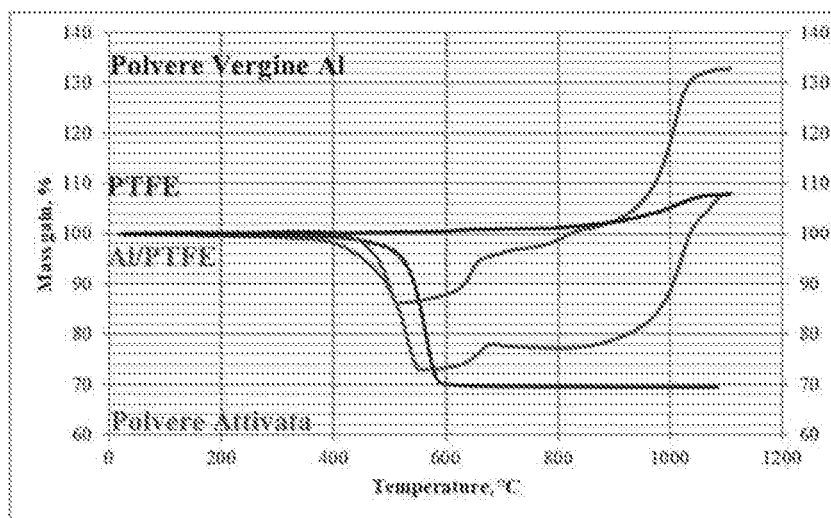


FIG. 27

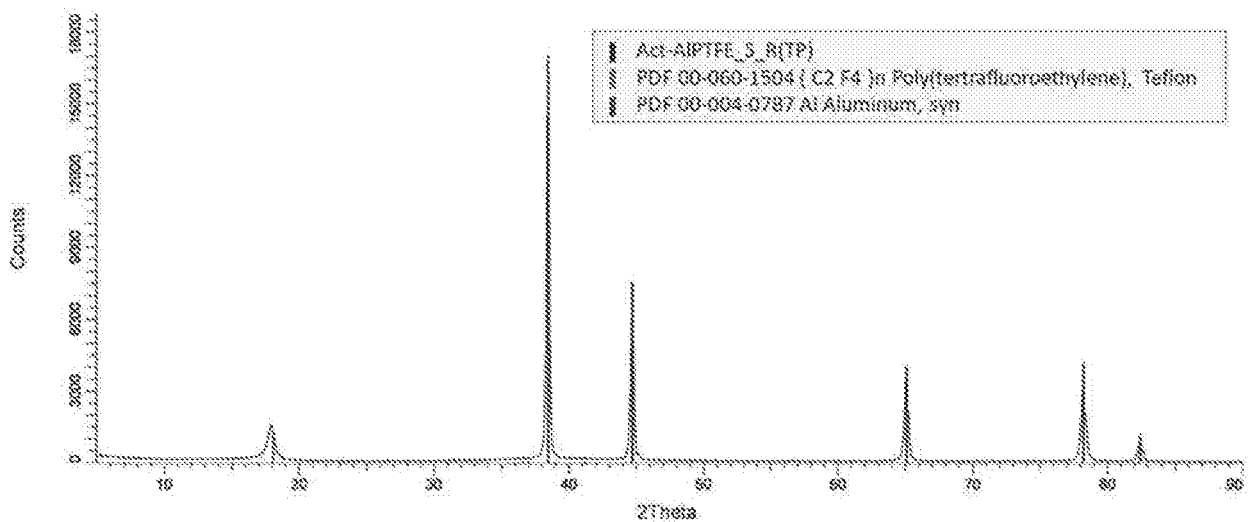


FIG. 28

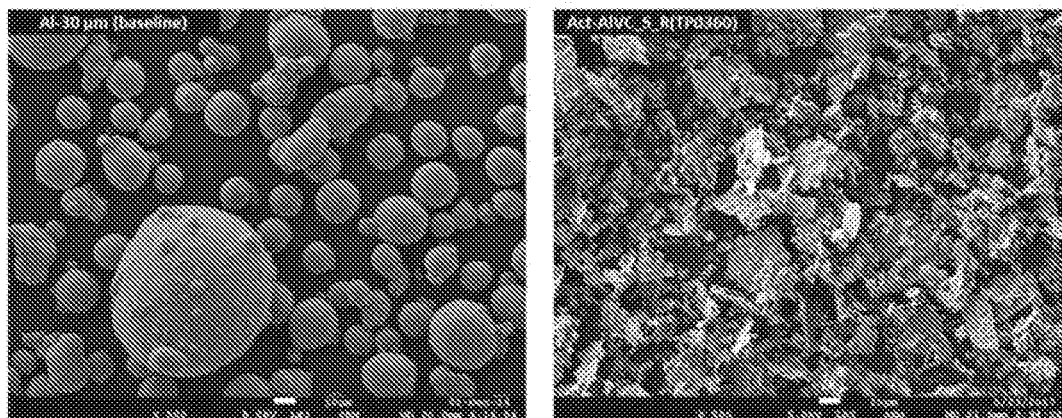


FIG. 29



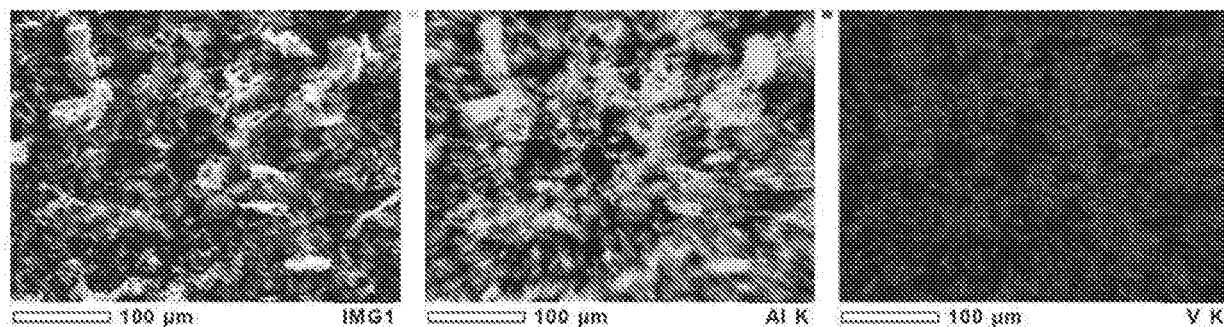


FIG. 30

FIG. 31

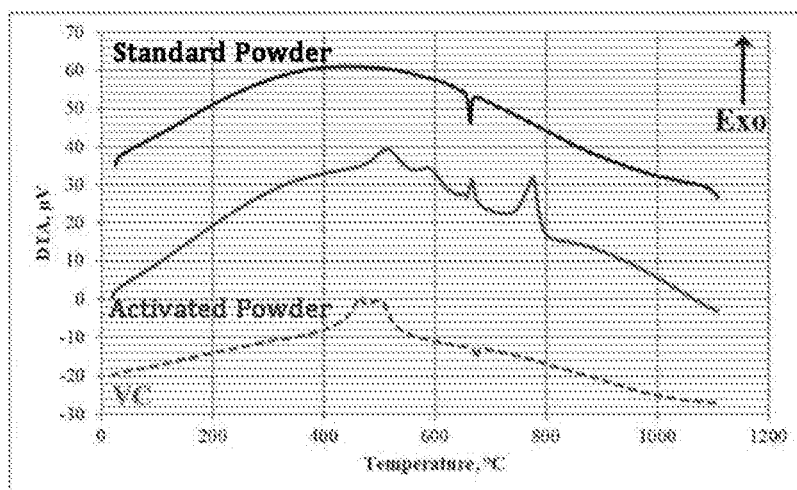
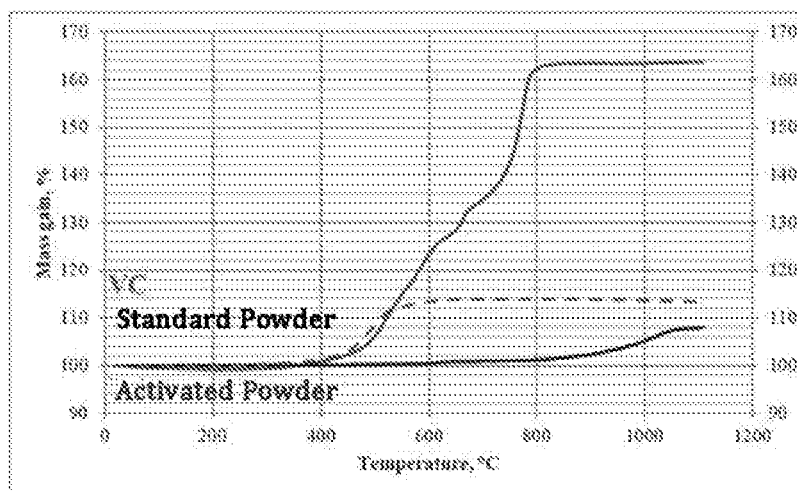


FIG. 32



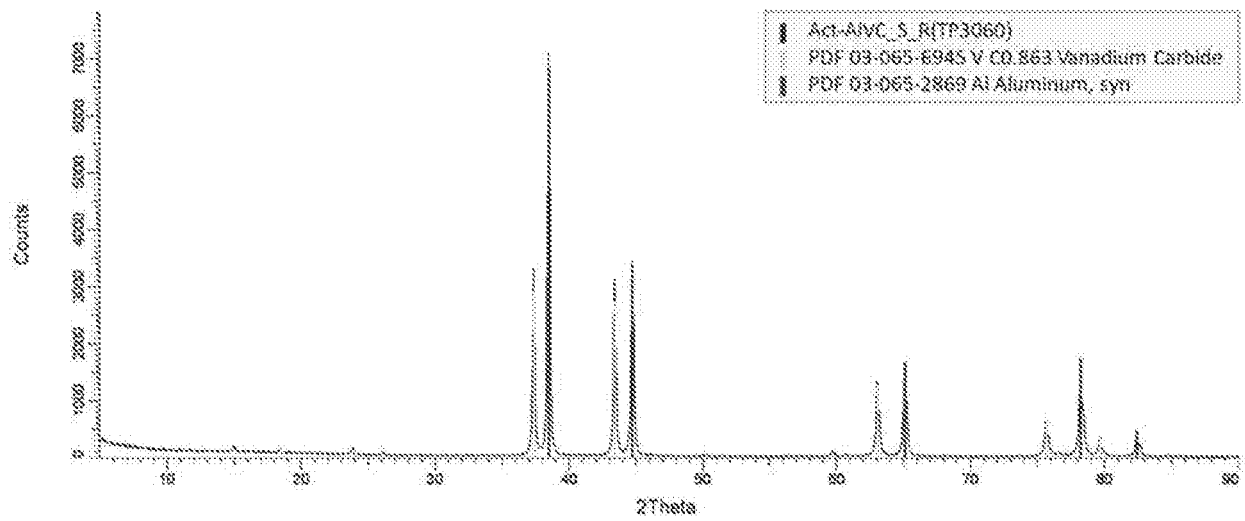


FIG. 33

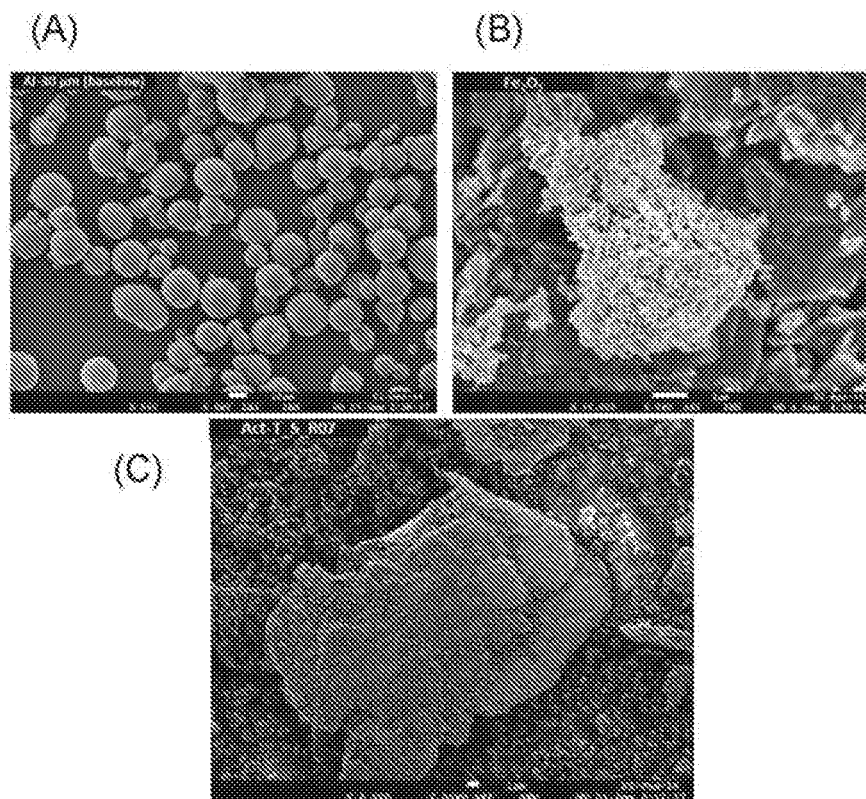


FIG. 34

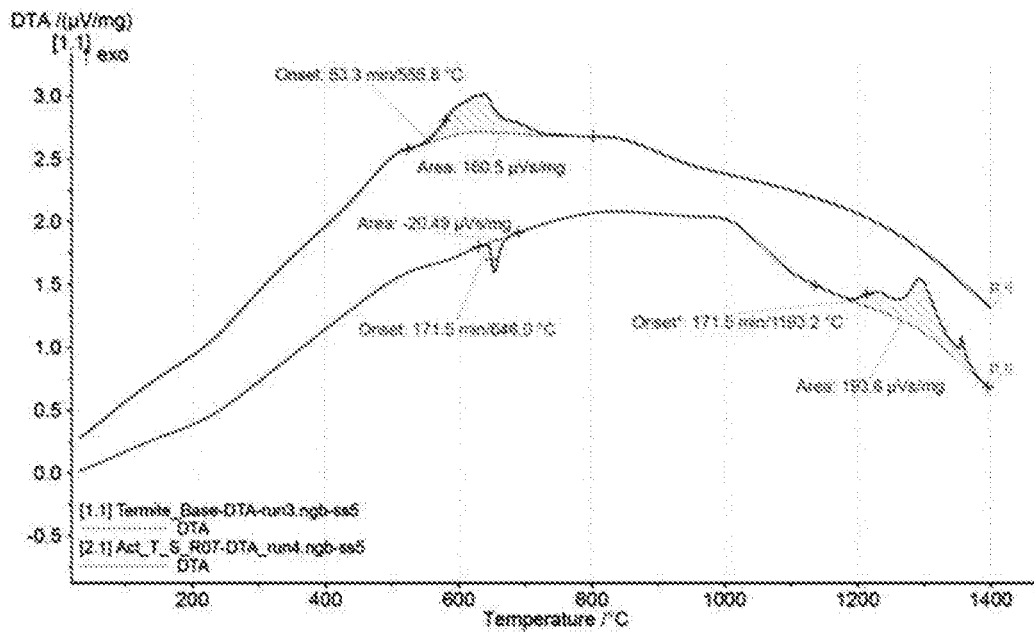


FIG. 35

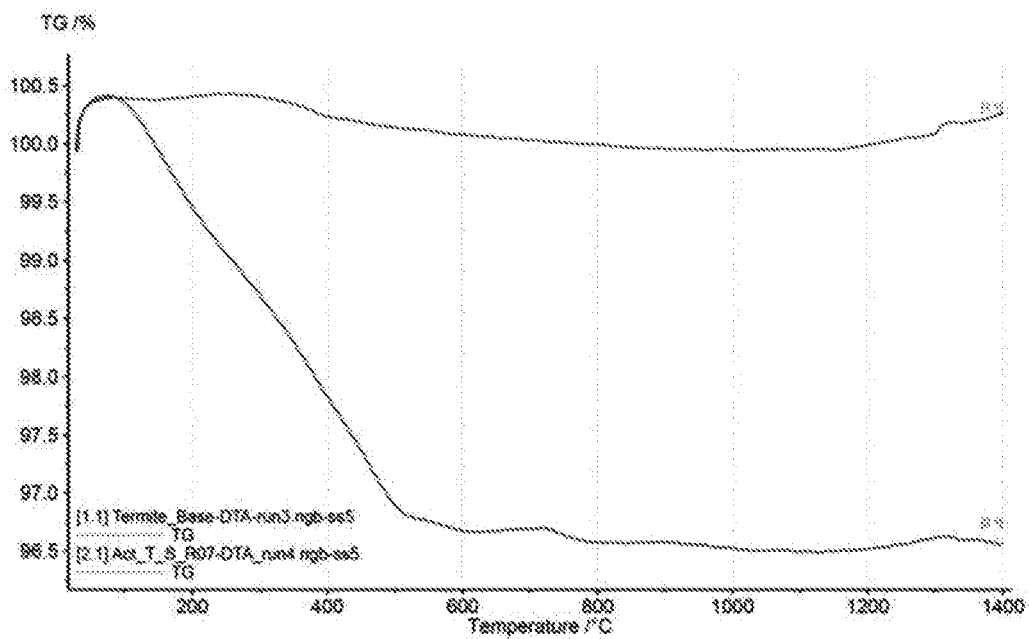


FIG. 36

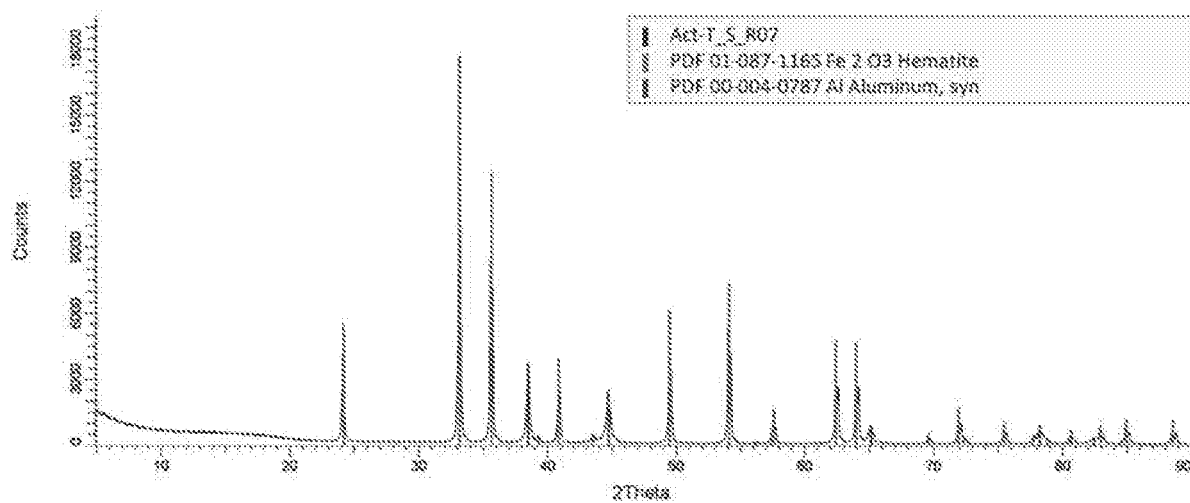


FIG. 37

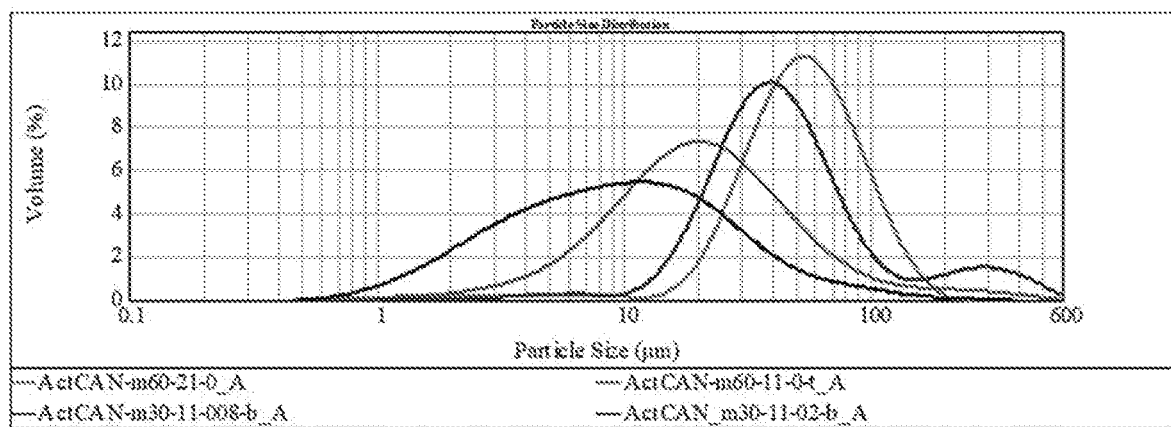


FIG. 38

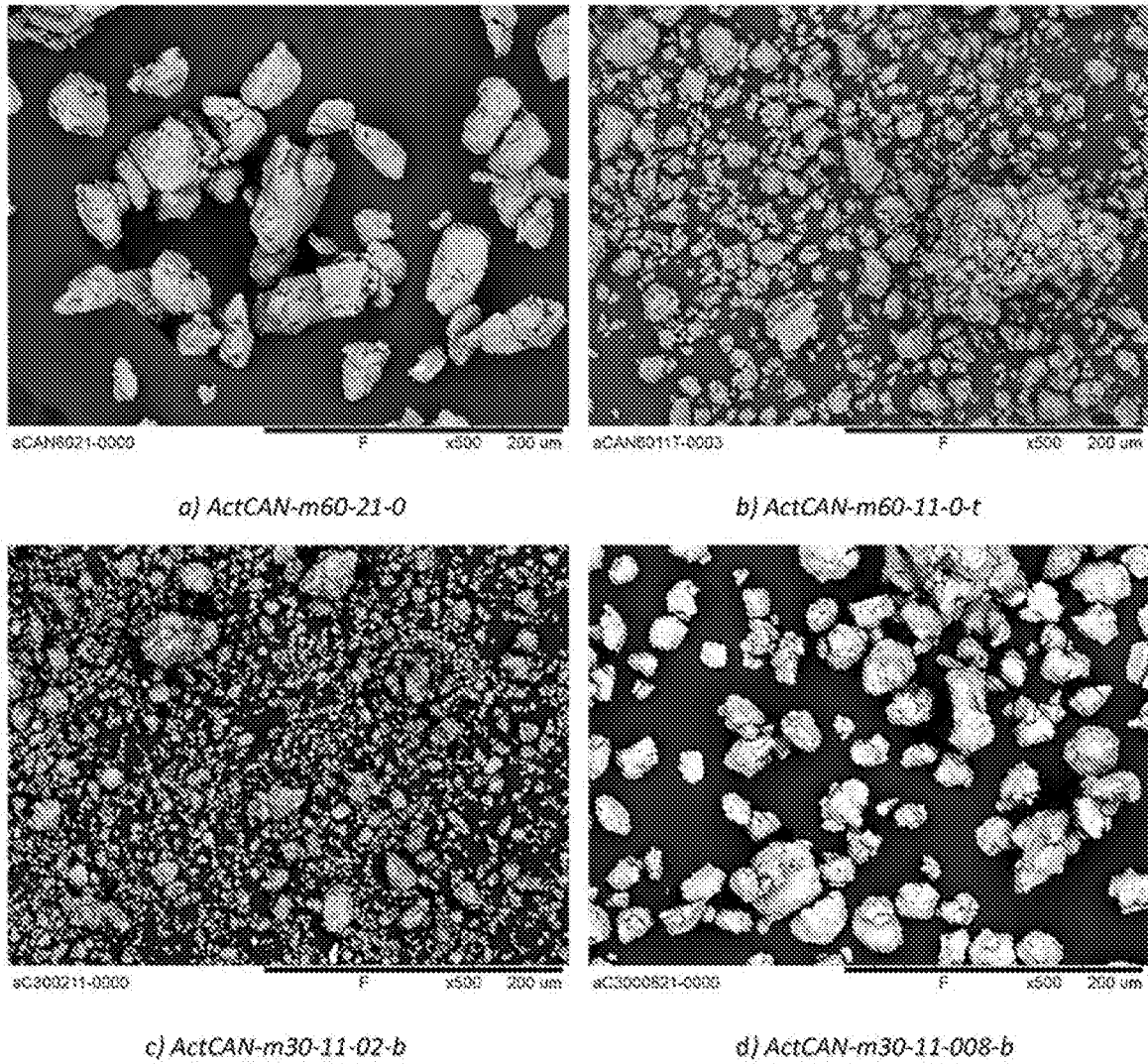


FIG.39

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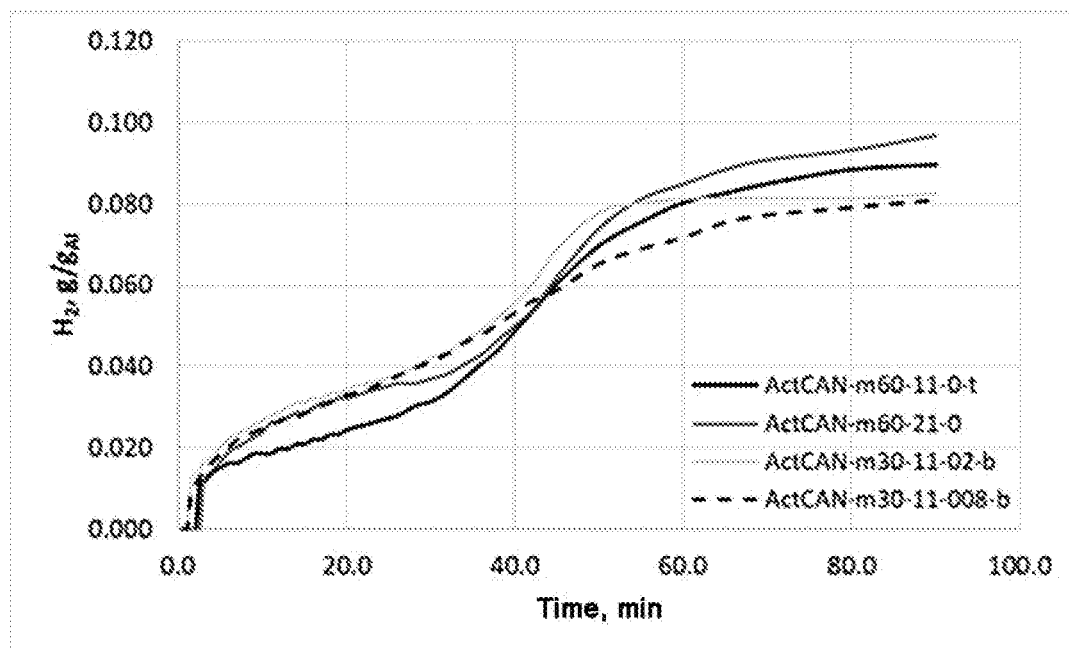


FIG. 40

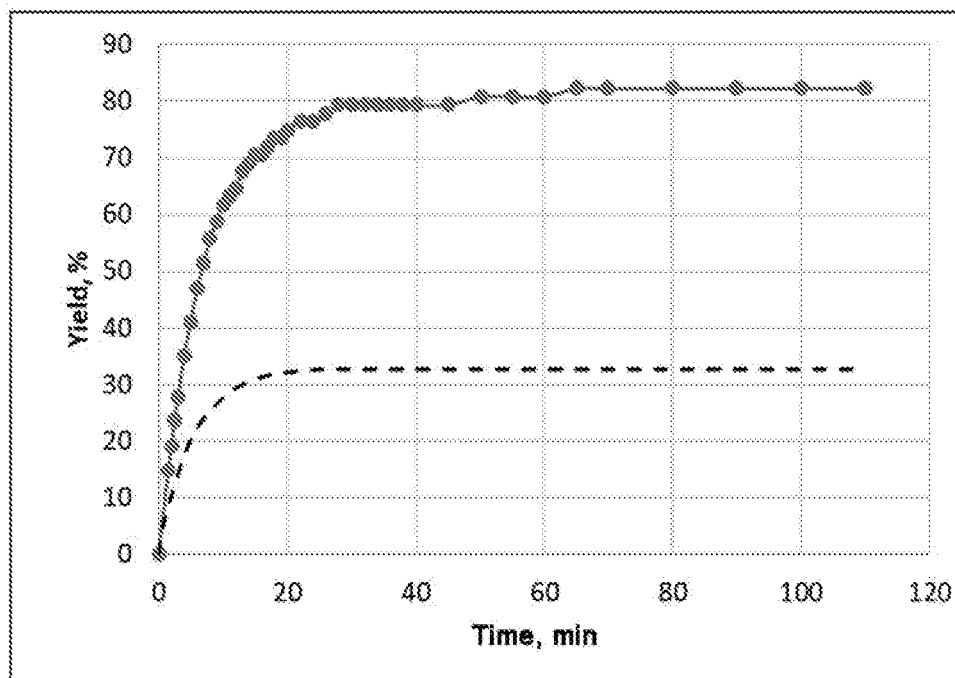
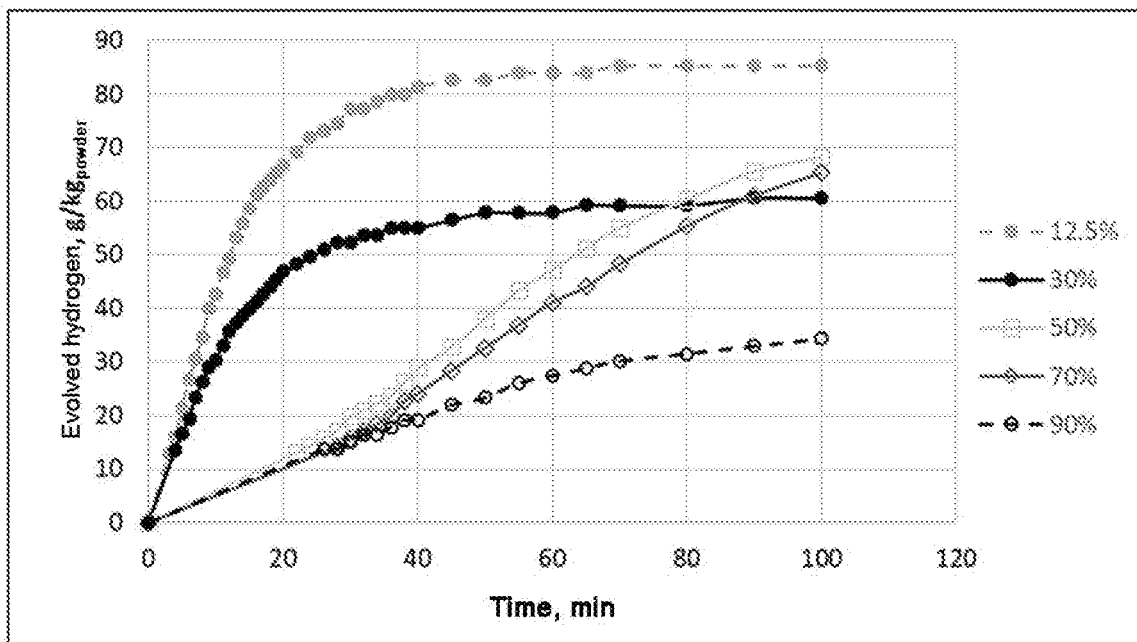


FIG. 41

A



B

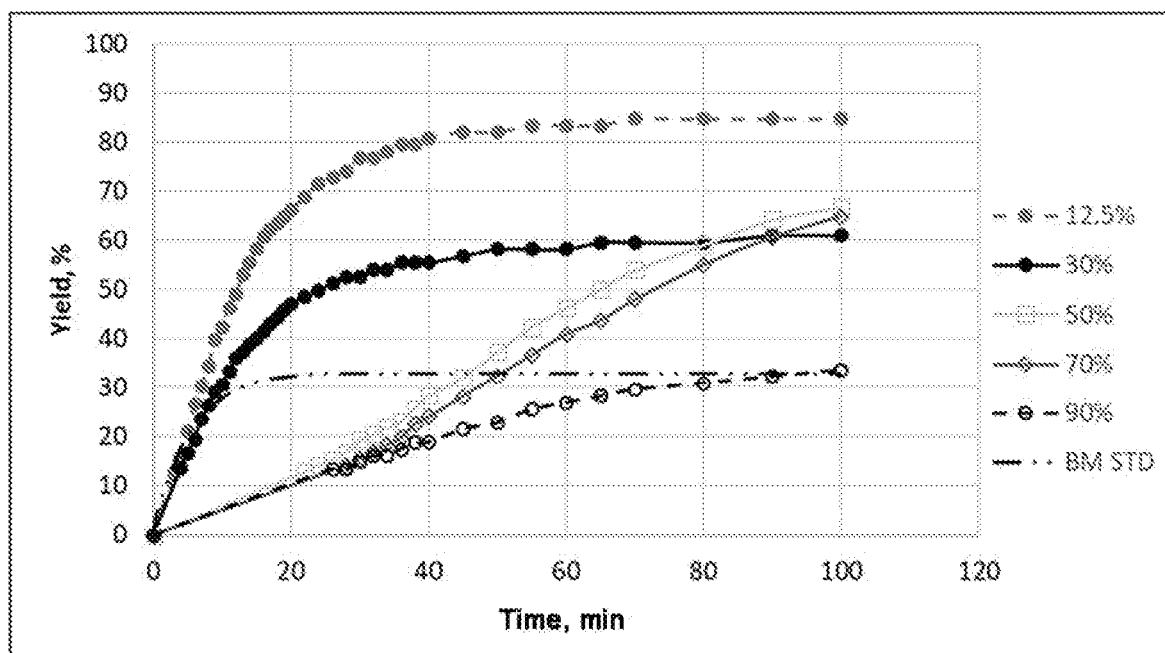
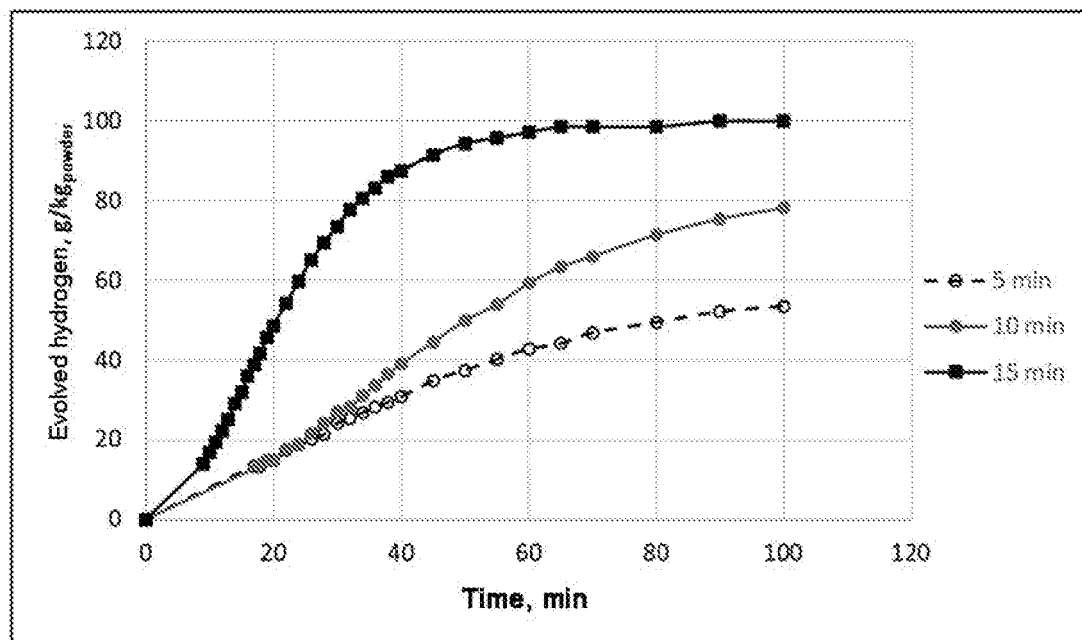


FIG. 42

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A



B

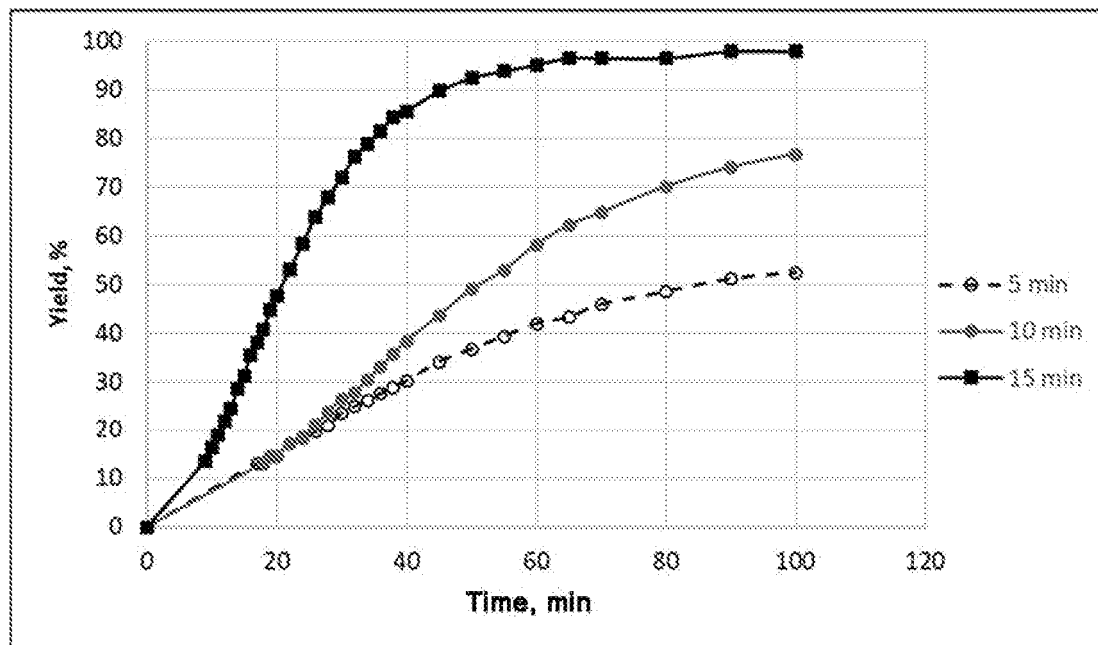


FIG. 43



# INTERNATIONAL SEARCH REPORT

International application No  
PCT/IB2018/059128

## A. CLASSIFICATION OF SUBJECT MATTER

INV. B02C17/14 B02C17/04 B02C17/18  
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)  
B02C

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)

EP0-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 2016/317391 A1 (BHARATWAJ BALAJI [US] ET AL) 3 November 2016 (2016-11-03)	1-12,14
A	paragraph [0008] - paragraph [0042]; claims 1-11	13,15
A	----- CN 103 316 742 B (SUN HARMONICS LTD) 8 April 2015 (2015-04-08) abstract	7
A	----- EP 2 202 017 A1 (KOREA ADVANCED INST SCI & TECH [KR]) 30 June 2010 (2010-06-30) paragraph [0020]	9
A	----- US 7 188 993 B1 (HOWE HAROLD W [US] ET AL) 13 March 2007 (2007-03-13) column 3, line 40 - column 4, line 17; figures 1-17	1
	-----	

☐ 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

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Date of the actual completion of the international search

14 March 2019

Date of mailing of the international search report

22/03/2019

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Fax: (+31-70) 340-3016

Authorized officer

Swiderski, Piotr

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2018/059128

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