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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
22 March 2018 (22.03.2018)

WIPO | PCT

(10) International Publication Number
WO 2018/053243 A1

(51) International Patent Classification:
B22F 3/11 (2006.01)

(21) International Application Number:
PCT/US2017/051747

(22) International Filing Date:
15 September 2017 (15.09.2017)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/395,721 16 September 2016 (16.09.2016) US

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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, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, 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, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *of inventorship (Rule 4.17(iv))*

Published:
— *with international search report (Art. 21(3))*

WO 2018/053243 A1

(54) Title: RAPID FABRICATION PROCESS OF POROUS ALUMINUM MATERIALS

(57) Abstract: Disclosed herein are porous aluminum materials with increased consolidation and hardness, and processes for their preparation using ultrasonic vibration.

Rapid Fabrication Process of Porous Aluminum Materials

RELATED APPLICATION

This application claims the benefit of priority to U.S. Provisional Patent Application serial number 62/395,721, filed September 16, 2016.

BACKGROUND

Current methods for fabricating porous aluminum materials involve using temperatures near or above the melting point of aluminum (about 660 ℃) under an inert atmosphere. These processes are based on sintering and spacer removal methods, such as an aluminum melt-foaming agent process (see, e.g., Byakova, et al. *Advances in Materials Science Engineering* 2014 pp. 1-9), investment casting (see, e.g., Jinnapat, et al., *Metals* 2011 1:49-64), and melt-gas injection (see, e.g., Surace et. al. *Advances in Materials Science Engineering* 2009 pp. 1-9). All of these methods can require over an hour at peak temperature to complete. The requirement for an inert atmosphere and the hold time at that temperature significantly increase the overall cost of fabrication. The resulting products can be further oxidized if exposed to oxygen at elevated temperatures. In addition, many known processes produce gaseous side products that necessitate protective measures and can increase production costs.

Porous aluminum materials have utility in a wide range of applications. For example, they can be used to produce cathode current collectors for high energy-density rechargeable lithium ion batteries. Hu et al. *Advanced Energy Materials* 2011 1:1012-1017. These materials are also useful as sound damping and energy absorption in vehicles. Furthermore, foam-based compact heat exchangers can be fabricated using porous aluminum materials with a large exchange surface, high permeability and high effective thermal conductivities. Thus, a need exists for an alternative approach to producing porous aluminum materials with increased operational simplicity and efficiency, greater cost effectiveness, and increased consolidation quality.

SUMMARY

Disclosed are methods of preparing a porous aluminum material, comprising the steps of:

a) applying a pressure of about 5-80 MPa to a mixture of aluminum powder and a salt spacer material;

b) heating the mixture to a temperature of about 100-550 °C and increasing the pressure to about 30-100 MPa for about 3 minutes;

c) applying ultrasonic vibration to the mixture for about 2-4 seconds;

d) allowing the mixture to cool at ambient temperature and pressure; and

e) washing the mixture in water using an ultrasonic cleaning tank;

thereby producing the porous aluminum material.

Also disclosed are porous aluminum materials produced by a process comprising the steps of:

a) applying a pressure of about 5-80 MPa to a mixture of aluminum powder and a salt spacer material;

b) heating the mixture to a temperature of about 100-550 °C and increasing the pressure to about 30-100 MPa for about 3 minutes;

c) applying ultrasonic vibration to the mixture for about 2-4 seconds;

d) allowing the mixture to cool at ambient temperature and pressure; and

e) washing the mixture in water using an ultrasonic cleaning tank.

BRIEF DESCRIPTIONS OF THE DRAWINGS

FIG. 1A shows mixing Al powder with NaCl particles.

FIG. 1B shows the converter apparatus with the die placed on the heater plate. The punch is placed on top of the die, and the sonotrode is lowered on the powder mixture to apply uniaxial pressure and high-frequency vibration.

FIG. 1C shows the consolidated material being placed in water to dissolve NaCl.

FIG. 1D shows the material being washed in an ultrasonic cleaning tank to remove NaCl.

FIG. 1E shows the skeleton of the porous aluminum material.

FIG. 2A shows a scanning electron micrograph (SEM) image of the as-received Al powders.

FIG. 2B shows the SEM image of the NaCl particles.

FIG. 2C shows the size distribution of the Al powders.

FIG. 2D shows the size distribution of the as-received NaCl particles.

FIG. 3 shows a schematic diagram of the ultrasonic powder consolidation procedure outlined in Example 1.

FIG. 4A shows an optical microscopy (OM) image of the microstructures in the cell wall regions of sample No. 1.

FIG. 4B shows an OM image of the microstructures in the cell wall regions of sample No. 2.

FIG. 4C shows an OM image of the microstructures in the cell wall regions of sample No. 3.

FIG. 4D shows an OM image of the microstructures in the cell wall regions of sample No. 4.

FIG. 4E shows an OM image of the microstructures in the cell wall regions of sample No. 5.

FIG. 4F shows an OM image of the microstructures in the cell wall regions of sample No. 6.

FIG. 5A shows an OM image of the microstructures in the cell wall regions of sample No. 7.

FIG. 5B shows an OM image of the microstructures in the cell wall regions of sample No. 8.

FIG. 5C shows an OM image of the microstructures in the cell wall regions of sample No. 9.

FIG. 5D shows an OM image of the microstructures in the cell wall regions of sample No. 10.

FIG. 5E shows an OM image of the microstructures in the cell wall regions of sample No. 11.

FIG. 5F shows an OM image of the microstructures in the cell wall regions of sample No. 12.

FIG. 6A shows an SEM image of sample No. 3 at 1 μm magnification.

FIG. 6B shows an SEM image of sample No. 4 at 1 μm magnification.

FIG. 7A shows an OM image of a cross-section of sample No. 2 fabricated with 4 seconds of ultrasonic vibration followed by 5 minutes of ultrasonic washing.

FIG. 7B shows an OM image of a cross-section of sample No. 4 fabricated with 4 seconds of ultrasonic vibration followed by 5 minutes of ultrasonic washing.

FIG. 7C shows an OM image of a cross-section of sample No. 6 fabricated with 4 seconds of ultrasonic vibration followed by 5 minutes of ultrasonic washing.

FIG. 7D shows an OM image of a cross-section of sample No. 8 fabricated with 4 seconds of ultrasonic vibration followed by 5 minutes of ultrasonic washing.

FIG. 7E shows an OM image of a cross-section of sample No. 10 fabricated with 4 seconds of ultrasonic vibration followed by 5 minutes of ultrasonic washing.

FIG. 7F shows an OM image of a cross-section of sample No. 12 fabricated with 4 seconds of ultrasonic vibration followed by 5 minutes of ultrasonic washing.

FIG. 8A shows an OM image of a cross-section of sample No. 3 at 500 μm magnification after 1 minute of ultrasonic washing in ambient air.

FIG. 8B shows an OM image of a cross-section of sample No. 4 at 500 μm magnification after 5 minutes of ultrasonic washing in ambient air.

FIG. 8C shows an OM image of a cross-section of sample No. 4 at 500 μm magnification after 5 minutes of ultrasonic washing under an argon atmosphere.

FIG. 9A shows a SEM image of sample No. 4 at 500 μm magnification.

FIG. 9B shows a SEM image of sample No. 4 at 200 μm magnification.

FIG. 9C shows a SEM image of sample No. 4 at 100 μm magnification.

FIG. 9D shows a SEM image of sample No. 4 at 50 μm magnification.

FIG. 9E shows a SEM image of sample No. 4 at 10 μm magnification.

FIG. 9F shows a SEM image of sample No. 4 at 5 μm magnification.

FIG. 9G shows a SEM image of sample No. 10 at 200 μm magnification.

FIG. 9H shows a SEM image of sample No. 10 at 100 μm magnification.

FIG. 9I shows a SEM image of sample No. 10 at 10 μm magnification.

FIG. 10A shows a high magnification optical micrograph of sample No. 3 at 10 μm. This sample No. 3 was prepared in ambient air.

FIG. 10B shows a corresponding SEM image of sample No. 3 at 10 μm. This sample No. 3 was prepared in ambient air.

FIG. 10C shows a high magnification optical micrograph of sample No. 4 at 10 μm. This sample No. 4 was prepared in ambient air.

FIG. 10D shows a corresponding SEM image of sample No. 4 at 10 μm. This sample No. 4 was prepared in ambient air.

FIG. 10E shows a high magnification optical micrograph of sample No. 4 at 10 μm. This sample No. 4 was prepared under Ar atmosphere.

FIG. 10F shows a corresponding SEM image of sample No. 4 at 10 μm. This sample No. 4 was prepared under Ar atmosphere.

FIG. 11A shows the Vickers hardness and percentage of dissolved mass of sample Nos. 2, 4 and 6.

FIG. 11B shows the Vickers hardness and percentage of dissolved mass of sample Nos. 8, 10 and 12.

FIG. 12A shows the Vickers hardness test results and estimated dislocation density of sample Nos. 3 and 4.

FIG. 12B is an OM image of the Vickers indentation on the cell wall region of sample No. 3.

FIG. 12C is an OM image of the Vickers indentation on the cell wall region of sample No. 4 prepared in ambient air.

FIG. 12D is an OM image of the Vickers indentation on the cell wall region of sample No. 4 prepared under argon atmosphere. Each TEM is shown at 10 μm magnification.

FIG. 13A shows a SEM image of sample No. 3.

FIG. 13B shows a higher magnification SEM image of sample No. 3. This sample No. 3 was prepared in ambient air.

FIG. 13C shows a plot of counts vs. Energy (KeV) for aluminum and oxygen in sample No. 3.

FIG. 13D shows a SEM image of sample No. 4 at 10 μm. This sample No. 4 was prepared in ambient air.

FIG. 13E shows a magnification of sample No. 4 at 1 μm. This sample No. 4 was prepared in ambient air.

FIG. 13F shows a plot of counts vs. Energy (KeV) for aluminum and oxygen in sample No. 4. This sample No. 4 was prepared in ambient air.

FIG. 13G shows a SEM image of sample No. 4. This sample No. 4 was prepared in ambient air.

FIG. 13H shows a higher magnification SEM image of sample No. 4. This sample No. 4 was prepared under Ar atmosphere.

FIG. 13I shows a plot of counts vs. Energy (KeV) for aluminum and oxygen in this sample No. 4. This sample No. 4 was prepared under Ar atmosphere.

FIG. 14 shows an SEM image of sample No. 4 prepared in ambient air with four spots where energy-dispersive X-ray spectroscopy (EDS) was performed.

FIG. 15A shows an OM image of a cross-section of sample No. 13 at 500 μm.

FIG. 15B shows an OMimage of a cross-section of sample No. 14 at 500 μm.

FIG. 15C shows an OMimage of a cross-section of sample No. 15 at 500 μm.

FIG. 15D shows an OMimage of a cross-section of sample No. 16 at 500 μm.

FIG. 16A shows an OMimage of a cross-section of sample No. 17 at 500 μm.

FIG. 16B shows an OMimage of a cross-section of sample No. 17 at 50 μm.

FIG. 16C shows an OMimage of a cross-section of sample No. 17 at 10 μm.

FIG. 17A shows a TEM image of interparticle boundaries in sample No. 18.

FIG. 17B shows a TEM image of interparticle boundaries in sample No. 19.

FIG. 18A shows a TEM image of interparticle boundaries in sample No. 3 at 1.0 μm.

FIG. 18B shows a TEM image of interparticle boundaries in sample No. 3 at 500 nm.

FIG. 18C shows a TEM image of interparticle boundaries in sample No. 4 at 1.0 μm.

FIG. 18D shows a TEM image of interparticle boundaries in sample No. 4 at 500 nm.

DETAILED DESCRIPTION

Definitions

The term "ambient" as it pertains to air temperature and pressure, respectively, refers to a temperature range of 15-27 °C and the pressure exerted by a column of mercury 29.92 inches (760 mm) high, or 1013 millibars (101.3 kilopascals).

The term "mixture" refers to the product obtained by any process that brings two or more components within contact of one another such that each component retains its chemical identity and properties. The resulting mixture may have different properties than the individual components. A mixture can be attained by shaking, blending, stirring, agitation, and other methods known in the art. A mixture may be heterogeneous, having non-uniform texture and composition, or homogenous where all components have different identities but are in the same phase. As used herein, a mixture is not limited by its particle size or the particle size of its individual components.

The term "in-plane ultrasonic vibration" refers to a process whereby a sample is physically contacted by vibration at a frequency of above 20 KHz that is aligned parallel to the surface to which the pressure is applied. The physical contact can be directly on the sample or through an intermediate solid such as a punch. The vibration can be applied using a sonotrode.

The term "washing" as used herein refers to any process by which a solid sample is placed in a liquid permeable container and then partially or fully submerged in a liquid, such as water, in a larger tank. *See, e.g.,* FIG. 1D. One or more transducers placed outside the tank are used to contact the sample with sound waves at a frequency of above 20 KHz (ultrasonic frequency). These sound waves can be aligned in a single plane or contact the sample at two or more planes of direction. The washing may thus occur when the sample is

motionless or when the sample is moved about in space, such as by pulling, pushing, swaying, turning, rotating, swiveling, or other means known in the art.

A numerical range expressed in the form "about x-y units," e.g., "about 5-10 minutes," means "about x units to about y units," e.g., "about 5 minutes to about 10 minutes."

Disclosed herein are methods of preparing a porous aluminum material, comprising the steps of:

a) applying a pressure of about 5-80 MPa to a mixture of aluminum powder and a salt spacer material;

b) heating the mixture to a temperature of about 100-550 °C and increasing the pressure to about 30-100 MPa for about 3 minutes;

c) applying ultrasonic vibration to the mixture for about 2-4 seconds;

d) allowing the mixture to cool at ambient temperature and pressure; and

e) washing the mixture in water using an ultrasonic cleaning tank;

thereby producing the porous aluminum material.

Also disclosed are porous aluminum materials produced by a process comprising the steps of:

a) applying a pressure of about 5-80 MPa to a mixture of aluminum powder and a salt spacer material;

b) heating the mixture to a temperature of about 100-550 °C and increasing the pressure to about 30-100 MPa for about 3 minutes;

c) applying ultrasonic vibration to the mixture for about 2-4 seconds;

d) allowing the mixture to cool at ambient temperature and pressure; and

e) washing the mixture in water using an ultrasonic cleaning tank.

In some embodiments, the salt spacer material is NaCl. In other embodiments, the salt spacer material can be KCl or $AlK(SO_4)_2 \bullet 12(H_2O)$. In certain embodiments, the weight percent ratio of Al powder:salt spacer material is from about 10:90 to about 50:50, such as about 20:80, further such as about 15:85. In some embodiments, wherein the Al powder has a size distribution ranging from about 5-100 μm, such as from about 8-56 μm. In other

embodiments, the salt spacer material is NaCl and is particulate with a size distribution of about 100-500 μm, such as about 210-420 μm.

In some embodiments, the pressure in steps a) and b) is uniaxial and applied using a sonotrode. The pressure can be, for example, about 10 MPa, about 60 MPa or about 80 MPa. In some embodiments, the temperature in step b) ranges from about 400 °C - 500 °C, such as about 400 °C, about 450 °C, or about 500 °C. In certain embodiments, wherein the ultrasonic vibration in step c) ranges from about 1-50 KHz (e.g., 20 KHz) with a 9 mm amplitude. The ultrasonic vibration can be normal vibration on in-plane vibration, and be applied for about 1-10 seconds, such as about 2 or about 4 seconds.

In some embodiments, the ultrasonic washing occurs for about 1-10 minutes, such as about 5 minutes. During step e), the salt spacer material is removed. In certain embodiments, greater than or equal to about 95% of the salt spacer material is removed during step e). The resulting porous aluminum material has greater than or equal to about 85% porosity. This porosity can be attained with a starting weight percent ratio of Al powder:salt spacer material from about 10:90 to about 40:60, such as about 20:80. In some embodiments, the porous aluminum material has a thickness of less than or equal to about 2 mm, such as about 1.20 mm. The processes disclosed herein can occur in an ambient atmosphere or under inert atmosphere, such as argon.

The present method uses aluminum powder with a salt spacer material and proceeds at a temperature at least about 120 °C below current processes and at a lower pressure. The method uses an ultrasonic powder consolidation that occurs within about 3 minutes and does not produce gaseous side products. The time period includes a holding time at an elevated temperature for about 3 minutes, followed by applying in-plane vibration for a few seconds. The process is conducted in the open air, in the presence of oxygen. The ultrasonic vibration-assisted powder repacking helps increase initial compact densification, decrease surface oxide disruption, enable metallurgical bonding between deformed particles, and create formation of strain hardened aluminum cell walls that provided the strength of the porous aluminum material product.

Ultrasonic vibration enables a consolidation process for producing porous aluminum from aluminum powder and spacer material, such as NaCl, KCl, or $AlK(SO_4)_2 \bullet 12(H_2O)$. The vibration can be in-plane or normal vibration. The temperature can range from about 100-550 °C with pressure in the range of about 30-100 MPa. The rapid fabrication process

occurs below the melting point of aluminum and benefits from high strain-rate plastic deformation. After ultrasonic fabrication treatment, the material is strong enough to withstand ultrasonic washing with water to remove the spacer material, giving an aluminum product with greater than or equal to about 85% interconnected porosity and uniform morphology. The aluminum particles are not further oxidized during the heating and consolidation process as the ultrasonic vibration disrupts the oxide on the particles, facilitating immediate metallurgical bonding before further oxidation can take place. Thus, the process can be conducted in the open air without a protective inert atmosphere. However, the process performs equally well when conducted under an inert atmosphere, such as argon.

During the consolidation process, the ultrasonic vibration period leads to porous aluminum material having much higher degrees of densification than those produced without ultrasonic vibration. In some embodiments, the vibration is applied for about 4 seconds. Vibration can be applied for up to about 10 seconds. Increasing the consolidation temperature and pressure increases densification in the cell wall regions of the porous aluminum material. Holding the material at a high temperature during ultrasonic vibration serves to increase flow stress which is favorable for creating plastic deformation. Interparticle boundaries are completely filled. If ultrasonic vibration is not used, the aluminum material only strain hardens to a certain extent, leaving particle interstices unfilled. These materials suffer from poor alignment of particles and unfilled triple junctions, indicating a weaker consolidation was achieved.

An ultrasonic washing test longer than one minute would severely destroy the aluminum skeletons of the specimens consolidated without ultrasonic vibration. However, the Al cell skeletons of the specimens fabricated with 4 seconds of ultrasonic vibration remained intact with a disc shape after a 5 min ultrasonic washing test, which indicated that the ultrasonic vibration during consolidation needs to be long enough (4 s) to increase both densification and bonding in the Al cell walls.

The morphology of the porous aluminum material can depend on the weight ratio of aluminum to salt spacer material. A lower ratio, such as about 15:85 Al:NaCl, can create larger pores that enables more efficient washing after vibration. However, the larger pores result in a material with less strength. Hardness can be achieved with a higher weight ratio, such as 20:80 Al:NaCl, undergoing increased hold temperatures, such as about 450 °C to 500 °C, while also increasing the pressure, such as from about 60 MPa to 80 MPa. Such

materials can withstand more rigorous ultrasonic washing, such that the fraction of NaCl remaining after washing in the final product decreases.

The morphology of the porous aluminum material also depends upon the thickness, where thicker materials, such as about 2 mm, have increased cell elongation and distribution with increasing pressure. The pressure used during the ultrasonic vibration can be adjusted based on the thickness of the material. For example, a pressure of about 30-40 MPa may not be as effective as a pressure of about 60-80 MPa in creating a material that is about 1.2 mm thick.

Energy-Dispersive X-ray Spectroscopy (EDS) is an exemplary method that can determine the amount of oxidation in the porous aluminum material. Oxidation of aluminum products made by conventional methods is a significant detriment. The resulting aluminum product has a thin, low atomic density and an amorphous oxide layer. Here, the lack of oxidation in the presently disclosed processes conducted in ambient air underscore the lower fabrication cost and ease of operation in producing the present porous aluminum material. When measured by EDS, porous aluminum material prepared with no ultrasonic vibration had a larger amount of oxygen remaining at the particle boundaries than material prepared with ultrasonic vibration.

EXAMPLE*:* Ultrasonic Powder Consolidation

Materials

The disclosed porous aluminum materials are manufactured using an ultrasonic powder consolidation process as illustrated in FIGs. 1-3. A non-limiting exemplary sequence of steps in the process is described below. Aluminum powder was obtained using gas atomization, and the mean diameter size was 25 micrometer. The mean diameter of the NaCl particles was 300 micrometer. The ultrasonic welding unit was a STAPLA Condor welding unit. A Shimadzu model HMV-2T was used to test the Vickers hardness of the porous aluminum material with a load of 245.2 MN and a run time of 5s. Similar microhardness testers and ultrasonic washers known in the art would be suitable for this process.

Exemplary Process

1. Mix Al powder with NaCl particles to a desired ratio as shown in FIG. 1A. FIGs. 2A, 2B, 2C and 2D illustrate an SEM image and particle size distribution for the Al powder and NaCl particles, respectively.

2. Place the Al-NaCl mixture in the die above the heater plate of the ultrasonic welding unit as shown in FIG. 1B.

3. Place the punch on top of the powder mixture in the die as shown in FIG. 1B.

4. Lower the sonotrode onto the powder mixture to apply uniaxial pressure as shown in FIG. 1B.

5. Heat the powder mix/die to the consolidation temperature at a rate of 1 °C/s according to the diagram shown in FIG. 3.

6. Hold for about 3 minutes at the consolidation temperature according to the diagram shown in FIG. 3.

7. Apply in-plane ultrasonic vibration (20KHz, 9 mm amplitude) for 4 s according to the diagram shown in FIG. 3.

8. Turn off heater to allow the consolidated material and the die to cool in ambient air according to the diagram shown in FIG. 3.

9. Remove the consolidated material from the die.

10. Place the consolidated material in water to dissolve NaCl as shown in FIG. 1C.

11. Wash the material in an ultrasonic cleaning tank to remove NaCl as shown in FIG. 1D.

12. Test the Al skeleton for integrity as diagrammed in FIG. 1E.

The above process was used to produce porous aluminum materials manufactured at different ratios of Al:NaCl, temperatures, pressures, and vibration times as shown in Table 1. In an alternative process, step 9 occurs after step 7, such that the consolidated material cools outside of the die.

TABLE 1

	Sample symbol Sample thickness: 1.20 ± 0.05 mm	Weight ratio of Al: W (%)	Temperature: T (°C)	Pressure: P (MPa)	Vibration time: V (s)
No.1	W20-T450-P60-V0	20	450	60	0
No.2	W20-T450-P60-V4	20	450	60	4
No.3	W20-T500-P60-V0	20	500	60	0
No.4	W20-T500-P60-V4	20	500	60	4
No.5	W20-T500-P80-V0	20	500	80	0
No.6	W20-T500-P80-V4	20	500	80	4
No.7	W15-T450-P60-V0	15	450	60	0
No.8	W15-T450-P60-V4	15	450	60	4
No.9	W15-T500-P60-V0	15	500	60	0
No.10	W15-T500-P60-V4	15	500	60	4
No.11	W15-T500-P80-V0	15	500	80	0
No.12	W15-T500-P80-V4	15	500	80	4

Densification in the cell wall region of porous materials fabricated at different conditions

FIGs. 4A-F show that for sample Nos. 1-6, significant metallurgical consolidation was achieved in the Al cell walls of the materials consolidated 500 °C with 4 s of ultrasonic vibration at a weight ratio of 20% Al/NaCl (W20). Likewise, FIGs. 5A-F show that sample Nos. 7-12 demonstrated desired metallurgical consolidation at 500 °C with 4 s of ultrasonic vibration at a weight ratio of 15% Al/NaCl (W15).

The samples with 4-second ultrasonic vibration had much higher densification than those without ultrasonic vibration for both weight ratios (W15 and W20). Increasing the consolidation temperature and pressure increased densification in the cell wall regions of the porous aluminum material.

FIGs. 6A and 6B compare the effect of no ultrasonic vibration in sample Nos. 3 and 4 seconds of ultrasonic vibration in sample No. 4 in ambient air. The high strain-rate plastic deformation in sample No. 4 disrupted oxide films, resulting in better metallurgical bonding and strain hardening. The rise in temperature during the ultrasonic consolidation process also served to decrease flow stress which is favorable for creating plastic deformation.

As shown in FIG. 6A, consolidation of sample No. 3, which was not exposed to ultrasonic vibration, caused particles to deform and strain-harden, thereby leaving unfilled interstices. FIG. 6B illustrates that sample No. 4, which was subjected to 4s of ultrasonic vibration during consolidation, resulted in high strain-rate deformation. This deformation caused excess vacancies to increase by many orders of magnitude. These vacancies enhanced diffusion, lowered the melting point and limited strain hardening. Thus, this porous aluminum material had better densification and bonding.

Ultrasonic washing stability of porous aluminum materials

An ultrasonic washing test longer than one minute would break down the Al skeletons of the specimens consolidated without ultrasonic vibration. However, the Al cell skeletons of the specimens fabricated with 4 seconds of ultrasonic vibration remained intact with a disc shape after a 5 min ultrasonic washing test. These results indicated that the ultrasonic vibration during consolidation needs to be long enough (4 s) to increase both densification and bonding in the Al cell walls.

Dissolving the spacer material (NaCl) in still water and subsequently ultrasonic washing the material in water left well-consolidated skeletal Al structures in sample Nos. 2, 4, 6, 8, 10, and 12 as seen in Figs. 7A-7F, respectively. The OMs (optical microscopy) were taken after 5 minutes of ultrasonic washing of the ultrasonically consolidated specimens. The samples consolidated at 450 °C, FIGs. 7A and 7D, lost some of the Al at in the edge regions during the ultrasonic washing, but little Al loss occurred in the samples consolidated at 500 °C: FIGs. 7B, 7C, 7E, and 7F.

FIGs. 8A and 8B compare the lack of ultrasonic vibration in sample Nos. 3 vs. 4 seconds of ultrasonic vibration in sample No. 4, showing the greater consolidation quality and geometric control achieved with ultrasonic vibration. Sample No. 3 was prepared with 1 minute of ultrasonic washing as the material would not withstand a longer period of washing. The consolidation effects can be seen especially at the cylindrical surface of the samples. In comparing sample No. 4 in FIG. 8B that was prepared in ambient air to sample No. 4 in FIG. 8C that was prepared under argon atmosphere, the observed morphology was similar.

Morphology of Porous Aluminum Material

Sample Nos. 6 and 12 were consolidated under 80 MPa, as shown in FIGs. 7C and 7F. These samples exhibited somewhat flattened cells. Thus, 60 MPa was determined to

give advantageous results. Flattened cells may pose difficulty in removing the spacer material and in device performance, such as battery cathode current collectors.

SEM images in FIGs. 9A-9I show an interconnected pore structure in the consolidated porous Al material of sample Nos. 4 (W20) and 10 (W15) at increasing magnification levels. Images of sample No. 4 at increasing levels of magnification illustrated the density of pores in the final material. Compared to sample No. 4, sample No. 10 had increased pore connectivity which is beneficial to more thoroughly remove NaCl particles. Sample No. 10 had thinner cell walls that sample No. 4 (W20), illustrating the greater strength of material at a W20 weight ratio.

FIGs. 10A and 10B show many voids in the sample No. 3 material that was prepared without ultrasonic vibration. FIGs. 10C and 10D illustrate the increased plastic deformation of the sample No. 4 aluminum particles in the material formed with ultrasonic vibration. As observed in FIGS. 10E and 10F, the observed morphology was similar.

Vickers Hardness of Porous Aluminum Material

FIG. 11A shows the Vickers hardness and % fraction of dissolved mass in sample Nos. 2, 4 and 6, which each had a W20 weight ratio. Increasing the hold temperature from 450 °C to 500 °C, while also increasing the pressure from 60 MPa to 80 MPa, resulted in a harder porous aluminum material that had significantly less mass remaining after the ultrasonic washing step.

FIG. 11B shows the Vickers hardness and % fraction of dissolved mass in sample Nos. 8, 10 and 12, which each had a W15 weight ratio. These materials had a lower Vickers hardness compared to the W20 samples and a higher % fraction of dissolved mass in each sample. These results demonstrate the benefits of using a weight ratio of at least W20 on the increased hardness of the porous aluminum material, and the greater washing efficiency to remove salt spacer material at the end of production.

FIG. 12A illustrates the Vickers hardness test results and estimated dislocation density of sample Nos. 3 and 4, where the sample No. 4 V4 material was harder than the sample No. 3 V0 material. The Vickers indentation on the cell wall region of sample No. 3 (FIG. 12B) and sample No. 4 (FIG. 12C) showed a higher dislocation density (determined by transmission electron microscopy) resulting from the application of ultrasonic vibration. Each of these samples were prepared in ambient air. Sample No. 3 material was prepared with 1 minute of ultrasonic washing, and each sample No. 4 material was prepared with 5

minutes of ultrasonic washing. Without the ultrasonic vibration step in the preparation of sample No. 3, this material would not withstand a longer ultrasonic washing step to remove the NaCl spacer material. FIG. 12D illustrates the Vickers indentation on the cell wall region of sample No. 4 prepared under argon atmosphere.

These experiments demonstrate that an inert atmosphere is not necessary to achieve the high consolidation and densification of the present porous aluminum material. Aluminum oxidation is well-known in the art, such as thermal processes described in Trunov, M.A. et al., *Combustion Theory and Modeling* 2006 10:603-623, and Jeurgens, L.P.H. et al., *Journal of Applied Physics* 2002 92:1649-1656. In known processes, oxidation can occur using low consolidation temperatures, such as 500 °C, that are held for a short time, such as 3 minutes. The resulting aluminum product has a thin, low atomic density and an amorphous oxide layer. Here, the lack of oxidation in processes conducted in ambient air underscore the lower fabrication cost and ease of operation in producing the present porous aluminum material.

Energy-Dispersive X-ray Spectroscopy (EDS) Results

FIG. 13A shows a SEM image of sample No. 3 at 10 μm, while FIG. 13B shows a magnification of sample No. 3 in Table 1 at 1 μm. This sample No. 3 was prepared in ambient air. A spot on the micrograph was chosen for elemental analysis using EDS. FIG. 13C illustrates the ratio of aluminum (Al) to oxygen (O) at that "EDS Spot 1" location.

FIG. 13D shows a SEM image of sample No. 4 at 10 μm, while FIG. 13E shows a magnification of sample No. 4 at 1 μm. This sample No. 4 was prepared in ambient air. A spot on the micrograph was chosen for elemental analysis using EDS. FIG. 13F illustrates the ratio of aluminum (Al) to oxygen (O) at that "EDS Spot 2" location.

FIG. 13G shows a SEM image of sample No. 4 in at 10 μm, while FIG. 13H shows a magnification of sample No. 4 at 10 μm. This sample No. 4 was prepared under Ar atmosphere. A spot on the micrograph was chosen for elemental analysis using EDS. FIG. 13I illustrates the ratio of aluminum (Al) to oxygen (O) at that "EDS Spot 3" location.

In comparing FIG. 13C with FIGs. 13F and 13I, a lesser amount of oxygen was incorporated into the porous aluminum material when ultrasonic vibration was used in the consolidation process.

FIG. 14 also indicates four places where EDS was performed. This elemental analysis indicated that pure aluminum was present in the particle-particle interface at EDS spots 1 and 2. EDS spots 3 and 4 showed a minor amount of oxygen within the interior of the particle. Table 2 provides the results of the eZAF Smart Quant analysis.

TABLE 2

eZAF Smart Quant Results

	Element	Weight %	Atomic %	Net Int.	Error %
EDS Spot 1	AlK	100.00	100.00	196.57	6.31
EDS Spot 2	AlK	100.00	100.00	199.29	6.29
EDS Spot 3	O K	2.13	3.53	8.49	21.29
	AlK	97.87	96.47	213.32	6.30
EDS Spot 4	O K	2.32	3.84	9.32	16.72
	AlK	97.68	96.16	214.54	6.24

Varying Ultrasonic Powder Consolidation Parameters

TABLE 3

Sample No.	Sample Symbol	Wt. Ratio of Al: W (%)	Temperature T (°C)	Pressure: P (MPa)	Vibration Time: V (s)
13	W20-T500-P30-V4	20	500	30	4
14	W20-T500-P35-V4	20	500	35	4
15	W20-T500-P40-V4	20	500	40	4

16	W20-T500-P40-V4	20	500	45	4
17	W20-T450-P40-V5	20	450	40	5
18	W20-T500-P100-V4	20	500	100	4
19	W20-T500-P100-V0	20	500	100	0

Sample Nos. 13-17 were fabricated using the ultrasonic powder consolidation process described above using the parameters in Table 3. The heating hold time was 5 minutes and the process was conducted in ambient air for sample Nos. 13-16. FIGs. 15A-15D illustrate SEM cross-section images of each of these samples at 500 μm. The resulting porous aluminum material was 2 mm thick and exhibited increased cell elongation and distribution with increasing pressure. For sample No. 17, the heating hold time was 3 minutes and the process was conducted in ambient air. FIGs 16A-16C illustrate OM cross-section images of sample No. 17 at 500, 50, and 10 μm, respectively. The resulting porous aluminum material was 1.2 mm thick and demonstrated that 40 MPa pressure was insufficient to obtain high quality consolidation. These experiments illustrate the necessity to adjust the pressure based on the desired thickness of the porous aluminum material.

FIG. 17A shows a TEM image of Sample No. 18 produced using ultrasonic vibration. The interparticle boundaries were completely filled and bonded to each other. In contrast, sample No. 19 produced without ultrasonic vibration as shown in FIG. 17B resulted in poor alignment of particles and unfilled triple junctions, indicating a weaker consolidation was achieved.

FIGs. 18A and 18B show TEM images of Sample No. 3 produced without using ultrasonic vibration. The interparticle boundaries show poor alignment of particles and unfilled triple junctions, indicating a weaker consolidation was achieved. In contrast, FIGs 18C and 18D show TEM images of Sample No. 4 produced with using ultrasonic vibration. The interparticle boundaries were completely filled and bonded to each other.

Incorporation by Reference

All publications and patents mentioned herein are hereby incorporated by reference in their entirety as if each individual publication or patent was specifically and individually indicated to be incorporated by reference. In case of conflict, the present application, including any definitions herein, will control.

Equivalents

While specific embodiments of the subject invention have been discussed, the above specification is illustrative and not restrictive. Many variations of the invention will become apparent to those skilled in the art upon review of this specification and the claims below. The full scope of the invention should be determined by reference to the claims, along with their full scope of equivalents, and the specification, along with such variations.

CLAIMS

1. A method of preparing a porous aluminum material, comprising the steps of:

a) applying a pressure of about 5-80 MPa to a mixture of aluminum powder and a salt spacer material;

b) heating the mixture to a temperature of about 100-550 °C and increasing the pressure to about 30-100 MPa for about 3 minutes;

c) applying ultrasonic vibration to the mixture for about 2-4 seconds;

d) allowing the mixture to cool at ambient temperature and pressure; and

e) washing the mixture in water using an ultrasonic cleaning tank;

thereby producing the porous aluminum material.

2. The method of claim 1, wherein the salt spacer material is NaCl.

3. The method of claim 1 or 2, wherein the weight percent ratio of Al powder:salt spacer material is from about 10:90 to about 50:50.

4. The method of any one of the preceding claims, wherein the weight percent ratio of Al powder:salt spacer material is about 20:80.

5. The method of any one of the preceding claims, wherein the weight percent ratio of Al powder:salt spacer material is about 15:85.

6. The method of any one of the preceding claims, wherein the Al powder has a size distribution ranging from about 5-100 μm.

7. The method of any one of the preceding claims, wherein the Al powder has a size distribution ranging from about 8-56 μm.

8. The method of claim 2, wherein the NaCl is particulate with a size distribution of about 100-500 μm.

9. The method of claim 8, wherein the NaCl is particulate with a size distribution of about 210-420 μm.

10. The method of any one of the preceding claims, wherein the pressure in steps a) and b) is uniaxial and applied using a sonotrode at 10 MPa.

11. The method of any one of the preceding claims, wherein the temperature in step b) is about 400 °C.

12. The method of any one of claims 1-10, wherein the temperature in step b) is about 450 °C.

13. The method of any one of claims 1-10, wherein the temperature in step b) is about 500 °C.

14. The method of any one of the preceding claims, wherein the pressure in step b) is about 60 MPa.

15. The method of any one of claims 1-13, wherein the pressure in step b) is about 80 MPa.

16. The method of any one of the preceding claims, wherein the ultrasonic vibration in step c) ranges from about 1-50 KHz with an amplitude of about 9 mm.

17. The method of any one of the preceding claims, wherein the ultrasonic vibration in step c) is at about 20 KHz with an amplitude of about 9 mm.

18. The method of any one of the preceding claims, wherein the ultrasonic vibration is in-plane vibration.

19. The method of any one of the preceding claims, wherein the ultrasonic vibration in step c) is applied for about 1-10 seconds.

20. The method of any one of the preceding claims, wherein the ultrasonic vibration in step c) is applied for about 4 seconds.

21. The method of any one of claims 1-19, wherein the ultrasonic vibration in step c) is applied for about 2 seconds.

22. The method of any one of the preceding claims, wherein the ultrasonic washing occurs for about 1-10 minutes.

23. The method of any one of the preceding claims, wherein the ultrasonic washing occurs for about 5 minutes.

24. The method of any one of the preceding claims, wherein the salt spacer material is removed during step e).

25. The method of claim 24, wherein greater than or equal to about 95% of the salt spacer material is removed during step e).

26. The method of any one of the preceding claims, wherein the porous aluminum material has greater than or equal to about 85% porosity.

27. The method of claim 18, wherein the weight percent ratio of Al powder:salt spacer material is from about 10:90 to about 40:60.

28. The method of any one of the preceding claims, wherein the porous aluminum material has a thickness of less than or equal to about 2 mm.

29. The method of any one of the preceding claims, wherein the porous aluminum material has a thickness of about 1.20 mm.

30. The method of any one of the preceding claims, wherein the method occurs in ambient atmosphere.

31. The method of any one of claims 1-29, wherein the method occurs in an inert atmosphere.

32. The method of claim 30, wherein the inert atmosphere is an argon atmosphere.

33. A porous aluminum material produced by a process comprising the steps of:

a) applying a pressure of about 5-80 MPa to a mixture of aluminum powder and a salt spacer material;

b) heating the mixture to a temperature of about 100-550 °C and increasing the pressure to about 30-100 MPa for about 3 minutes;

c) applying ultrasonic vibration to the mixture for about 2-4 seconds;

d) allowing the mixture to cool at ambient temperature and pressure; and

e) washing the mixture in water using an ultrasonic cleaning tank.

34. The method of claim 33, wherein the salt spacer material is NaCl.

35. The method of claim 33 or 34, wherein the weight percent ratio of Al powder:salt spacer material is from about 10:90 to about 50:50.

36. The method of any one of the preceding claims, wherein the weight percent ratio of Al powder:salt spacer material is about 20:80.

37. The method of any one of the preceding claims, wherein the weight percent ratio of Al powder:salt spacer material is about 15:85.

38. The method of any one of the preceding claims, wherein the Al powder has a size distribution ranging from about 5-100 μm.

39. The method of any one of the preceding claims, wherein the Al powder has a size distribution ranging from about 8-56 μm.

40. The method of claim 34, wherein the NaCl is particulate with a size distribution of about 100-500 μm.

41. The method of claim 40, wherein the NaCl is particulate with a size distribution of about 210-420 μm.

42. The method of any one of the preceding claims, wherein the pressure in steps a) and b) is uniaxial and applied using a sonotrode at 10 MPa.

43. The method of any one of the preceding claims, wherein the temperature in step b) is about 400 °C.

44. The method of any one of claims 1-42, wherein the temperature in step b) is about 450 °C.

45. The method of any one of claims 1-42, wherein the temperature in step b) is about 500 °C.

46. The method of any one of the preceding claims, wherein the pressure in step b) is about 60 MPa.

47. The method of any one of claims 1-45, wherein the pressure in step b) is about 80 MPa.

48. The method of any one of the preceding claims, wherein the ultrasonic vibration in step c) ranges from about 1-50 KHz with an amplitude of about 9 mm.

49. The method of any one of the preceding claims, wherein the ultrasonic vibration in step c) is at about 20 KHz with an amplitude of about 9 mm.

50. The method of any one of the preceding claims, wherein the ultrasonic vibration is in-plane vibration.

51. The method of any one of the preceding claims, wherein the ultrasonic vibration in step c) is applied for about 1-10 seconds.

52. The method of any one of the preceding claims, wherein the ultrasonic vibration in step c) is applied for about 4 seconds.

53. The method of any one of claims 1-51, wherein the ultrasonic vibration in step c) is applied for about 2 seconds.

54. The method of any one of the preceding claims, wherein the ultrasonic washing occurs for about 1-10 minutes.

55. The method of any one of the preceding claims, wherein the ultrasonic washing occurs for about 5 minutes.

56. The method of any one of the preceding claims, wherein the salt spacer material is removed during step e).

57. The method of claim 56, wherein greater than or equal to about 95% of the salt spacer material is removed during step e).

58. The method of any one of the preceding claims, wherein the porous aluminum material has greater than or equal to about 85% porosity.

59. The method of claim 50, wherein the weight percent ratio of Al powder:salt spacer material is from about 10:90 to about 40:60.

60. The method of any one of the preceding claims, wherein the porous aluminum material has a thickness of less than or equal to about 2 mm.

61. The method of any one of the preceding claims, wherein the porous aluminum material has a thickness of about 1.20 mm.

62. The method of any one of the preceding claims, wherein the method occurs at ambient atmosphere.

63. The method of any one of claims 1-62, wherein the method occurs in an inert atmosphere.

64. The method of claim 63, wherein the inert atmosphere is an argon atmosphere.

FIG. 1A

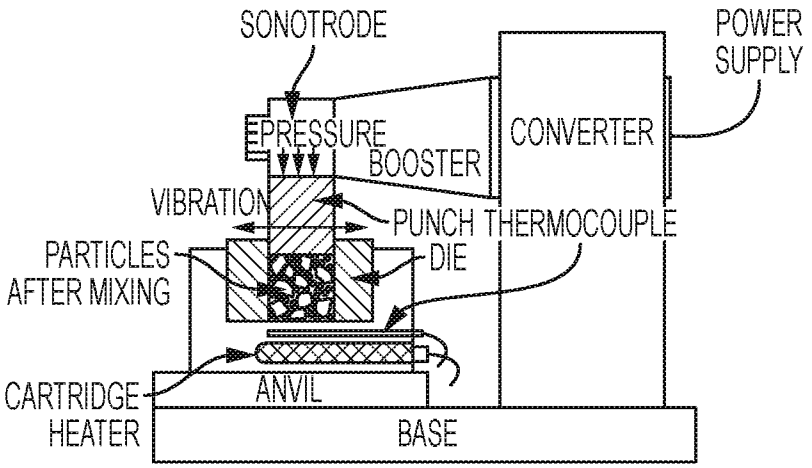

FIG. 1B

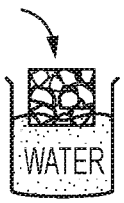

FIG. 1C

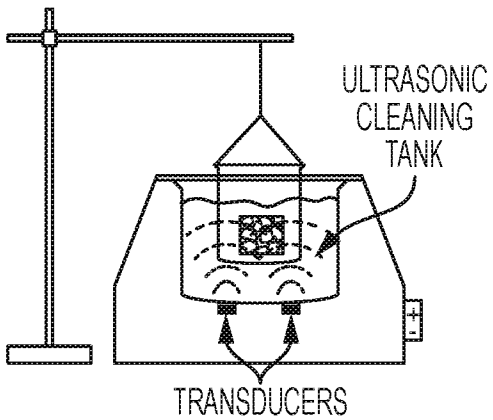

FIG. 1D

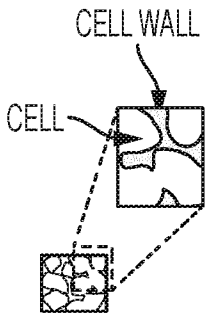

FIG. 1E

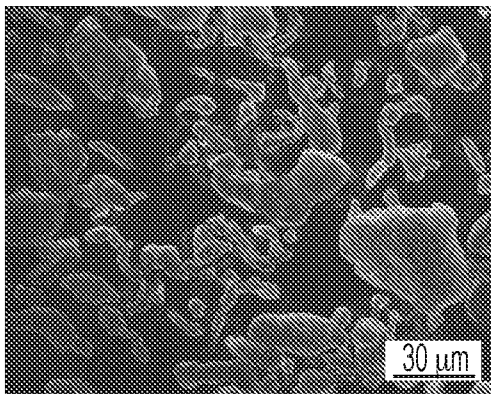

FIG. 2A

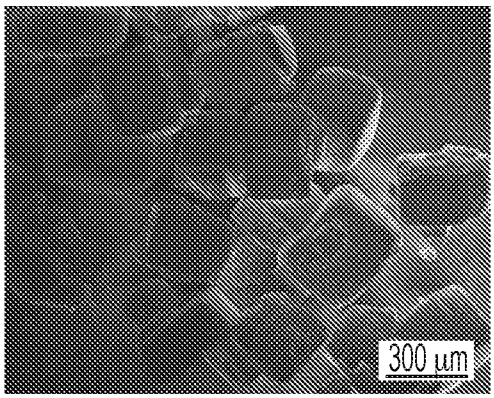

FIG. 2B

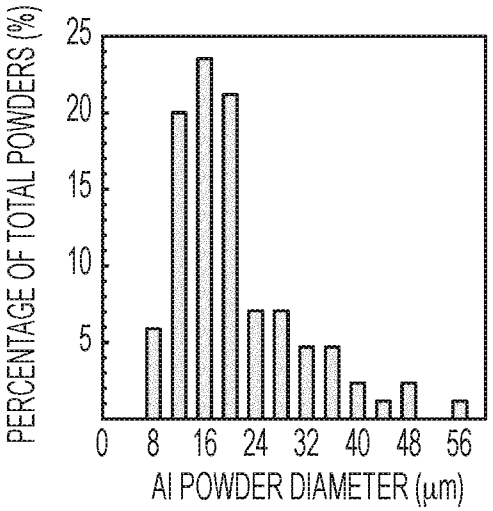

FIG. 2C

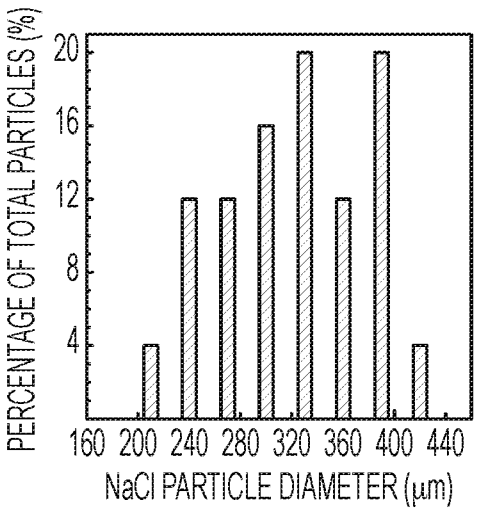

FIG. 2D

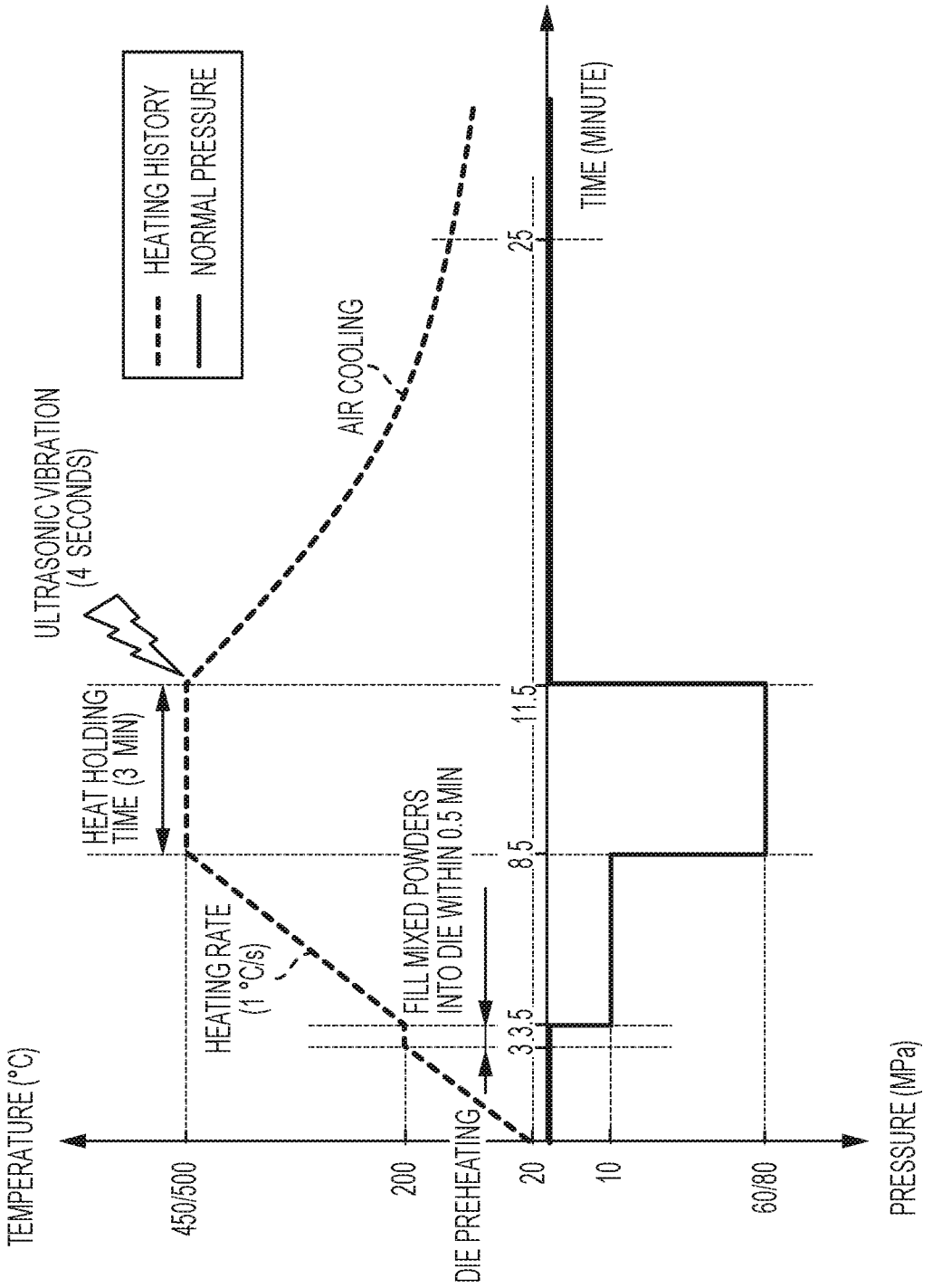
HEATING HISTORY
NORMAL PRESSURE
ULTRASONIC VIBRATION
(4 SECONDS)
AIR COOLING
HEAT HOLDING
TIME (3 MIN)
HEATING RATE
(1 °C/s)
FILL MIXED POWDERS
INTO DIE WITHIN 0.5 MIN
DIE PREHEATING
TEMPERATURE (°C)
450/500
200
20
TIME (MINUTE)
25
11.5
8.5
3.5
10
60/80
PRESSURE (MPa)

FIG. 3

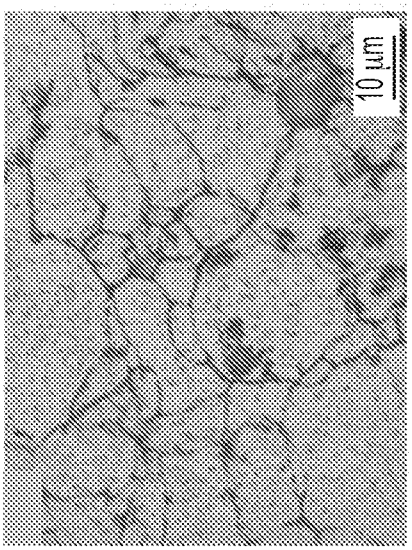

FIG. 4E

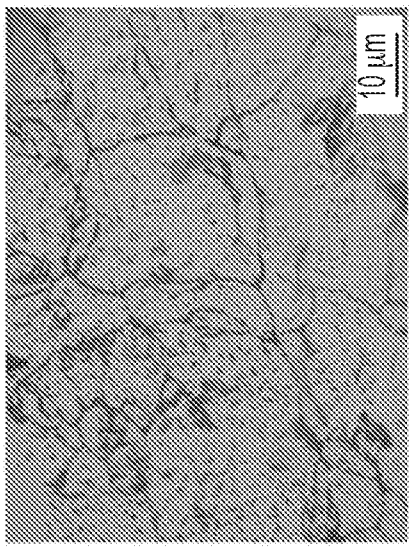

FIG. 4F

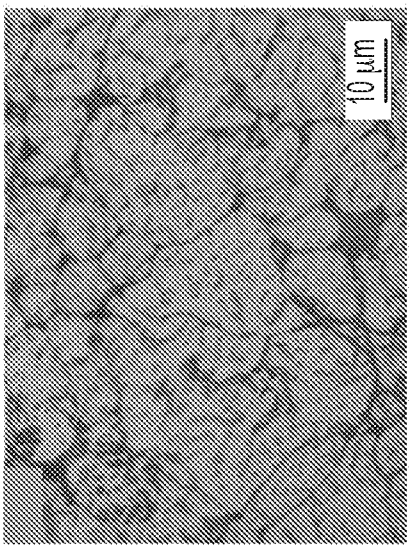

FIG. 4C

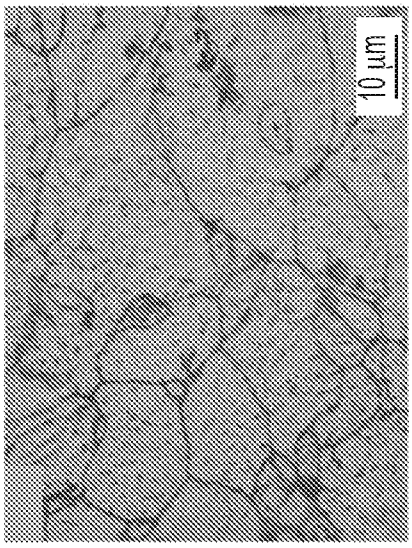

FIG. 4D

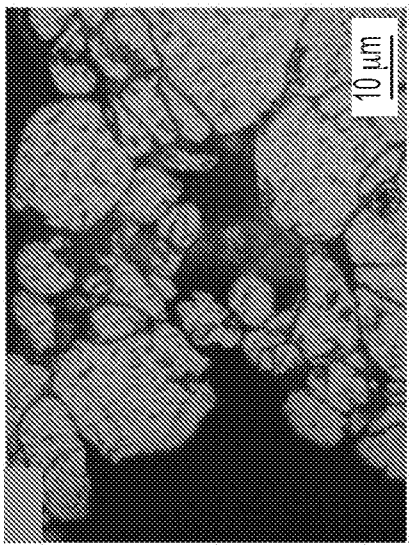

FIG. 4A

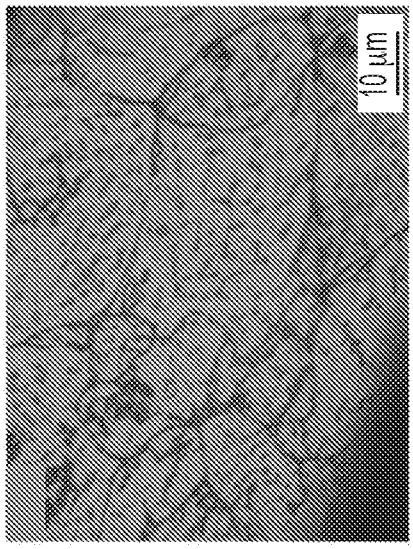

FIG. 4B

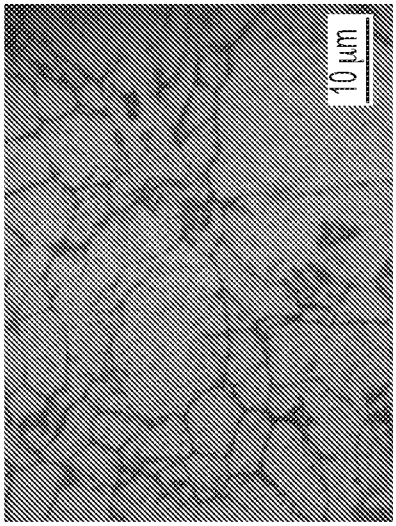

FIG. 5E

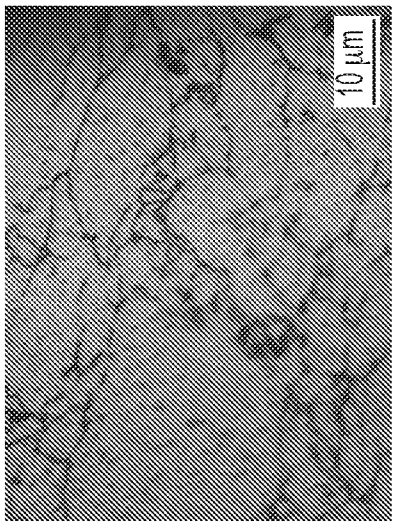

FIG. 5F

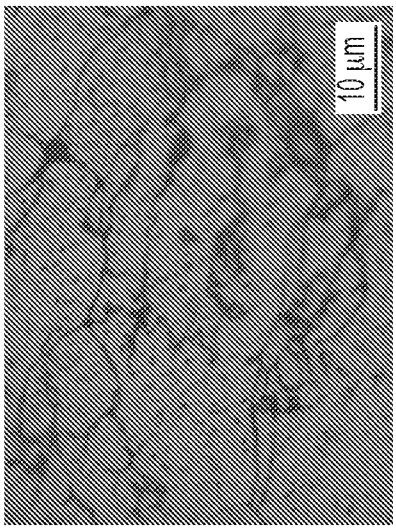

FIG. 5C

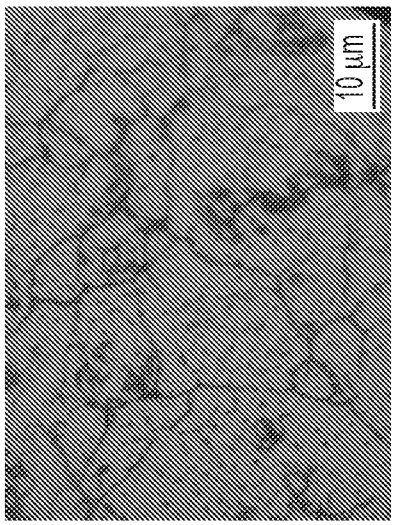

FIG. 5D

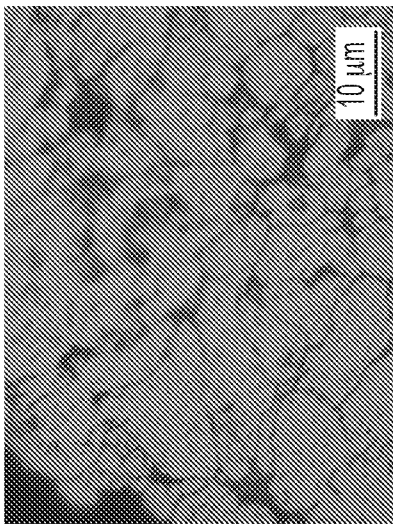

FIG. 5A

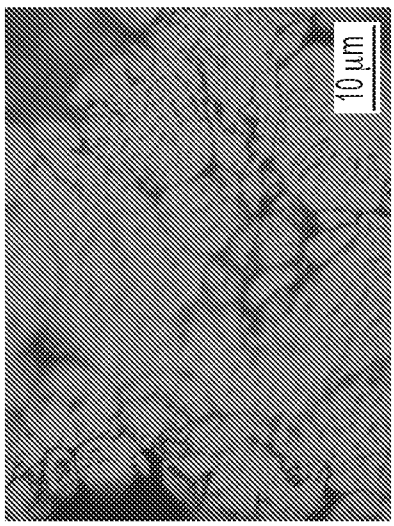

FIG. 5BD

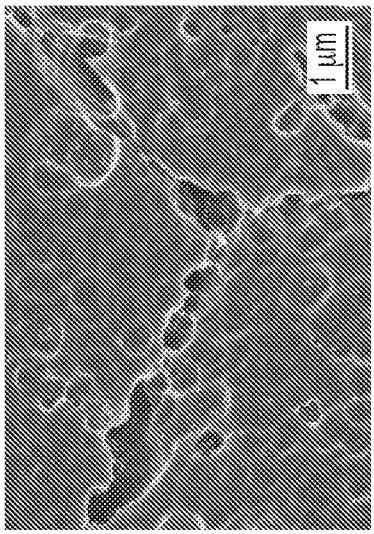

FIG. 6B

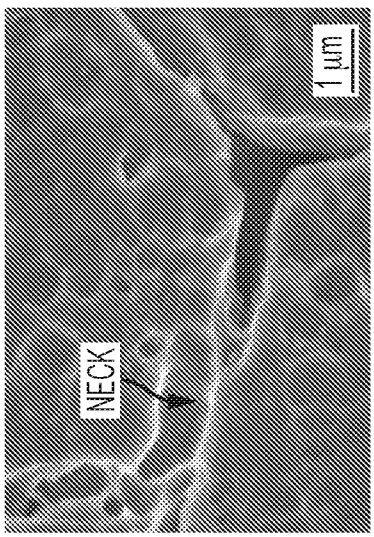

FIG. 6A

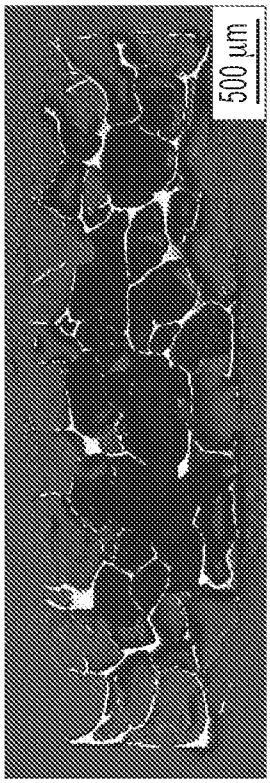

FIG. 7B

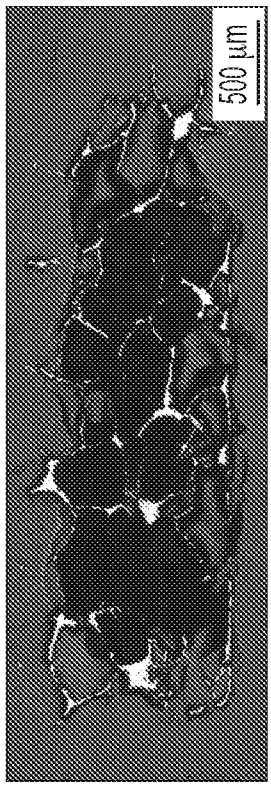

FIG. 7D

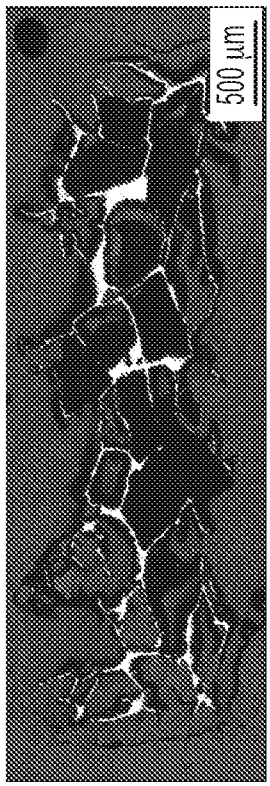

FIG. 7F

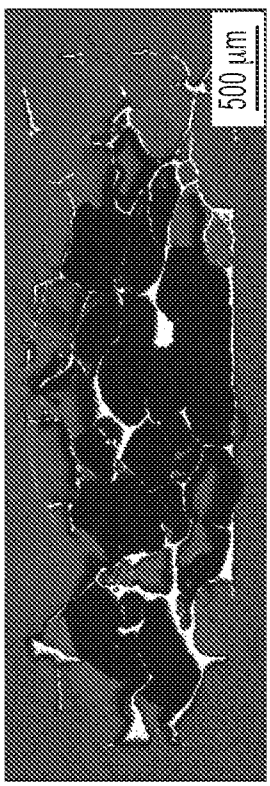

FIG. 7A

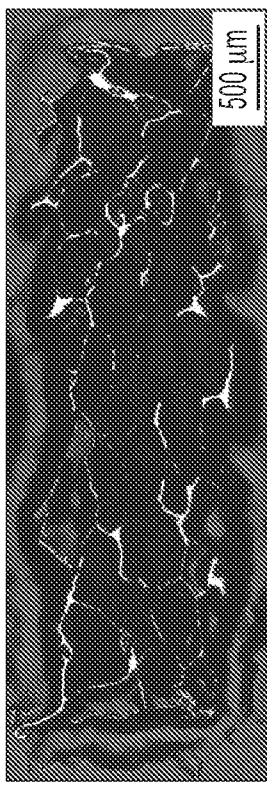

FIG. 7C

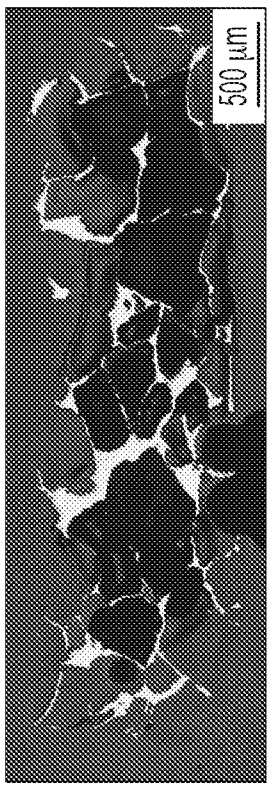

FIG. 7E

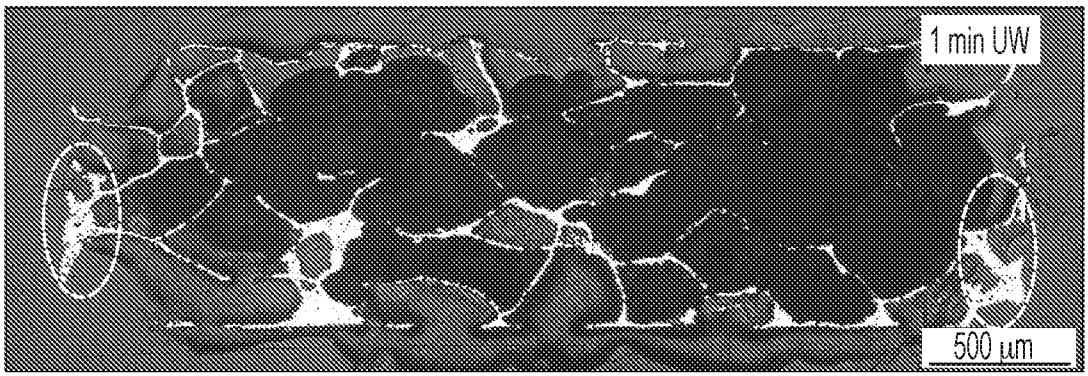

FIG. 8A

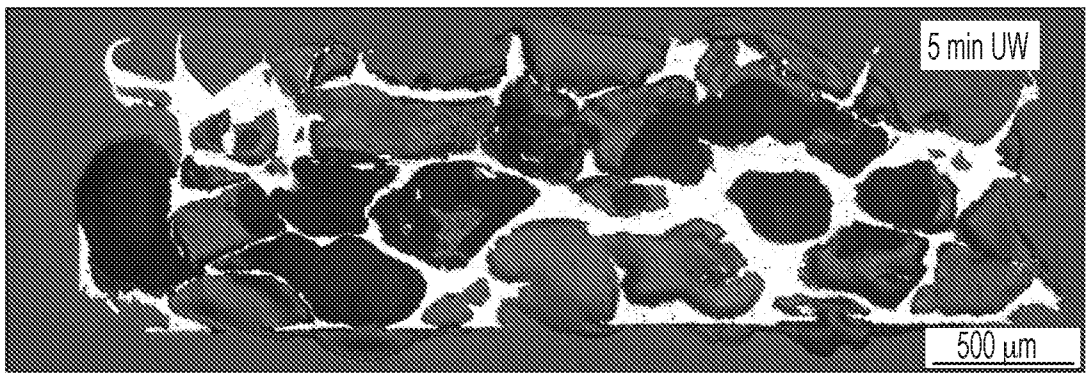

FIG. 8B

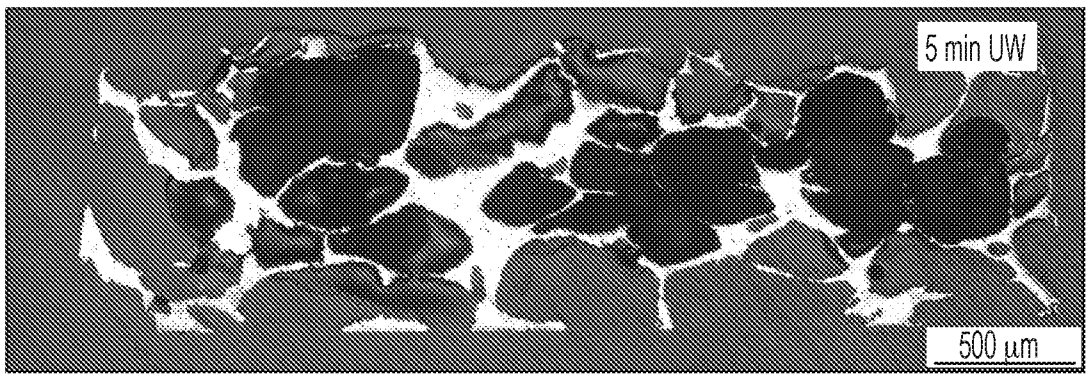

FIG. 8C

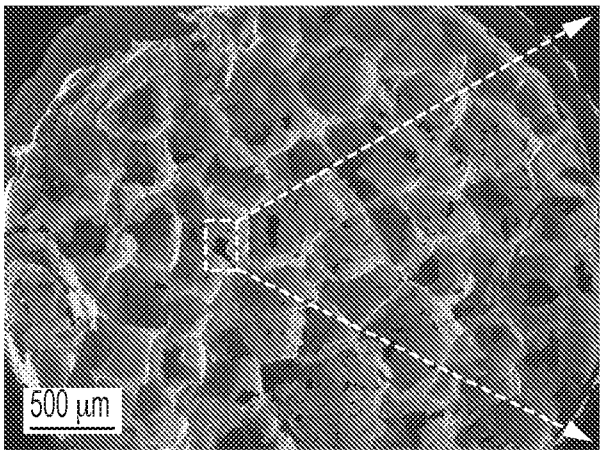

FIG. 9A

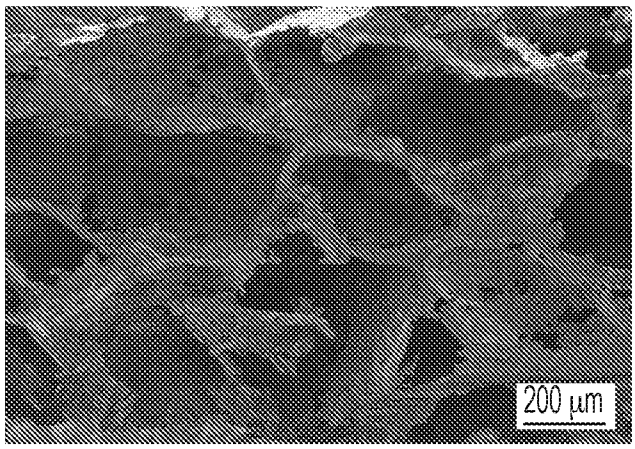

FIG. 9B

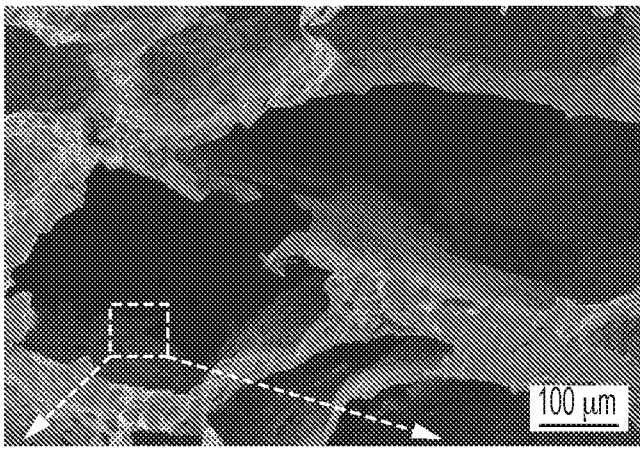

FIG. 9C

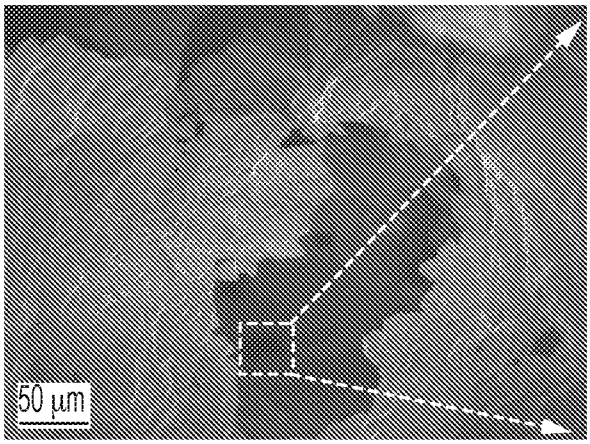

FIG. 9D

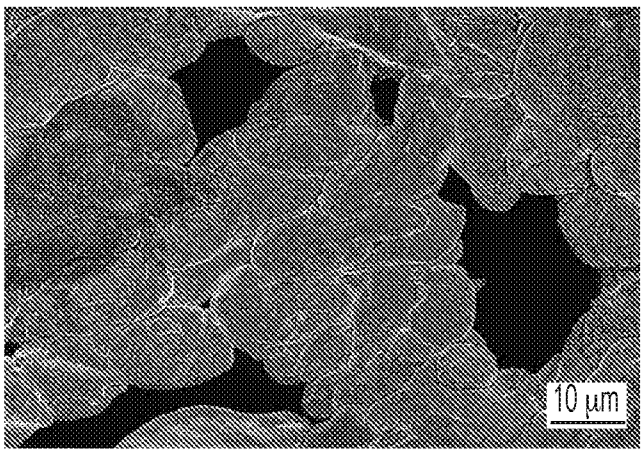

FIG. 9E

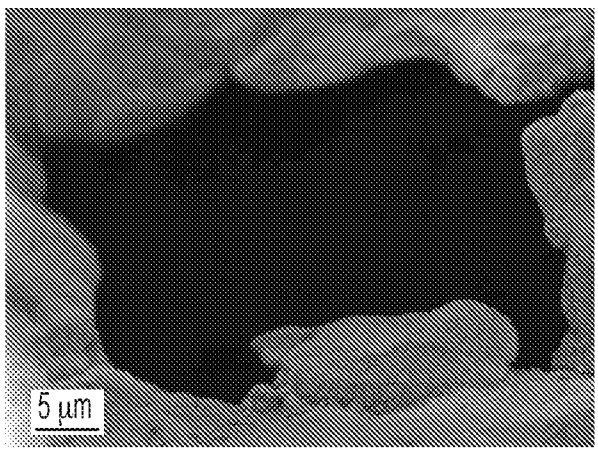

FIG. 9F

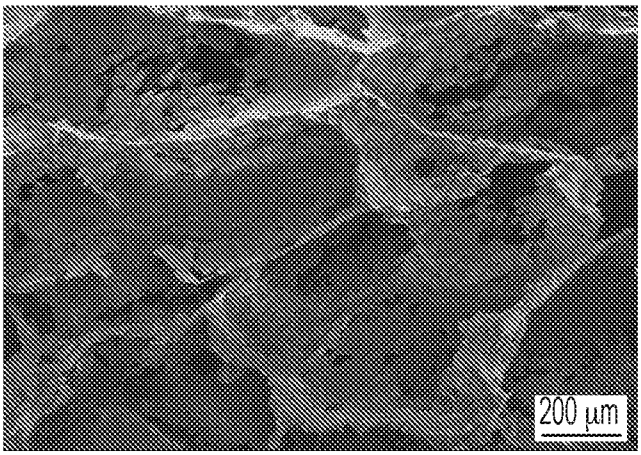

FIG. 9G

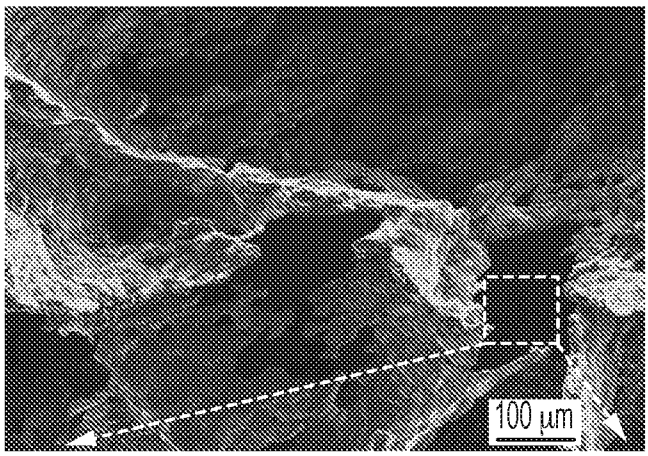

FIG. 9H

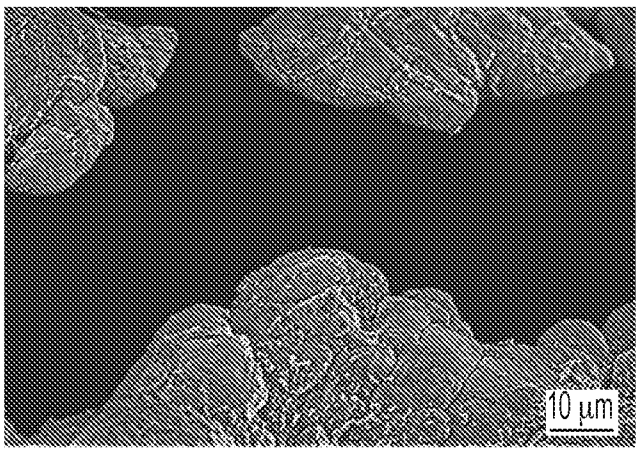

FIG. 9I

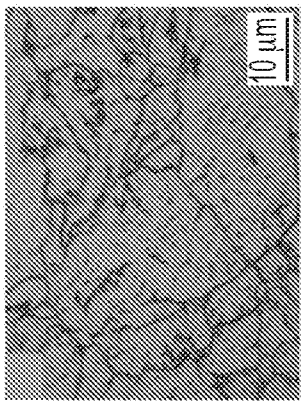

FIG. 10E

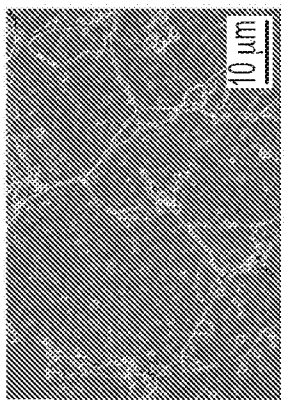

FIG. 10F

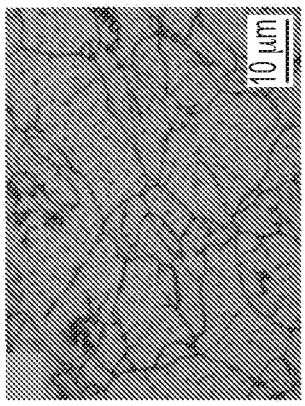

FIG. 10C

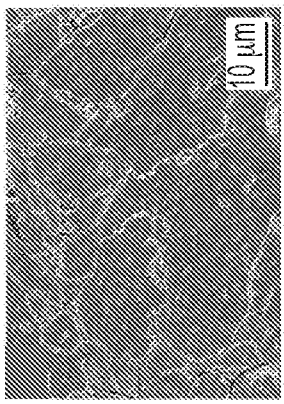

FIG. 10D

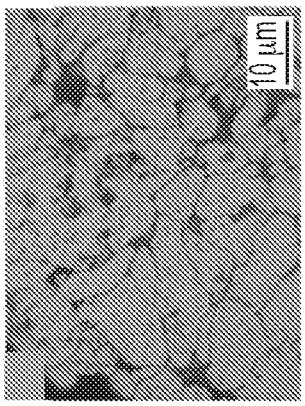

FIG. 10A

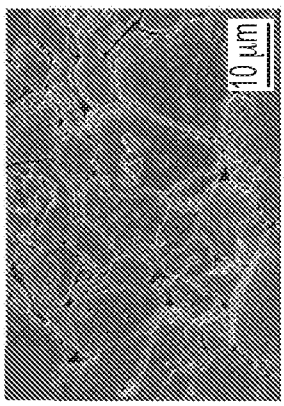

FIG. 10B

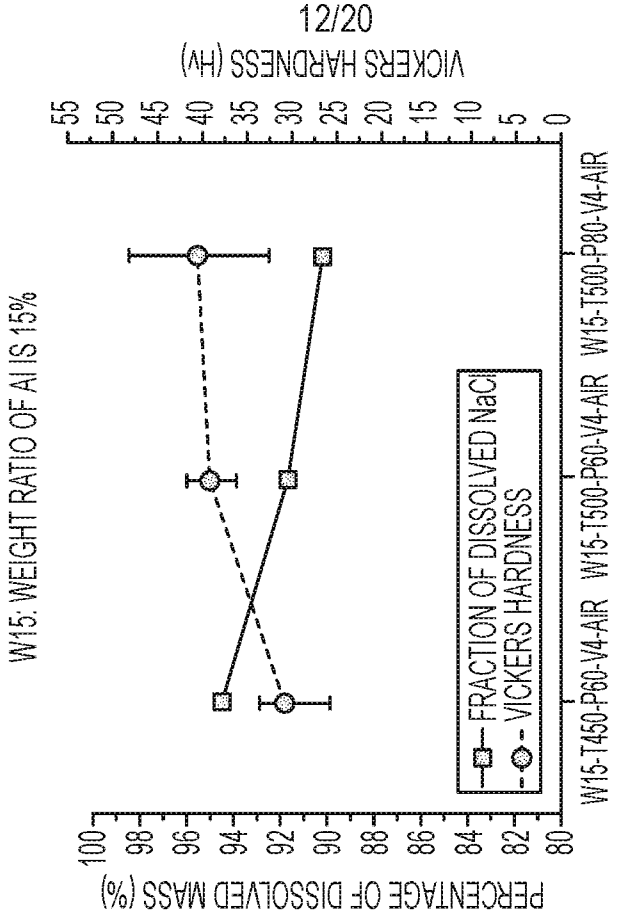

FIG. 11B

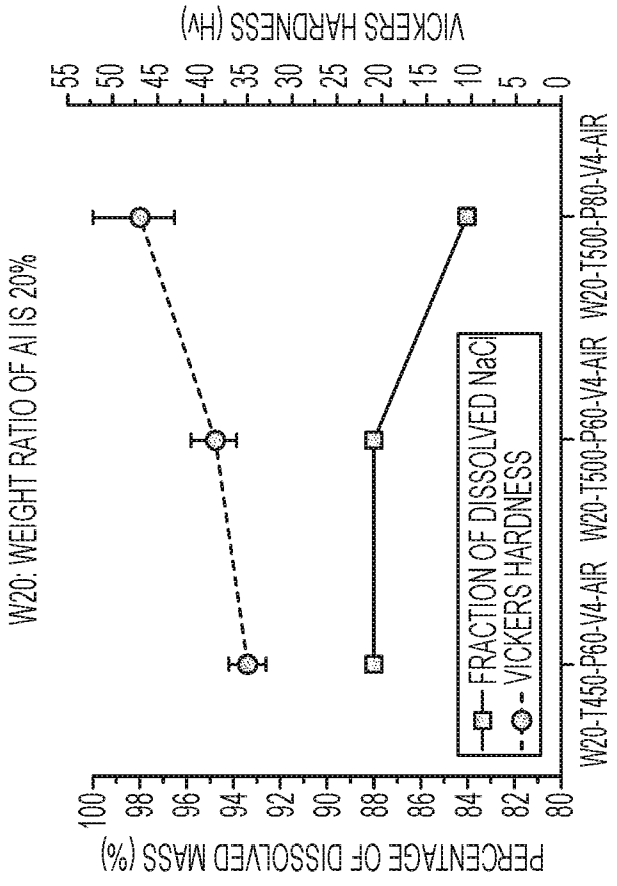

FIG. 11A

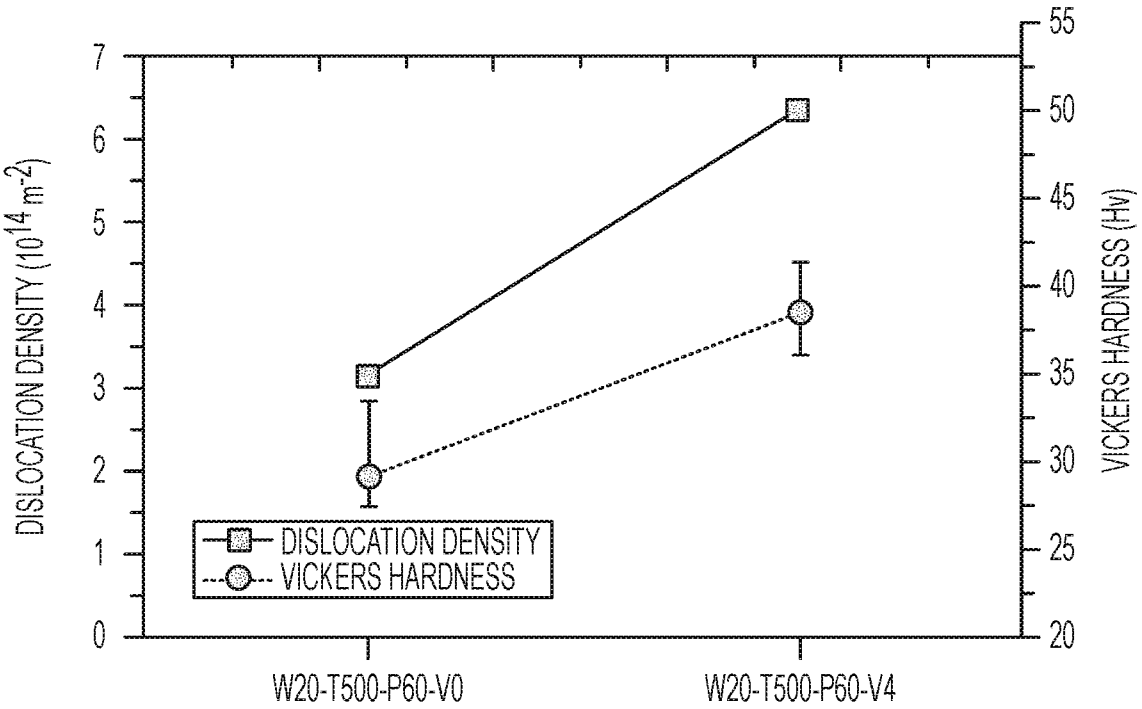

FIG. 12A

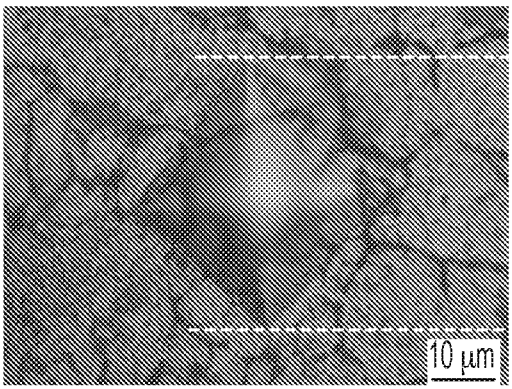

FIG. 12B

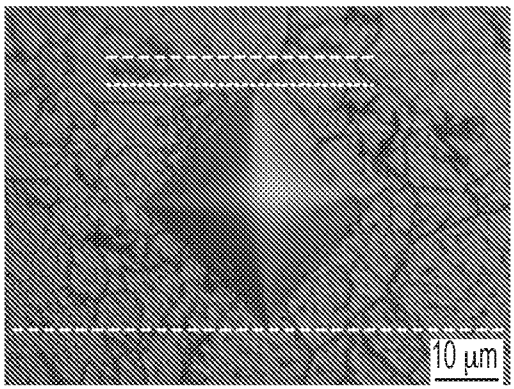

FIG. 12C

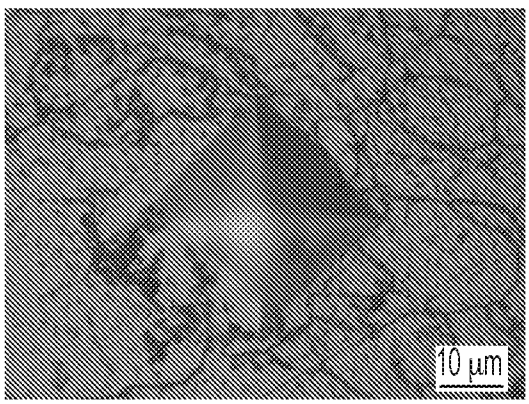

FIG. 12D

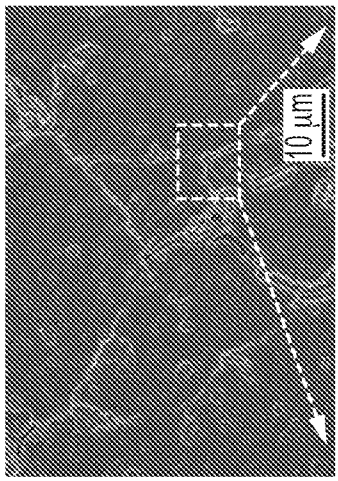

FIG. 13G

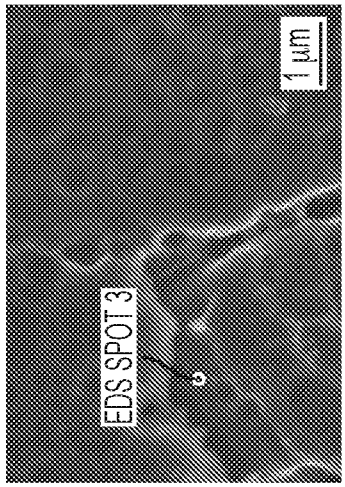

FIG. 13H

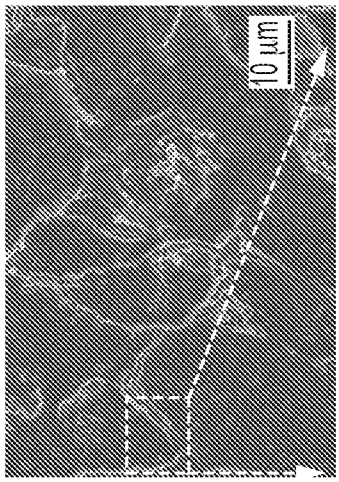

FIG. 13D

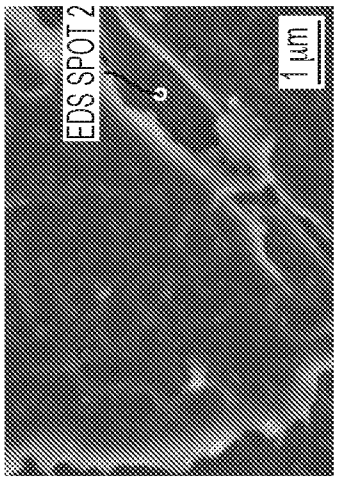

FIG. 13E

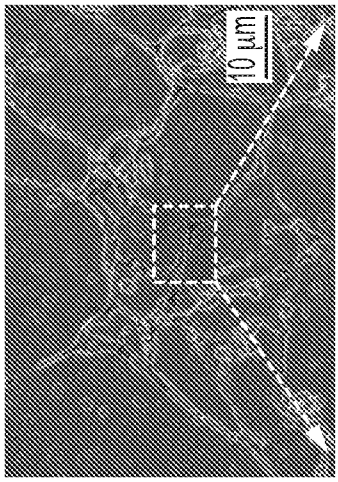

FIG. 13A

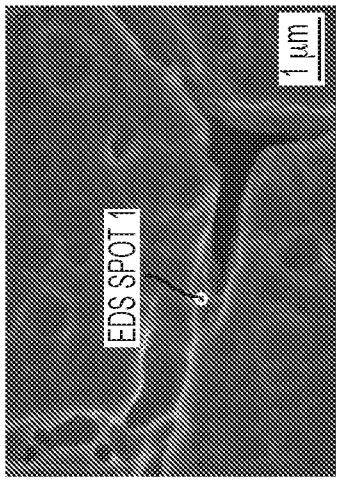

FIG. 13B

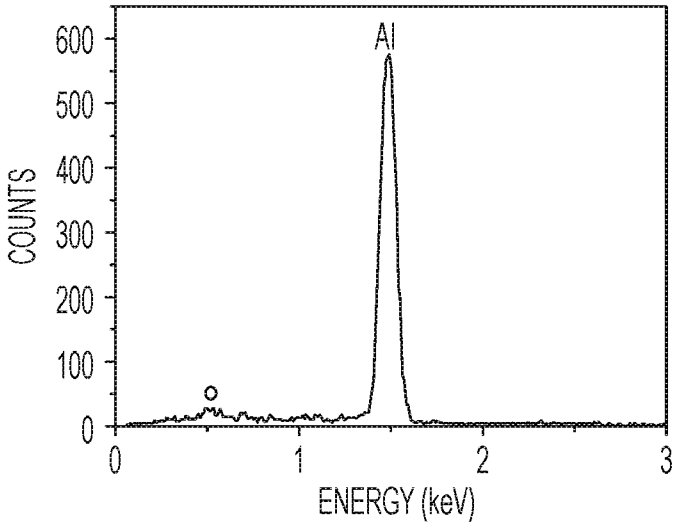

FIG. 13C

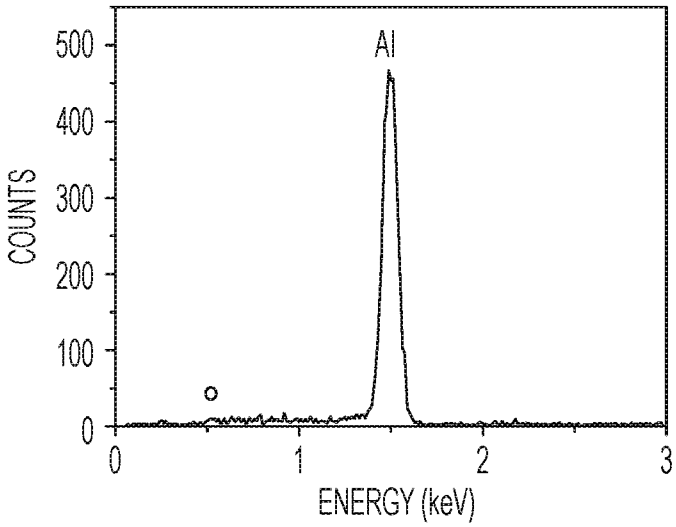

FIG. 13F

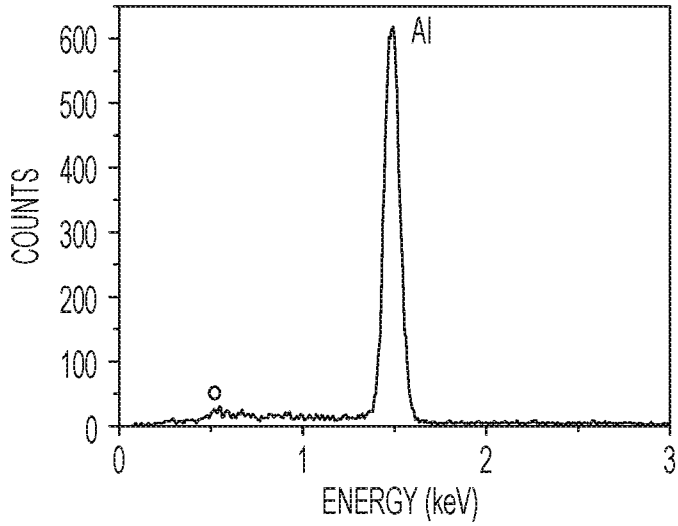

FIG. 13I

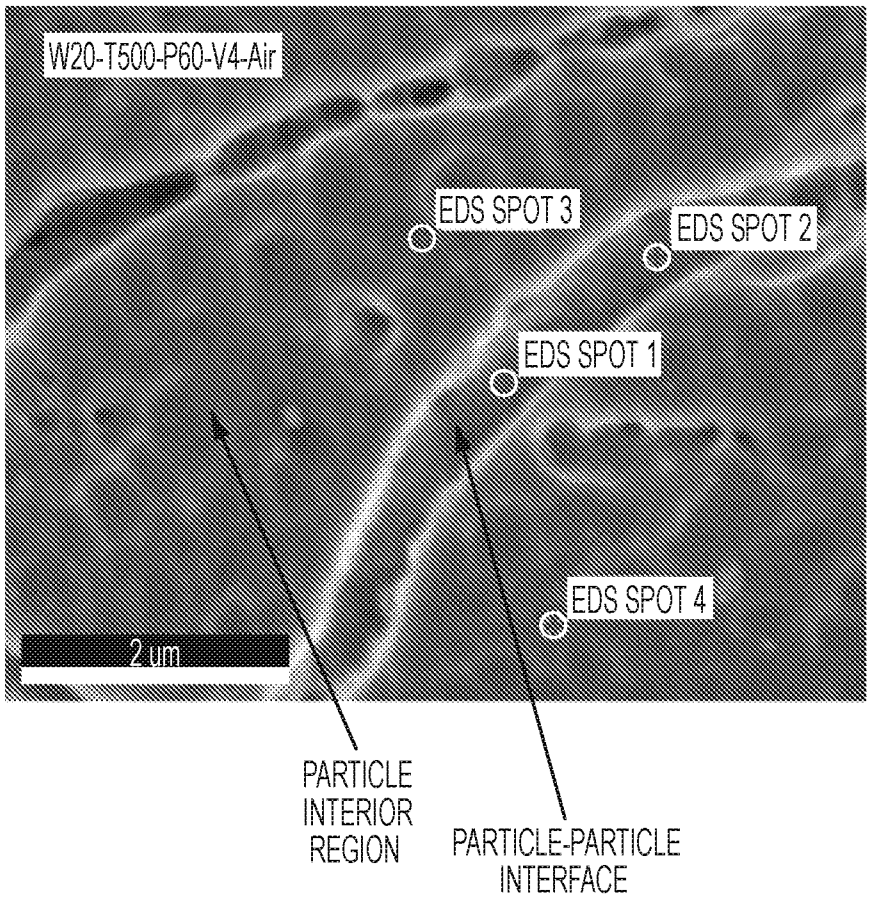
W20-T500-P60-V4-Air
EDS SPOT 3
EDS SPOT 2
EDS SPOT 1
EDS SPOT 4
2 um
PARTICLE INTERIOR REGION
PARTICLE-PARTICLE INTERFACE

FIG. 14

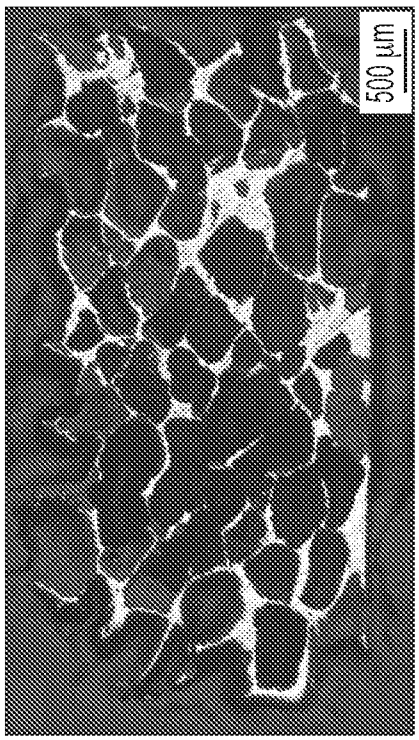

FIG. 15B

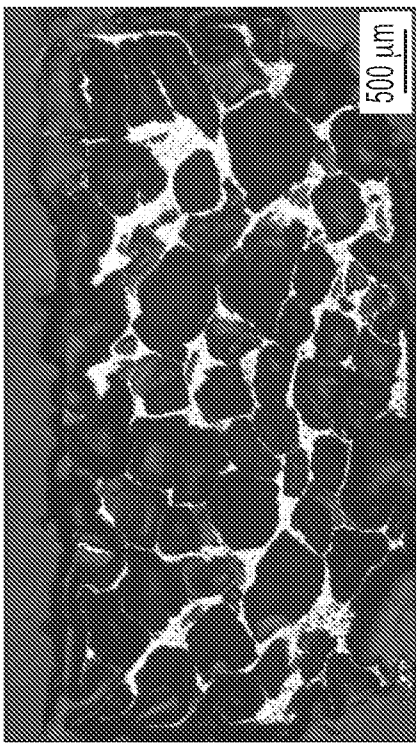

FIG. 15A

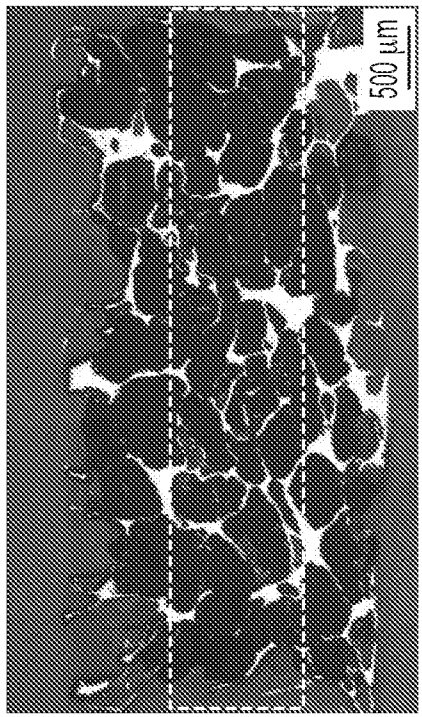

FIG. 15D

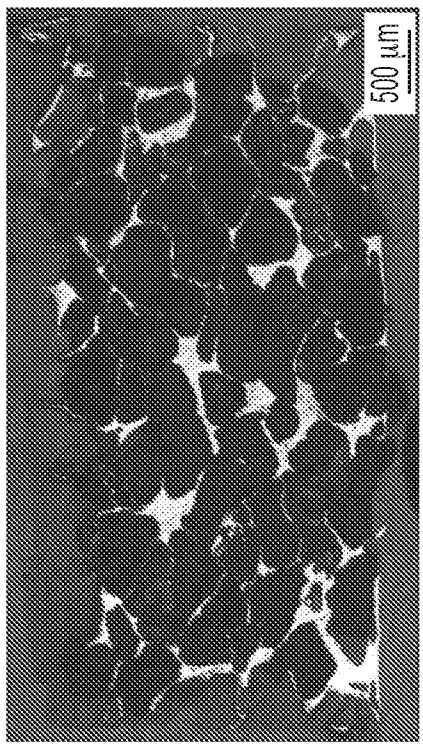

FIG. 15C

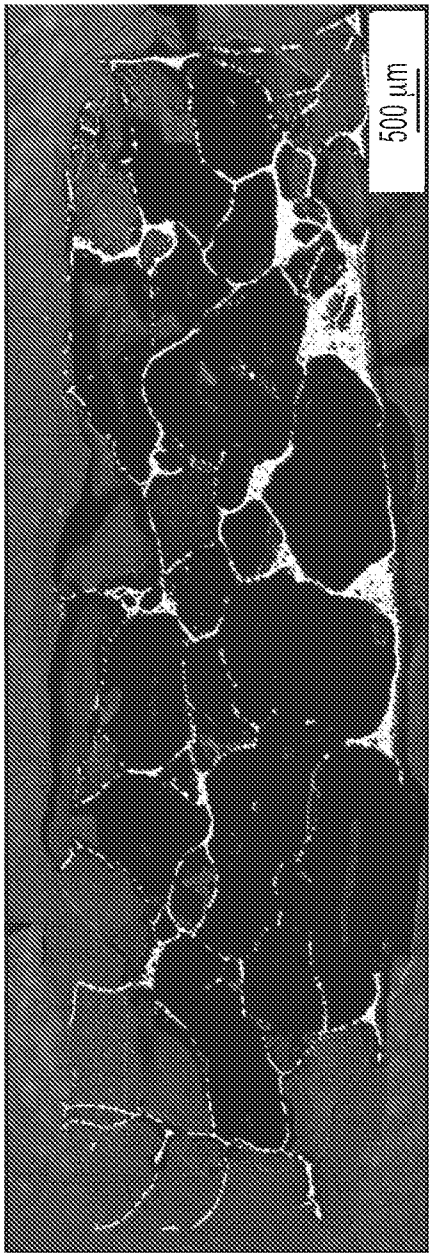

FIG. 16A

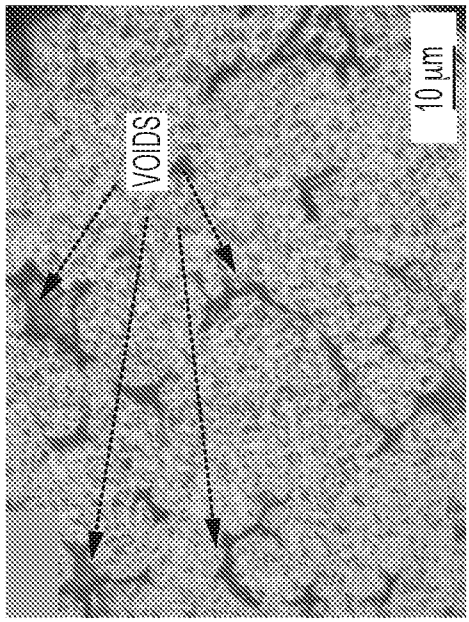

FIG. 16C

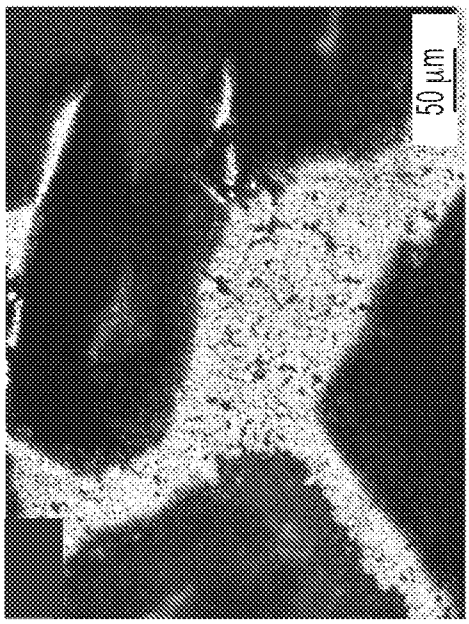

FIG. 16B

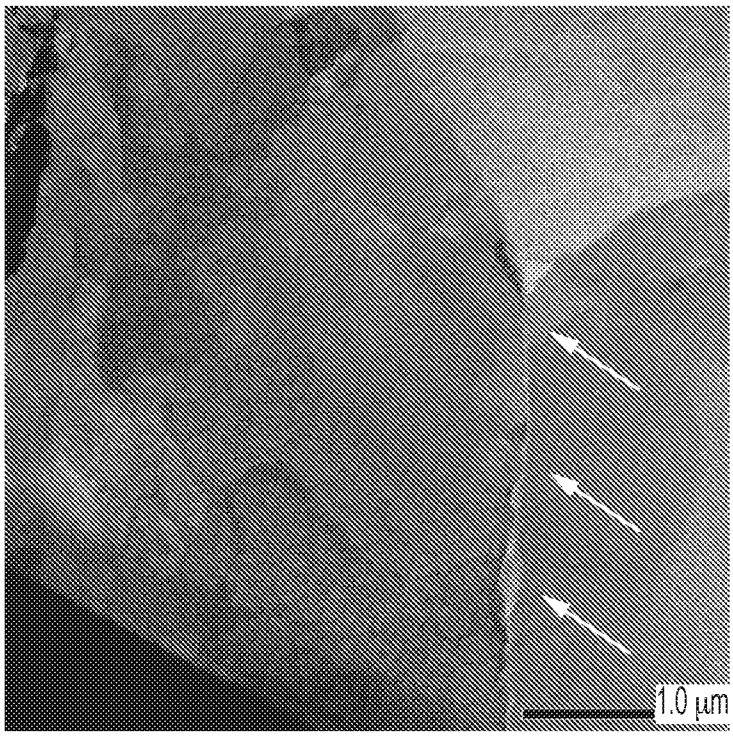

FIG. 17A

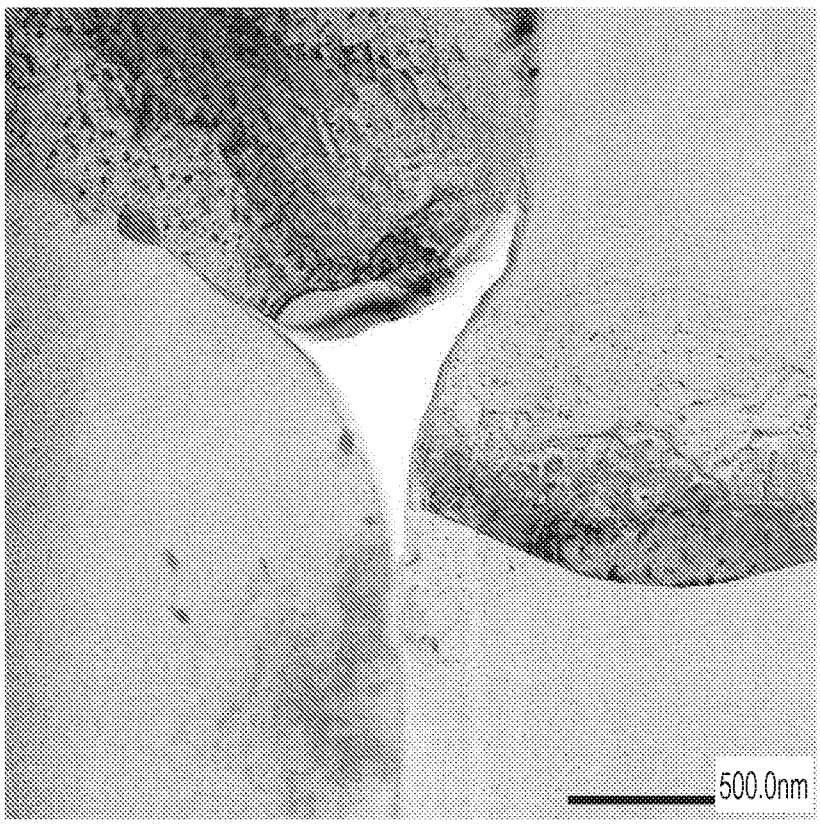

FIG. 17B

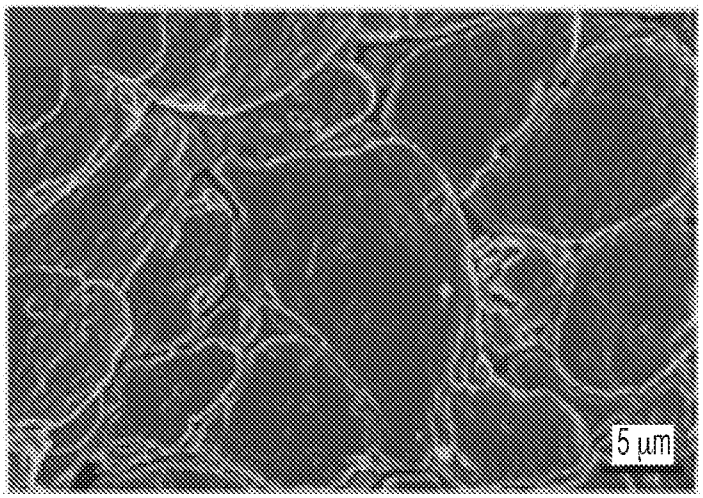

FIG. 18A

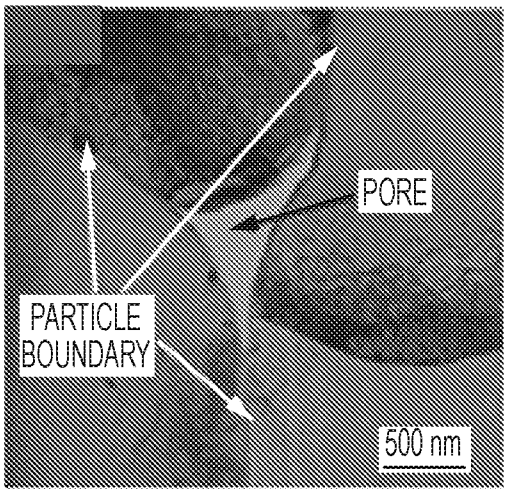

FIG. 18B

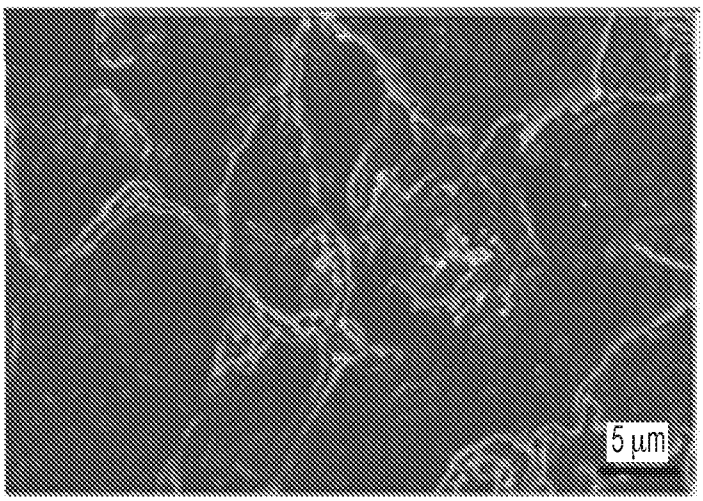

FIG. 18C

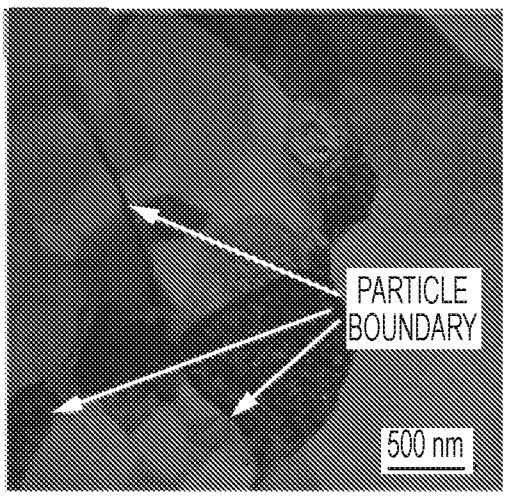

FIG. 18D

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/051747

A. CLASSIFICATION OF SUBJECT MATTER
INV. B22F3/11
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)
B22F

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)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 755 809 A2 (UNIV LIVERPOOL [GB]) 28 February 2007 (2007-02-28) paragraphs [0009], [0010] -----	33-64
X	EP 1 201 337 A1 (FUTURE METAL CO LTD [KR]) 2 May 2002 (2002-05-02) paragraphs [0005], [0010] examples 1, 2 claims 1, 2 -----	33-64
A	JP 2014 062317 A (UNIV SAGA) 10 April 2014 (2014-04-10) paragraphs [0044] - [0046] claims 1, 3-5 -----	1-32
A	US 2010/003158 A1 (ANDO TEIICHI [US] ET AL) 7 January 2010 (2010-01-07) claim 1 -----	1-32

☐ 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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 November 2017	05/12/2017

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Järvi, Tommi

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2017/051747

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1755809 A2	28-02-2007	AT 404309 T	15-08-2008
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		WO 2008094624 A1	07-08-2008