

(19)



(11)

EP 3 944 914 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

02.02.2022 Bulletin 2022/05

(51) International Patent Classification (IPC):

B22F 9/08 ^(2006.01) **B22F 9/10** ^(2006.01)
B22F 9/14 ^(2006.01) **B22D 11/06** ^(2006.01)
B22D 11/16 ^(2006.01)

(21) Application number: **20188662.9**

(22) Date of filing: **30.07.2020**

(52) Cooperative Patent Classification (CPC):

B22D 11/0611; B22D 11/0642; B22D 11/0651;
B22D 11/16; B22D 13/00; B22D 23/003;
B22F 9/082; B22F 9/10; B22F 9/14;
B22F 2009/0836; B22F 2009/088; B22F 2009/0892

(84) Designated Contracting States:

AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR

Designated Extension States:

BA ME

Designated Validation States:

KH MA MD TN

(72) Inventors:

- **MICOULET, Alexandre**
68229 Mannheim (DE)
- **SPATZ, Joachim P.**
70569 Stuttgart (DE)

(74) Representative: **Manitz Finsterwald**

Patent- und Rechtsanwaltspartnerschaft mbB
Martin-Greif-Strasse 1
80336 München (DE)

(71) Applicant: **Max-Planck-Gesellschaft zur**
Förderung der
Wissenschaften e.V.
80539 München (DE)

(54) **NOZZLE AND METHOD FOR FORMING MICRODROPLETS**

(57) The invention relates to a nozzle for producing microdroplets of metal using gas flow, to a nozzle for producing microdroplets using electrodispersion, to a combination of a melt spinner for forming elongate metal fibers with a nozzle and to a method of forming microdroplets using at least one of a gas flow and electrodispersion.

EP 3 944 914 A1

Description

[0001] The invention relates to a nozzle for producing metal droplets using gas flow and to a nozzle for producing metal droplets using electrodispersion. Furthermore, the invention relates to a combination of a melt spinner for forming elongate metal fibers with a nozzle according to the invention and to a method of forming microdroplets using at least one of gas flow and electrodispersion.

[0002] A known method to produce metal strands out of metal droplets is the process of melt spinning. Melt spinning is a technique used for rapid cooling of metal liquids. A thin stream of metal liquid is then dripped onto the circumferential surface of a fast rotating wheel where it undergoes rapid solidification. This technique is used to form elongated strands of materials such as metals or metallic glasses. The cooling rates achievable by melt-spinning are of the order of $10^4 - 10^7$ Kelvin per second (K/s). The process can continuously produce thin ribbons of material.

[0003] In this connection it should be noted that a strand can be understood as an element of which the length is at least twice its width, while the geometry of its cross section may be round, oval, half-oval, rectangular, quadratic, triangular or such a related geometry.

[0004] A special role is assigned to metal strands and/or fibers with a lateral dimension in the micrometer range, i.e. 1 to 50 micrometers, and a length of several millimeters or centimeters. These materials, as individual fibers, mesh of fibers or bunch of fibers, also in combination with other materials play a central role in a whole series of applications for the improvement of the most diverse properties. Examples of such applications are metallic wool and tissues, 3-dimensional electrodes for batteries and accumulators, catalysis, conductive plastics for touch sensitive systems, such as, displays and artificial hands in the field of robots, anti-electrostatic textiles and plastics, mechanically reinforced textiles, plastics and cement for lightweight and heavy construction, filter materials for use in environments subjected to mechanical and/or chemical stress or catalysis.

[0005] An important aspect for the improvement of metal strand based material functions is a large surface area to weight ratio and the ability to manufacture and process such strands in an industrially relevant process. This signifies: adjustable lengths, widths and cross section geometries of metal strands, reproducibility and economic manufacturing methods and low process costs with a high material yield per unit time.

[0006] Nowadays, the industrially relevant manufacture of functional materials based on metal strands is restricted to a strand width of about $50\mu\text{m}$ and larger. These methods are based on drawing, template, rolling or extrusion processes. Fibers of stainless steel with a width of down to 8 micrometers are manufactured by a complicated drawing process starting from a bundle of larger diameter fibers, which are drawn to smaller diameters. For example, the fibers need to be coated with a

layer of copper in order to allow gliding of the fibers along one another. However, these methods have disadvantages when being utilized industrially because they are restricted to a few materials only, require long process times and costly fabrication- and post-fabrication processes. The method is generally restricted to only a few kinds of metal.

[0007] Conventionally known apparatuses for producing metal strands via melt-spinning processes usually let molten metal flow on a lateral surface or a circumferential surface of a rotating wheel. This allows the metal melt to partly coat the rotating lateral or circumferential surface of the wheel with a certain thickness and to be "thrown off" the wheel as straight strand of defined thickness due to centrifugal forces originating from the rotation of the wheel once the metal is solidified.

[0008] In conventional melt spinners a continuous flow of liquid metal is brought in contact with the above mentioned rotating wheel to form the metal fibers. In order to be able to produce fibers in a micrometer scale it is well known that with finer continuous flows of molten metal even smaller metal fibers can be formed on said rotating wheel. Hence, one approach to produce even smaller fibers is to reduce the size of a nozzle opening, from which the molten metal is directed to the rotating wheel, such that the flow of molten metal is reduced to a minimum. Nevertheless, it has shown that this approach has its limits, since the size of the nozzle opening can only be reduced to a certain limit depending on the surface tension of the molten metal, because at some point the molten metal would simply - because of said surface tension - not exit the nozzle anymore.

[0009] It is therefore an object of the invention to provide a nozzle and a method for producing microdroplets of metal as well as a combination of a melt spinner with a nozzle, with which the size of the produced fibers can be decreased significantly in its width and length. This object is solved by the subject-matter of the independent claims.

[0010] By way of example a nozzle for producing microdroplets of metal, may comprise a reservoir for molten metal, a nozzle opening for directing the molten metal in a flow direction out of the reservoir and a channel connecting the reservoir with the nozzle opening, wherein the nozzle further comprises an external force generating device configured to apply an external force on a molten metal flow flowing in said channel with a force per unit area generated by the external force generating device at the molten metal being larger than a surface tension of the molten metal.

[0011] A nozzle is thus provided into which a continuous or quasi continuous flow of molten metal is guided and in which nozzle the continuous or quasi continuous flow of molten metal is separated into individual bunches or droplets.

[0012] In other words, a nozzle is provided, which is configured to let molten metal flow out of a reservoir into one end of a channel. As the molten metal flow moves

through the channel a force is applied on said molten metal flow in the channel or at the exit of the channel which so to say chops the molten metal flow into individual droplets, since the force applied on the molten metal flow is greater than a surface tension of the molten metal, if the force is not greater than the surface tension, the surface tension of the liquid molten metal would keep the flow continuous. By defining the speed at which the molten metal flow is chopped, the size of the droplets generated from the originally continuous molten metal flow can be controlled and thereby be pre-determined.

[0013] This means that the gist of the present invention is the application of an external force, e.g. in the form of an externally applied gas flow or electric field, to separate the molten metal flow into individual bunches of molten metal, whereas in prior art melt spinning applications the flow molten metal flow is interrupted by controlling the speed of the moving surface moving relative to the molten metal flow.

[0014] As an alternative, depending on the temperature used gas may be replaced by a liquid stream which chops metal flow apart. The condition that then applies is that the liquid stream is not permitted to come into contact with the rotating wheel in order to not interfere with the principle of metal fibre formation on the rotating wheel.

[0015] In particular, according to a first aspect of the invention a nozzle for producing microdroplets of metal using gas flow is provided. The nozzle comprises a reservoir for molten metal, a nozzle opening for directing the molten metal in a flow direction out of the reservoir and a channel connecting the reservoir with the nozzle opening. Furthermore, the nozzle comprises a gas flow generating device for generating and directing the gas flow to the molten metal through at least one supply opening into the channel, wherein the supply opening is located at the nozzle opening or crossing the molten metal flow channel by a defined angle. A force per unit area, which is generated by the gas flow at the molten metal, is larger than the surface tension of the molten metal.

[0016] In other words, a nozzle is provided in which the external force generating device is a gas supply by means of which the speed at which the molten metal flow is chopped is defined by the force of the gas flow on the molten metal flow.

[0017] In this connection it is noted that the reservoir can be a hollow space, which is configured to accommodate the molten metal. Hence, the reservoir can either be a tank filled with the molten metal or a kind of a connecting piece, which can be attached to a separate tank and which is configured to guide the molten metal from the tank into one end of the channel.

[0018] At a far end of the channel a nozzle opening is provided, through which the molten metal is directed in a flow direction. In order to be able to provide microdroplets instead of a flow of molten metal, a gas flow generating device is provided, which is configured to generate a flow of gas. Said flow of gas is then directed to the

flow of molten metal inside the channel through a supply opening in the channel. The gas supply opening can be located in the near vicinity of the nozzle opening, i. e. for example not further away than 10cm upstream from the nozzle opening, such that the gas flow is provided at the molten metal somewhere in the channel, preferably at the point right before the melt exits the nozzle.

[0019] In this connection it is noted that in general the expression "nozzle opening" relates to lowermost point downstream the melt, where the formed droplet exits the nozzle.

[0020] A diameter of the gas supply opening can lie in the range of 0.001 to 5mm, preferably in the range of 0.005 to 0.015mm. Such sizes of supply openings have been found beneficial in forming droplets of the desired size.

[0021] As already mentioned above, the force per unit area, which is applied at the molten metal by the gas flow needs to exceed the surface tension of the molten metal such that microdroplets are formed from the metal flow, which then move on to exit the nozzle through the nozzle opening. The interfacial tensions of liquid metals can have values of up to and more than 400 mN/m.

[0022] In this connection it is also noted that the gas flow can either be provided as a continuous flow of gas, i.e. the same amount of gas is supplied for a period of five minutes or longer. Or the gas flow can be provided as a "pulsed" gas flow, meaning that the gas flow pressure can be modulated periodically, e.g. the gas flow is provided at a different pressure for a millisecond. Naturally other cycle times of the pulsed gas can be provided. Furthermore, it is noted that the gas can be a fluid with a comparatively high boiling temperature selected above 20°C, in particular above 100°C. This might be applicable for low temperature melting metals and metal alloys based on Gallium, Indium or tin. This means in other words that the gas flow can also be replaced by a high-boiling liquid.

[0023] According to a first embodiment of the invention the gas flow generating device is configured to direct the gas flow perpendicular to or at an angle to the flow direction into the channel. Hence, the gas flow can be directed to the molten metal from a side such that the gas flow can "cut" through the melt. In some cases it might help when the gas flow is not provided at an exact perpendicular angle with respect to the flow direction but rather at an angle smaller than 90° between the gas flow and the flow direction of the melt.

[0024] According to another embodiment the channel comprises two or more supply openings to receive the gas flow from more than one side around the circumference of the nozzle. For some applications it can be helpful to provide more than one gas flow in order to form microdroplets out of the flow of metal melt.

[0025] In some cases, it might also be necessary to provide more than one gas flow in order to produce a plurality of microdroplets, which all comprise roughly the same volume such that fibers, which can be produced

out of the droplets, will all roughly comprise the same diameter.

[0026] In this connection it is noted that the gas in the gas flow can be air, Helium, N₂, Ar₂, CO₂ or a combination from the above.

[0027] According to a second aspect of the invention a nozzle for producing microdroplets of metal is provided, in particular a nozzle as described above, using electrodispersion. The nozzle comprises a reservoir for molten metal, a nozzle opening for directing the molten metal in a flow direction out of the reservoir and a channel connecting the reservoir with the nozzle opening. Furthermore, the nozzle comprises a first electrode such as a metal piece and a device to apply an electric field between the first electrode and the molten metal with a force per unit area generated by the electric field at the molten metal being larger than a surface tension of the molten metal.

[0028] In other words, also according to the second aspect of the invention, a nozzle is provided, which is configured to let molten metal flow out of a reservoir into a channel and then to chop the molten metal flow in or exiting said channel through the application of an external force into droplets of pre-determined size by varying the size of the force applied at the flow of molten metal and then guiding the droplets out of the nozzle opening. In the present case the external force generating device is an electric field generator.

[0029] It should be noted in this connection that also other types of external force generating devices can be used provided that they can be configured to apply an external force on the molten metal flow which is larger than a surface tension of the molten metal flow so that a continuous or quasi continuous molten metal flow can be separated into droplets of pre-determinable size.

[0030] In this connection the reservoir can be a hollow space, which is configured to accommodate the molten metal. Hence, the reservoir can either be a tank filled with the molten metal or some kind of a connecting piece, which can be attached to a separate tank and which is configured to guide the molten metal from the tank into one end of the channel.

[0031] At the far end of the channel a nozzle opening is provided, through which the molten metal is directed in a flow direction. In order to be able to provide microdroplets instead of a flow of molten metal, a first electrode such as a metal piece and device to apply an electric field between the first electrode and the molten metal is provided. That is to say, the device applies a voltage to the first electrode and the molten metal such that an electric field is generated between the first electrode and the molten metal. Said electric field induces a Coulomb force, which is able to break up the flow of molten metal into microdroplets.

[0032] The force per unit area, which is applied by said Coulomb force at the molten metal needs to exceed the surface tension of the molten metal such that microdroplets can be formed out of the metal flow. In this connec-

tion it is noted that interfacial tensions of liquid metals can value up and above 400 mN/m. The microdroplets can be formed directly after the melt exits the nozzle, i. e. right at the nozzle opening.

[0033] Furthermore, it is possible that the electric field is provided by the device such that the molten metal itself acts as a second electrode. It is also possible that one electrode may be the molten metal itself while the second electrode the rotating wheel. In an alternative embodiment a second - separate - electrode is provided at an opposite site of the molten metal such that the microdroplets are being formed when the molten metal flows through a space between said two electrodes. The second electrode can also be a piece of metal or even a wheel of a melt spinner.

[0034] It is known that increasing the applied voltage or decreasing the distance between two electrodes, i. e. for example the first electrode and the molten metal or the second separate electrode, leads to a higher electric field and thus also to a higher Coulomb force. Hence, there are several ways to increase the force per unit area high enough to overcome the surface tension of the molten metal.

[0035] The first, and if existing the second electrode, can be, for example, a piece of metal or any other kind of suitable material composition such as graphite powder as long as it is electrically conductive.

[0036] Depending on the exact composition of the molten metal it can in some cases also be favourable to provide two separate electrodes, whereas in other cases only one electrode with the molten metal itself acting as the second electrode may be sufficient in order to continuously produce the microdroplets.

[0037] Generally, it is also possible to provide a nozzle, which comprises the gas generating device as well as the first electrode and a device to generate an electric field between the first electrode and the molten metal flow such that a combination of both the gas flow and the electric field can be used to form the microdroplets.

[0038] Hence, it can also be possible to produce plasma such that the plasma can "cut" droplets from the flow of molten metal exiting the nozzle. However, it is also noted that usually some sort of gas is already present at the nozzle such that plasma could already be produced by the use of a nozzle using electrodispersion. According to a first embodiment the first electrode comprises an essentially cuboid shape with a length in the range of 1 to 5cm and a width in the range of 0.1 to 5cm. In this connection it is noted that the exact shape and size of the electrode may be very variable. Thus, different shapes and sizes can be chosen.

[0039] According to another embodiment the electric field generated between the first and the molten metal lies in the range of 1 V/cm to 1000 V/cm, preferably in the range of 10 V/cm to 800 V/cm, particularly in the range of 20 V/cm to 400 V/cm. The generated electric field only needs to be high enough such that the force per unit area, which is applied by the Coulomb force generated by the

electric field at the molten metal exceeds the surface tension of the molten metal in order to produce microdroplets out of the flow of molten metal.

[0040] It is further noted that the electric field can be generated by an alternating current or a direct current. Hence, the force per unit area applied to the molten metal can either be applied continuously or in a pulsed manner. However, applying alternating fields may limit the flow of current between the two electrodes.

[0041] According to another embodiment of the invention a cross-section of the channel in the flow direction of the molten metal comprises a rectangular or triangular shape. The precise shape of the channel may be chosen according to the composition of the molten metal and/or according to the type of nozzle, which is used, i.e. a nozzle using gas flow, electrodispersion, an external force generating device or maybe even combinations of the foregoing.

[0042] Regardless of the choice of the cross section in the flow direction, the cross-section of the channel in a plane perpendicular to the flow direction of the molten metal can be chosen to comprise a circular, rectangular, triangular, oval, polygonal or any other shape. Hence, the channel can comprise a cylindrical, cuboid, pyramidal, conical or any other shape. As already mentioned above, the tapered shapes can either be tapered in the flow direction of the molten metal or also against the flow direction.

[0043] Also, the channel can comprise a length in the range of 0.1 to 100mm, preferably 1 to 50mm, in particular 5 to 20mm. A limiting factor in the choice of length of the channel may be the how fast the flow of molten metal cools down and thus solidifies. A solidification of the molten metal inside the channel has to be avoided. Hence, the length of the channel has to be chosen accordingly. Currently, for some metals, an approximate length of about 10mm has proven to be a preferable length. In this connection it is also noted that if a gas is used to produce the metal droplets, said gas may not be too cold such that the metal solidifies before the droplets can be formed. Hence, it may be necessary to heat the gas, which is used to "cut" the flow of molten metal.

According to still another embodiment the nozzle opening comprises a circular, rectangular, triangular, oval, polygonal or any other shaped cross-section. In this connection it is noted that the cross section of the nozzle opening can correspond to the cross section of the channel in the plane perpendicular to the flow direction. Should this not be the case, the channel further comprises a transition area, in which the cross section of the channel transitions to the cross section of the nozzle opening.

[0044] According to an embodiment a rectangular nozzle opening can comprise a length in the range of 0.5 to 10cm, preferably 1 to 5 cm, and a width in the range of 10 to 500 μ m, preferably 20 to 200 μ m, in particular 30 to 100 μ m.

[0045] According to another embodiment a circular nozzle opening can comprise a diameter of 10 to 500 μ m,

preferably 20 to 200 μ m, in particular 30 to 100 μ m.

[0046] According to another embodiment of the invention the reservoir comprises an inner shape, which is connected with the channel via a channel opening in the inner shape, wherein the inner shape of the reservoir is rounded or sloped the channel opening such that the molten metal is guided to the nozzle opening.

[0047] The formed microdroplets can comprise a diameter in the range of 0.010 to 0.500mm, preferably in the range of 0.050 to 0.150mm.

[0048] Typical materials for the molten metal can be bronze, Au, Ag, cobalt-alloy, Fe-alloy, CuSi₁₋₁₅, AlSi₁₋₁₅ or stainless steel.

[0049] In a third aspect of the invention a combination of a melt spinner for forming elongate metal fibers with a nozzle according to the invention is provided. The melt spinner further comprises a rotatable wheel with a circumferential surface, at least one rotating planar surface and collection means for collecting solidified fibers formed on one of the circumferential surface and the rotating planar surface of the rotatable wheel from the molten metal and separated from the rotatable wheel by forces generated by the rotation of the rotatable wheel. Thus, the microdroplets, formed in or at the nozzle, are directed from the nozzle opening to either one of the circumferential and the tangential surface of the rotating wheel. In both cases the drops will be - as soon as they touch the respective surface of the wheel - elongated by the force of the rotating wheel until it solidifies to a fiber. After solidification the fiber will be thrown off the wheel by a force generated by the wheel. Said force can for example be a circumferential force such that after being thrown off the wheel, the collection means can catch the solidified fibers.

[0050] In this connection it is noted that in the case that a nozzle using electrodispersion is provided, the rotating wheel itself, which is usually made out of metal, can act as the first electrode such that the molten metal acts as the second electrode.

[0051] State of the art melt spinners, which can be used with the nozzles according to the invention are well known and are, for example, described in WO2017/042155 (which describes a so-called vertical melt spinner) and PCT/EP2020/063026 (which describes a so-called horizontal melt spinner).

[0052] With said state of the art melt spinners typical distances between the nozzle and the rotating wheel lie in the range between 1 and 30mm, whereas typical speeds for the rotating wheel lie in the range of 10 to 100m/s, preferably 20 to 75m/s. This leads to contact times of the droplets with the surface of the rotating wheel in the range of 1 to 10ms.

[0053] In a fourth aspect of the invention a method of forming microdroplets using at least one of an external force field, a gas flow and electrodispersion is provided. The method comprises the following steps of providing a flow of molten metal at a nozzle opening and applying a force per unit area at said nozzle opening on said flow

of molten metal, with said force per unit area being larger than a surface tension of said flow of molten metal. The nozzle can comprise the above mentioned features of the invention such that the force per unit area, which is applied at the nozzle opening originates from a gas flow and/or electrodispersion.

[0054] The invention will now be described in further detail by way of example only with reference to the accompanying drawings. In the drawings there are shown:

- Figs. 1a to 1c: different examples of nozzles according to the invention using gas flow;
- Fig. 1d: a further example of a nozzle according to the invention;
- Figs. 2a to 2d: different examples of nozzles according to the invention using electrodispersion;
- Fig. 3: an example of a horizontal melt spinner;
- Fig. 4: an example of a vertical melt spinner;
- Figs. 5a and 5b: experimental results and pictures of produced microdroplets;
- Fig. 6: scanning electron micrographs of a produced fibre;
- Fig. 7: a photograph of a cross section of a produced fiber;
- Figs. 8a to 8c: experimental results for distributions of fiber thicknesses and widths;
- Figs. 9a to 9c: experimental results for distributions of fiber thicknesses and widths;
- Fig. 10: a photograph of a produced bronze fiber;
- Fig. 11: a photograph of a plurality of produced bronze fibers;
- Figs 12a to 12c: experimental results for distributions of thicknesses and widths of produced fibers; and
- Fig. 13: experimental results for the variation of metal droplet volume by controlling the gas pressure which chops the continuous flow of metals in metal droplets.

[0055] Figs. 1a to 1c show different examples nozzles 10, each comprising a reservoir 12 filled with molten metal 14, a channel 16 and a nozzle opening 18. It can be seen that the nozzle opening relates to the last opening in a flow direction F of the molten metal 14, where the molten metal 14 actually leaves the nozzle 10.

[0056] The nozzles 10 shown in Figs. 1a to 1c each furthermore comprise two supply openings 20 for a gas flow, which is generated by a gas flow generating device (not shown). As can be seen the supply openings can either supply said gas flow in a direction perpendicular to the flow direction F of the molten metal 14 (see Fig. 1a) or at an angle smaller than 90° between the flow

direction F and a gas flow direction G (see Figs. 1b and 1c).

[0057] Regardless of the angle, the gas flow crosses the flow of molten metal 14 right at the nozzle opening 18 or right before the molten metal 14 exits the nozzle opening 18 such that a force per unit area generated by the gas flow at the molten metal 14 exceeds the surface tension of the molten metal 14 to form microdroplets 22.

[0058] In this connection it is noted that the gas flow can either be a continuous flow of gas or a pulsed flow of gas. The used gas can for example be N₂, Ar₂ or another gas such as CO₂.

[0059] The supply openings 20 shown in Figs. 1a to 1c each comprise a diameter in the range of 0.005 to 0.015mm, whereas the channel 16 comprises a diameter in the range of 0.050 to 0.250mm. Even though the expression "diameter" is used, it is clear that the cross section of both the supply openings 20 and the channel 16 do not necessarily have to be circular but can also be polygonal, triangular, rectangular, oval or any other shape.

[0060] The same applies also to the nozzle opening 18, which can have a circular cross section as well as a rectangular, triangular, oval or polygonal one.

[0061] The reservoir 12 shown in Figs. 1a to 1c is formed as a hollow space, which is configured to accommodate the metal melt. The hollow space comprises a channel opening 24 through which the metal melt 14 can flow into the channel 16. An inner shape of the reservoir 12 is rounded at the channel opening 24 such that the melt 14 can flow easily into the channel 16.

[0062] The reservoir 12 can either be a tank, which holds a bigger volume of melt 14, or a connecting piece, which is configured to be attached to a separate tank. Hence, the hollow space can either be big enough to hold a bigger volume of melt 14 or just as big to act as a connecting piece between the channel 16 and a separate tank.

[0063] Another example of a nozzle 10 using a gas flow to produce the microdroplets 22 is shown in Fig. 1d. Also in this embodiment a reservoir 12 for the molten metal is provided. The reservoir 12 further comprises a channel opening 24 through which a channel 16 is connected to the reservoir. At the far end of the channel 16 the nozzle 10 comprises a nozzle opening 18 through which the molten metal 14 can flow. Furthermore, one can see in Fig. 1d that the channel 16 comprises two gas flow channels 17 with respective supply openings through which one can direct a gas to the channel 16, which then chops the continuous flow of metal into a non-continuous flow such that droplets exit the opening 18.

[0064] It should also be noted that the supply openings 20 could be arranged at the nozzle opening 18 in order to separate the flow of molten metal 14 at the nozzle opening 18.

[0065] In the design shown in Fig. 1d, the two gas flow channels 17 first run in parallel to the channel 16 until they make a turn in the direction of the channel 16 such

that they meet the channel at the respective supply openings 20 of the channel 16. They can either meet the channel 16 such that the gas, which flows through the gas flow channels 17 "cuts" the molten metal 14 perpendicular to the flow direction F or at another defined angle.

[0066] In this connection it should be noted that the two gas flow channels 17 could also be arranged in a different manner and extend e.g. obliquely with respect to the channel 16 from their starting point.

[0067] Thus, it can be seen that the flow of gas can be provided at the nozzle at the reservoir 12 and in flow direction F. Such an embodiment can help to reduce the space needed for the nozzle 10 since the gas flow generating device can be provided at the reservoir 12 and thus, does not need any additional space next to the channel 16.

[0068] It is also possible that only one air flow channel 17 or more than two air flow channels 17 are provided. Hence, it is noted that the embodiment of Fig. 1d describes only an example and does not restrict the invention in any way.

[0069] A typical diameter of said air flow channel is about 1mm. Depending on the type of metal used said diameter can also vary. The typical gas pressure, with which the gas flows through the air flow channel 17 and through the supply opening 18, lies in the range from 100 to 10000mbar, preferably in the range of 800 to 1500mbar.

[0070] Said pressure can be dependent on the precise shape of the cross section of the air flow channel as well as the channel for the molten metal.

[0071] Figs. 2a to 2d show different examples of nozzles 10, which all use the concept of electrodispersion to form microdroplets 22 of molten metal 14. The shown nozzles 10 comprise generally the structure as the nozzles 10 of Figs. 1a to 1c expect for the part with the supply opening 20 since the nozzles 10 from Figs. 2a to 2d do not need a supply opening of any kind.

[0072] However, said nozzles 10 also comprise a reservoir 12 filled with molten metal 14, a channel 16 and a nozzle opening 18. Furthermore, said nozzles 10 comprise a first electrode 26, which can be designed in several different ways. As can be seen in Figs. 2c and 2d said first electrode 26 is a separate piece of metal, which is placed near the nozzle opening 18. A typical value for the spacing between the nozzle opening 18 and the first electrode 26 lies in the range from 4 to 6mm. Fig. 2d additionally shows a second piece of metal, which is used as a second electrode 30 such that the flow of molten metal 14 is guided through a space between said two electrodes 26, 30 such that the microdroplets 22 are formed therein.

[0073] As can be seen Fig. 2c, on the other hand, it is not necessary to provide a second separate electrode 30 since the molten metal 14 itself can act as the second electrode, meaning that the electric field is generated between the first electrode 26 and the molten metal 14.

[0074] In Figs. 2a and 2b, on the other hand, the first

electrode is realized by a (metal) surface 28, onto which the formed microdroplets 22 are directed. As will be described later in connection with Figs. 4 and 5, said surface 28 can be a circumferential or tangential surface of a rotating wheel of a so called melt spinner.

[0075] It should be noted that the channel 16 may comprises an approximate length selected in the range of 5 to 30 mm, in particular in the range of 8 to 15mm, whereas the diameter (or length) of the nozzle opening 18 lies in that range of 0.005 to 0.100mm.

[0076] Fig. 3 shows a typical horizontal melt spinner 32 for producing elongate metal strands comprising a nozzle 10 with a nozzle opening 18, which deposits drops of molten metal 14 in a deposition direction D onto a rotating planar surface 34 of a rotating wheel 36. In order to be able to deposit molten metal, the nozzle 10 comprises a heating device 38, which heats the metal inside the nozzle 10 to a temperature where the metal is in its liquid state.

[0077] The nozzle opening 18 may be of any geometry, usually circular, oval, rectangular, quadratic or triangular. The opening width can lie in the range of 10 μ m to 500 μ m. The nozzle direction N may vary from 90° with respect to the planar surface 34, i. e. it may be selected to lie in the range from 0° to 90°. Hence, the nozzle 10 could also be aligned parallel to the rotating planar surface 34 and still have a deposition direction D which is perpendicular, or any other angle, to the planar surface 34.

[0078] The diameter of the wheel 36 can range from centimeters to meters and the wheel material maybe of any choice, which withstands the metal molt deposition and fast rotation speed, in particular metal alloys such as copper, copper alloys, brass, nickel, iron, iron oxide, stainless steel or carbon based material such as graphite or carbide, ceramic materials. It is also possible that the wheel 36 is a wheel of a base material having a layer made of a metal or of a metal alloy of a ceramic material or of graphite or a vapor deposited carbon, for example a copper wheel 36 having a layer of graphite.

[0079] Because of the rotation of the wheel 36, the molten metal drops 22, which come into contact with the surface are entrained and thereby elongated by the wheel 36 to form elongate metal strands 40. These strands 40 remain on the surface until they are cooled down enough to solidify. For this purpose the rotating wheel 36 can be cooled by a cooling device to for example room temperature or even below by cooling with liquid nitrogen in order for the molten metal drops 22 to be able to solidify to metal strands 40. If the wheel 36 was not cooled at all it would eventually heat up because of its contact with the (hot) molten metal 14 and hence prevent the molten metal 14 to cool down sufficiently to solidify. Heating of the wheel can also affect its mechanical stability. The cooling device C is shown inside the rotatable wheel 36, but it is noted that does not necessarily have to be located inside the wheel. There are sufficiently many methods known to cool such devices.

[0080] Once the metal fibers 40 are solidified the cen-

trifugal forces which act on the metal fibers 40 due to the rotation of the wheel 36 will suffice in order to move the metal fibers 40 away from the planar surface. As the adhesion force between the solidified metal fibers 40 and the planar surface is less than the force acting on the metal fiber 40 due to the rotation of the planar surface. Thus, the solidified metal fibers 40 fly away from the wheel 36 in a direction transverse to the circumference of the wheel 36.

[0081] For collection of the solidified fibers 40 collection means 42 are provided, which basically catch the fibers 40 flying away from the rotating wheel 36.

[0082] A typical vertical melt spinner is shown in Fig. 4. Since the vertical melt spinner comprises several components, which are identical to the ones from the horizontal melt spinner, only the differences between these two will now be described.

[0083] The difference lies in the alignment of the rotating wheel 36 and hence the corresponding surface onto which the microdroplets 22 are guided. While the rotating wheel 36 of the horizontal melt spinner of Fig. 3 is aligned such that the microdroplets are being guided on one of its planar lateral surfaces 34, in the vertical melt spinner the rotating wheel 36 is aligned such that the microdroplets 22 are guided onto the circumferential surface 35 of the wheel. Hence, a rotation axis A of the rotating wheel 36 is aligned perpendicular to the flow direction F of the molten metal 14, whereas the rotation axis A of the horizontal melt spinner is aligned parallel to the flow direction F of the melt spinner.

[0084] Regardless of the alignment of the rotating wheel 36, the microdroplets 22 are elongated by the rotating wheel 36 just as described before in connection with Fig. 4.

[0085] Figs. 5a to 12c show different photographs and experimental results of the produced microdroplets 22 as well as the therewith produced fibers 40.

[0086] Figs. 5a shows a photograph of microdroplets 22, which are composed of bronze, whereas Fig. 5b shows experimental results for a size distribution of the diameter of microdroplets 22, which are composed of a cobalt-alloy. The diameter for both materials was constant throughout the experiment and in the range of 0.060 to 0.250mm. It has further shown that the ejection of the droplets 22 can also be held constant in the range of 1 to 10ms depending on the precise experimental settings. An increase of pressure, for example, has shown to have a minor influence on the microdroplet diameter, but a notable influence on the time laps between the ejection of two microdroplets.

[0087] The solidified fiber, which results from guiding the cobalt-alloy microdroplet 22 on a rotating wheel 36 of a horizontal or vertical melt spinner is shown in Fig. 6. It is observed that a small droplet remains at the very end of the produced fiber with a width of approximately 60 μ m. Said remaining droplet is shown in detail in the three bottom photographs. The width of the produced fiber is approximately 12 μ m.

[0088] A cross section of a produced bronze fiber is shown in Fig. 7. It can be seen that a typical cross section is asymmetric and comprises a straight part 44, which is contact with the wheel surface as well as a curved part 46 at the opposite side of the fiber 40. The parts with the highest curvature (left and right on the picture) result of poor wetting of the rotating wheel 36 by the melt 14. The maximal height of the fiber in this photograph is about 6 μ m.

[0089] Size distributions of the fiber thicknesses and widths are shown in Figs. 8a to 9c. The distributions are quite narrow and usually either Gaussian or log-normal distributions. Experiments have shown that parameters such as the wheel speed, roughness of the wheel surface, temperature of the melt and so on, can influence the landing of the microdroplet 22 on the wheel surface and thus the formation of the fiber. For a cobalt-alloy, the comparison of the size distributions indicates that the wheel surface speed influences the fiber geometry significantly. If the droplet diameter is kept constant as well as other experimental parameters, the increase of the wheel surface speed from 25m/s to 50m/s results in a decrease of thickness of 50% and decrease of width of 30% (comparison of Figs. 8a to 8c with 9a to 9c and Fig. 12).

[0090] If the microdroplet 22 diameter is reduced to 60 μ m (see Fig. 5a), the width of the fabricated fiber at standard experimental conditions is significantly below 10 μ m (see Fig. 10). A picture of a large amount of fibers produced with the said experimental settings is shown in Fig. 11.

[0091] The dropping process and its stability have shown to depend on the physical properties of the materials in contact at the microscopic scale, i.e. viscosity and surface tension of the melt, wetting of the nozzle surfaces by the melt (often sharply depending on the temperature) and the mechanical properties of the nozzle surfaces.

[0092] At the minimum required pressure difference and slightly above, three qualitative experimental observations are of crucial importance to support the dropping of the microdroplets: Firstly, the melt should not wet the nozzle (i. e. wetting angle $\gg 90^\circ$ but between contact angles from 0° to 90°);

[0093] Secondly, a reduced roughness of the surface of the rotating wheel is of advantage to improve the process stability. If the roughness of the nozzle surface is in the range of 0.05mm, it introduces a heterogeneous flow of melt. Hence, polishing the surface with a polishing paper, such as sandpaper with a grit size of down to a grain size of 0.003 mm has shown to be beneficial. In this connection sand paper with a grit size selected in the range of 20 to 500 can be selected preferably with a grit size of around 200 to 350.

[0094] As a third point experiments have shown that the borders of the nozzle opening should be as sharp as possible, i. e. rounded borders favor droplets of larger diameter. Hence, the sharper the borders, the smaller

the microdroplets can get.

[0095] Finally, Fig. 13 shows how the microdroplet volume varies if the gas pressure of the gas flow, which chops the continuous flow of metal in droplets is controlled to different values. One can clearly see that a control of the gas pressure is crucial in order to produce microdroplets with a volume down to several nanoliters.

[0096] Generally speaking, the volume of the microdroplets lies in the range of 0.1 to 20 nanoliters, in particular in the range of 2 to 9 nanoliters. In this connection a nozzle pressure, i. e. the pressure, with which the gas, e.g. Argon, is supplied in the channel to the molten metal, can be selected in the range of 900 mbar to 2000 mbar, in particular in the range of 1000 to 1500 mbar for a crucible pressure of 880 to 1050 mbar, in particular in the range of 900 to 1000 mbar, with the specific values being indicated in the drawing of Fig. 13. The term "crucible pressure" relates to the pressure exerted on the molten metal in the channel of the molten metal. In this connection it is noted that the nozzle pressure should not be much greater than the crucible pressure, as otherwise the molten metal can flow back into the gas passage for the gas flow.

Control of the liquid metal droplet volume by electrodispersion

[0097] As already mentioned above, the interfacial tension of liquid metals is very large, i.e. >400 mN/m. Therefore, liquid metals tend to form droplets in gas atmosphere or liquids to minimize their surface energy.

[0098] Electrodispersion techniques utilize a high electrical voltage to overcome the surface tension of a liquid meniscus at an orifice, allowing the breaking of the liquid into either monodisperse or polydisperse fine droplets.

[0099] Breakup of emerging liquid metal droplet occurs when the disruptive forces, i.e. the Coulomb force induced by the high voltage, overcome the interfacial tension that resists deformation of the droplet.

[0100] The liquid metal phase acts as the second electrode while for example a piece of solidified metal surface is the first electrode. In between the two electrodes an electric field is generated by a (not shown) device. Said electric field then generates a Coulomb force, which can overcome the interfacial tension that resists deformation of the droplet. Increasing the voltage or decreasing the distance between the two electrodes increases the electric field and thus also the Coulomb force, which is acting at the liquid interface.

Electrodispersion in combination with melt spinning

[0101] The control of a liquid metal droplet volume, which exits the nozzle of a crucible by electric fields can directly be applied to control the dimension of ultrafine metal fibers. Therefore, in some embodiments of the invention the liquid metal is contacted by one electrode while the second electrode is the rotating metal wheel or

an electrode, which is brought close to the exit of the nozzle. The thereby formed droplets with controlled volume are brought in contact with the rotating wheel, as described above, and an ultrafine metal fiber is pulled out of the droplet, which is in contact with the fast rotating wheel.

Control of liquid metal droplet volume by gas flow

[0102] A strong gas flow, which is brought close to the exit of a nozzle and crosses the linear flow of liquid metal from the exit, can overcome the surface tension of a fluid meniscus at an orifice, allowing the breaking of the liquid into either monodisperse or polydisperse fine droplets.

The possible set up for a nozzle as used in this setup has been explained above in connection with Figs. 1 to 4.

[0103] Generally, it is imaginable that both described methods, i.e. electrodispersion and gas flow, are realized in one single nozzle. With such a nozzle, the used method could for example be chosen according to the composition of the used molten metal. In some cases it can also be useful to apply both methods at the same time. Hence, the option to choose is can be given.

Claims

1. A nozzle for producing microdroplets of metal, the nozzle (10) comprising a reservoir (12) for molten metal (14), a nozzle opening (18) for directing the molten metal (14) in a flow direction (F) out of the reservoir (12) and a channel (16) connecting the reservoir (12) with the nozzle opening (18), wherein the nozzle (10) further comprises an external force generating device configured to apply an external force on a molten metal flow flowing in said channel (16) with a force per unit area generated by the external force generating device at the molten metal (14) being larger than a surface tension of the molten metal (14).
2. A nozzle for producing microdroplets of metal using gas flow, in particular in accordance with claim 1, the nozzle (10) comprising a reservoir (12) for molten metal (14), a nozzle opening (18) for directing the molten metal (14) in a flow direction (F) out of the reservoir (12) and a channel (16) connecting the reservoir (12) with the nozzle opening (18), wherein the nozzle (10) further comprises a gas flow generating device for generating and directing the gas flow to the molten metal (14) through at least one supply opening (20) into the channel (16), wherein the gas supply opening (20) is located at the nozzle opening (18), wherein a force per unit area generated by the gas flow at the molten metal (14) is larger than the surface tension of the molten metal (14).
3. The nozzle according to claim 1 or claim 2,

wherein the gas flow generating device, is configured to direct the gas flow perpendicular to or at an angle to the flow direction (F) of the channel (16).

4. The nozzle according to any one of the preceding claims,
wherein the channel (16) comprises two or more supply openings (20) to receive the gas flow from more than one side around the circumference of the nozzle (10). 5 10
5. The nozzle according to any one of the preceding claims,
wherein the gas in the gas flow is air, argon, Helium, N₂, Ar₂, CO₂ or combinations of the foregoing. 15
6. A nozzle for producing microdroplets of metal, in particular according to any one of claims 1 to 5, using electrodispersion, the nozzle (10) comprising a reservoir (12) for molten metal (14), a nozzle opening (18) for directing the molten metal (14) in a flow direction (F) out of the reservoir (12) and a channel (16) connecting the reservoir (12) with the nozzle opening (18), wherein the nozzle (10) further comprises a first electrode (26) such as a metal piece and a device to apply an electric field between the first electrode (26) and the molten metal (14) with a force per unit area generated by the electric field at the molten metal (14) being larger than a surface tension of the molten metal (14). 20 25 30
7. The nozzle according to claim 6,
wherein the first electrode (26) comprises an essentially cuboid shape, in particular with a length in the range of 1 to 5cm and a width in the range of 0.1 to 5cm. 35
8. The nozzle according to claim 6 or 7,
wherein the electric field generated between the first electrode (26) and the molten metal (14) has a field strength which lies in the range of 1 V/cm to 1000 V/cm, preferably in the range of 10 V/cm to 800 V/cm, particularly in the range of 20 V/cm to 400 V/cm. 40
9. The nozzle according to any one of claims 6 to 8,
wherein the electric field is generated by one of an alternating current and a direct current. 45
10. The nozzle according to any one of the preceding claims,
wherein a cross-section of the channel (16) in the flow direction (F) of the molten metal (14) comprises one of a square shape, a rectangular shape, a round shape, an oval shape, a polygonal shape and a triangular shape. 50
11. The nozzle according to anyone of the preceding claims, 55

wherein the cross-section of the channel (16) in a plane perpendicular to the flow direction (F) of the molten metal (14) comprises a circular, rectangular, triangular, oval, polygonal or any other shape.

12. The nozzle according to anyone of the preceding claims,
wherein the channel (16) comprises a length in the range of 0.1 to 100mm, preferably 1 to 50mm, in particular 5 to 20mm.
13. The nozzle according to any one of the preceding claims,
wherein the nozzle opening (18) comprises a circular, oval, square, rectangular, triangular, polygonal or any other shaped cross-section.
14. The nozzle according to claim 13,
wherein a rectangular nozzle opening (18) comprises a length in the range of 0.5 to 10cm, preferably 1 to 5 cm, and a width in the range of 10 to 500 μ m, preferably 20 to 200 μ m, in particular 30 to 100 μ m; or wherein a circular nozzle opening (18) comprises a diameter of 10 to 500 μ m, preferably 20 to 200 μ m, in particular 30 to 100 μ m.
15. The nozzle according to any one of the preceding claims,
wherein the reservoir (12) comprises an inner shape, which is connected with the channel (16) via a channel opening in the inner shape, wherein the inner shape of the reservoir (12) is rounded or sloped at the channel opening such that the molten metal (14) is guided to the nozzle opening (18).
16. The nozzle according to any one of the preceding claims,
wherein the formed microdroplets (22) comprise a size in the range of 0.010 to 500mm, preferably in the range of 0.050 to 150mm.
17. A combination of a melt spinner for forming elongate metal fibers with a nozzle (10) according to any one of the preceding claims, wherein the melt spinner (32) further comprises a rotatable wheel (36) with a circumferential surface (35), at least one rotating planar surface (34) and collection means (42) for collecting solidified fibers (40) formed on one of the circumferential surface (35) and the rotating planar surface (34) of the rotatable wheel (36) from the molten metal (14) and separated from the rotatable wheel (36) by forces generated by the rotation of the rotatable wheel (36).
18. A method of forming microdroplets using at least one of an external force field, a gas flow and electrodispersion, wherein the method comprises the following steps:

providing a flow of molten metal (14) at a nozzle opening (18); and
applying a force per unit area at said nozzle opening (18) by means of one of the on said flow of molten metal (14), with said force per unit area being larger than a surface tension of said flow of molten metal (14).

10

15

20

25

30

35

40

45

50

55

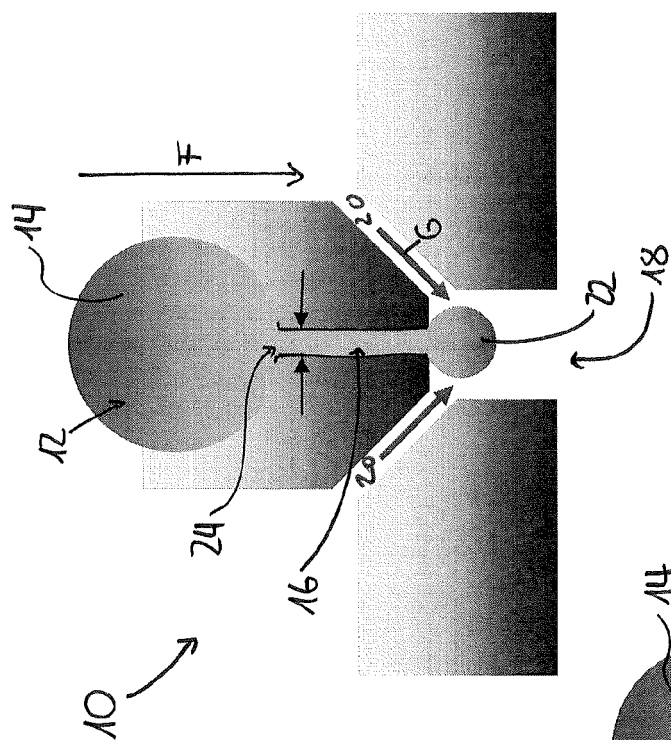


Fig. 1b

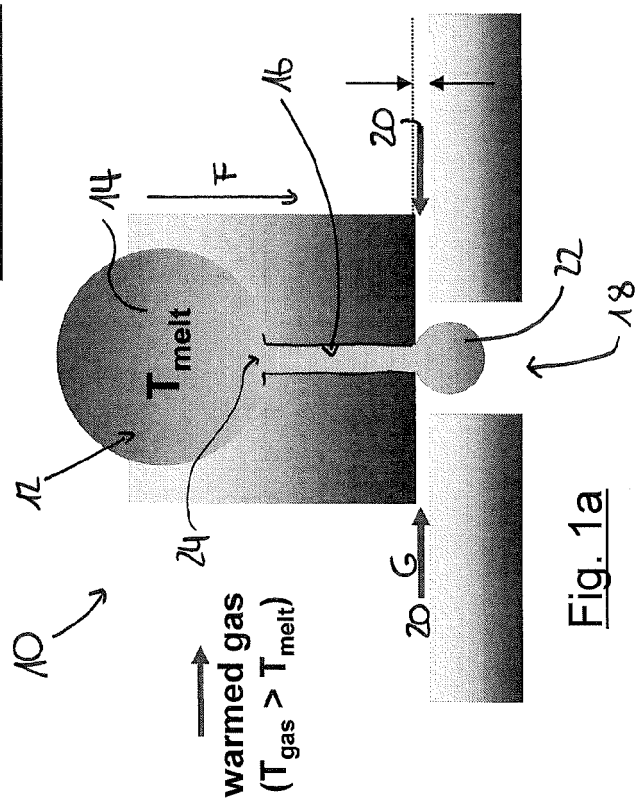


Fig. 1a

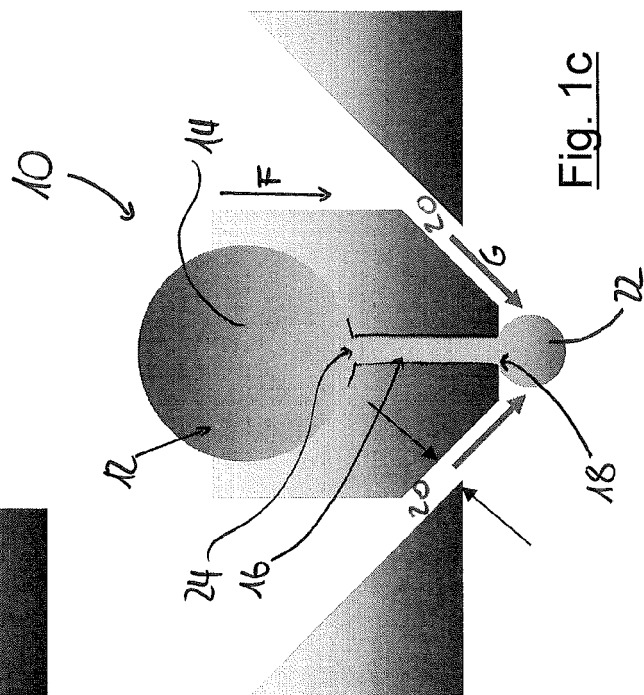


Fig. 1c

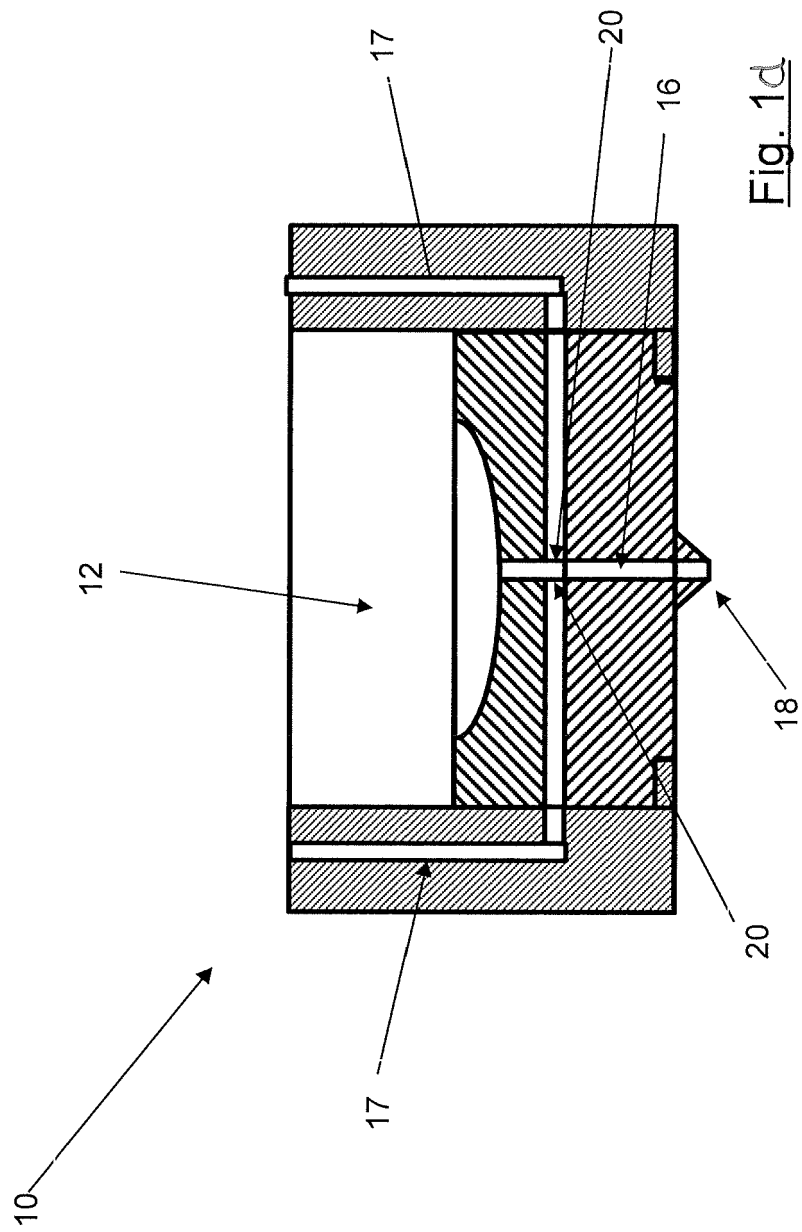


Fig. 1d

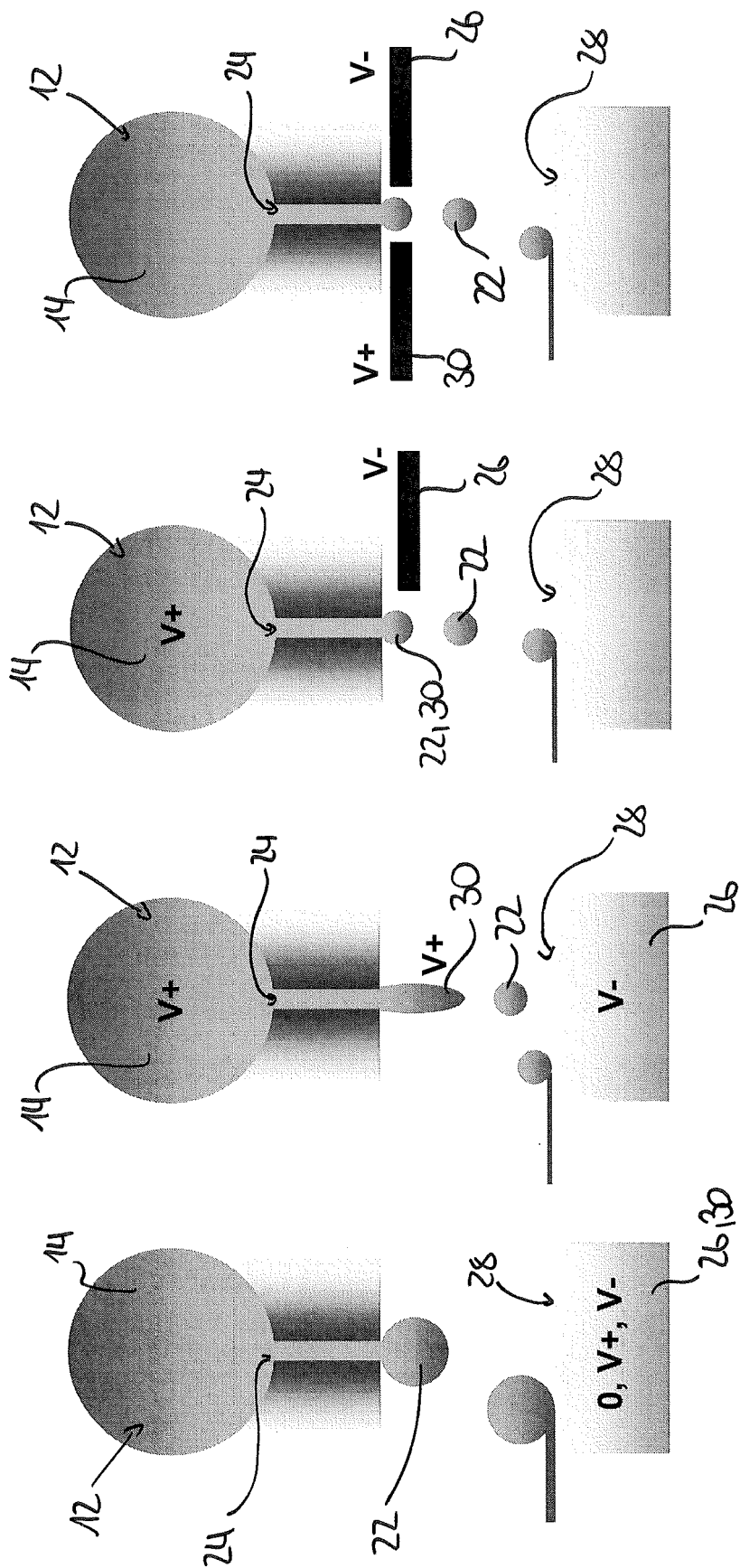


Fig. 2a

Fig. 2b

Fig. 2c

Fig. 2d

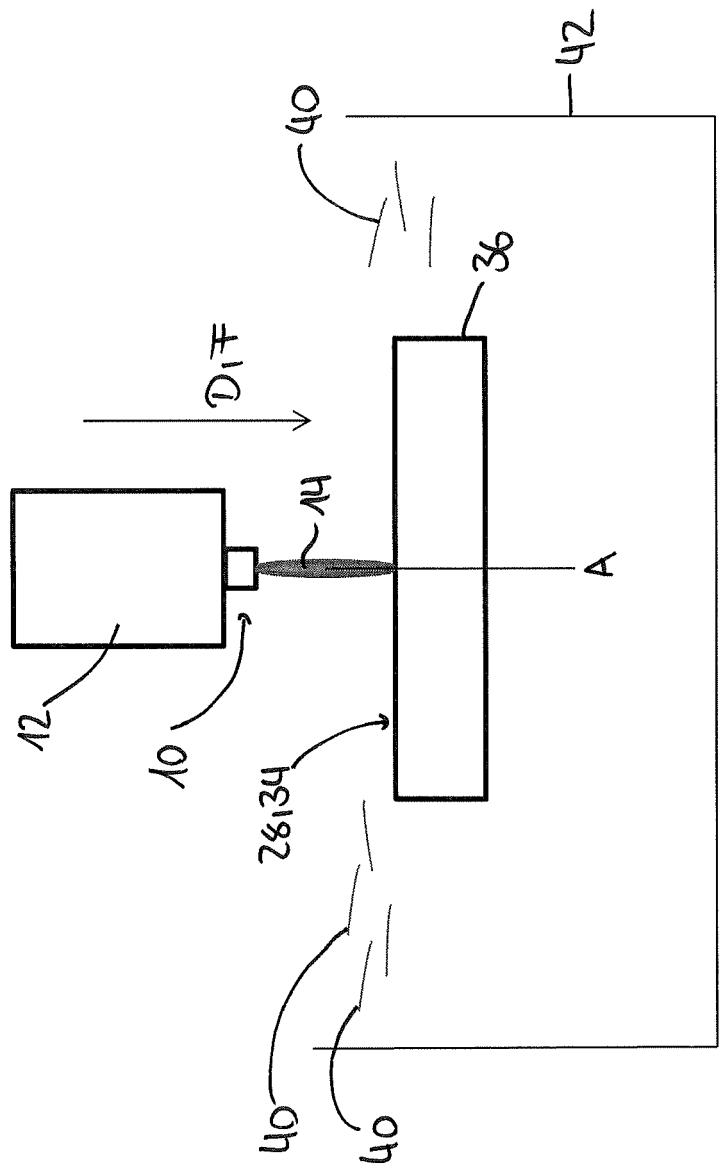


Fig. 3

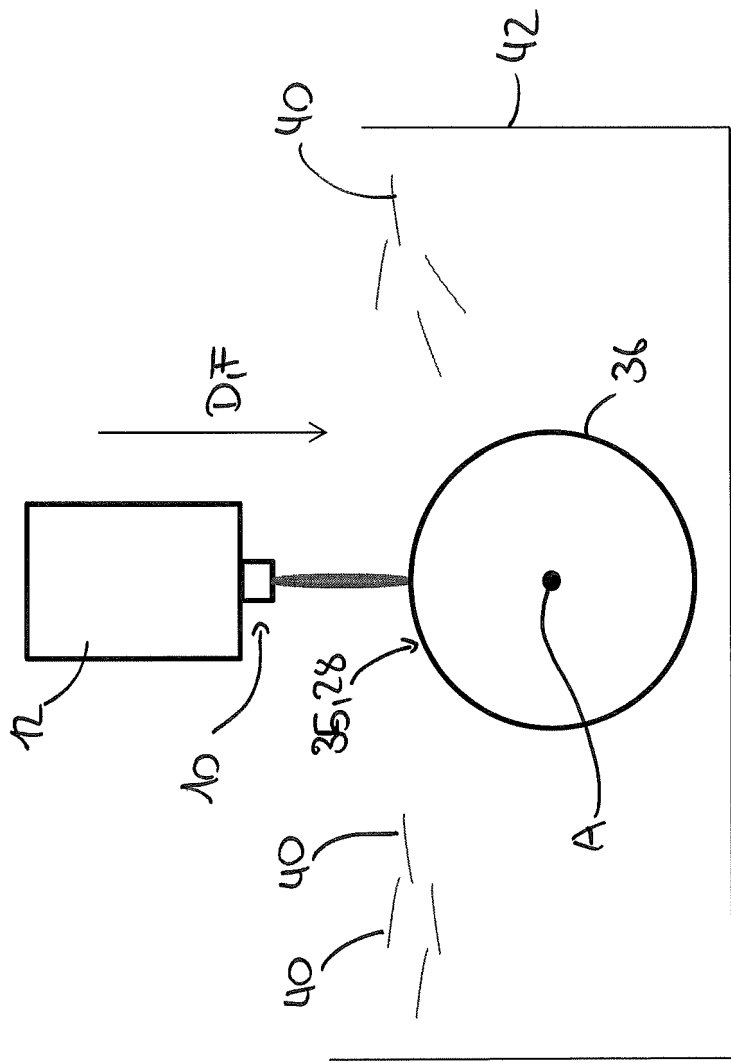


Fig. 4

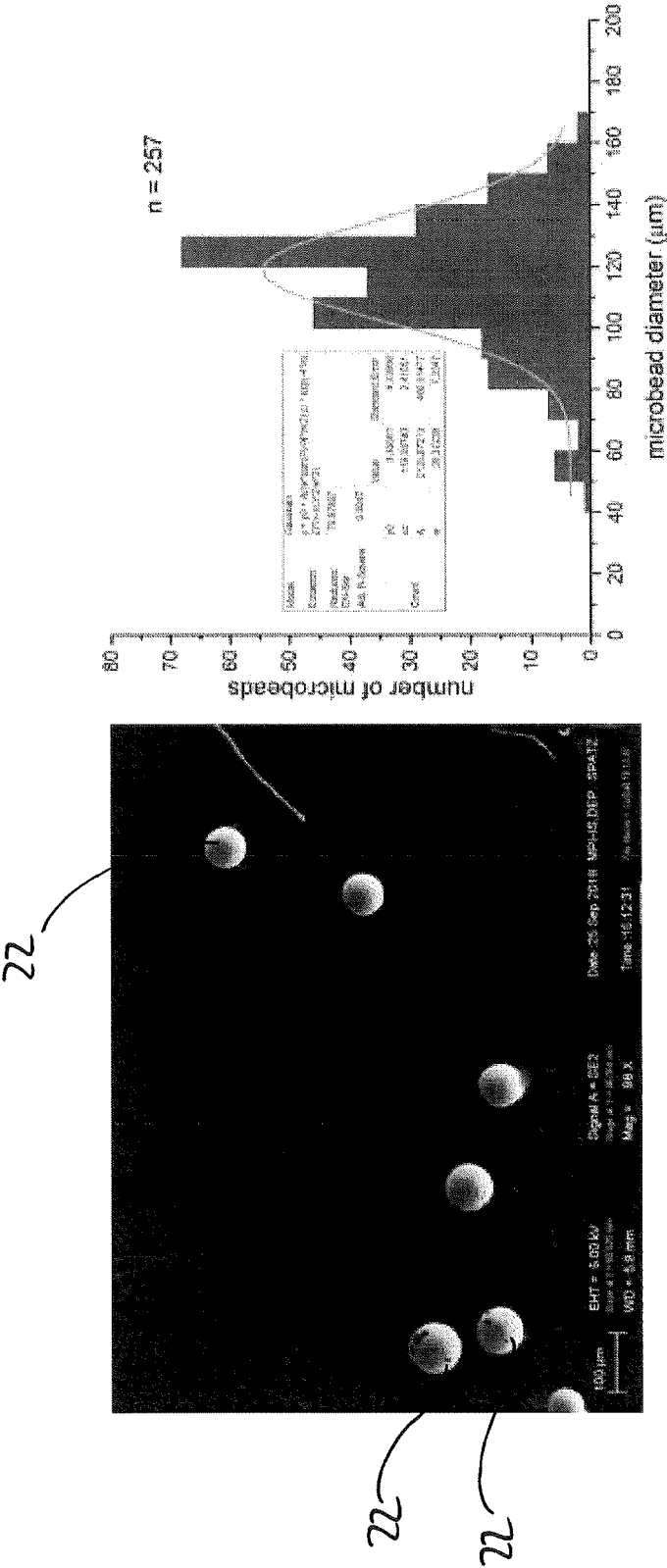


Fig. 5b

Fig. 5a

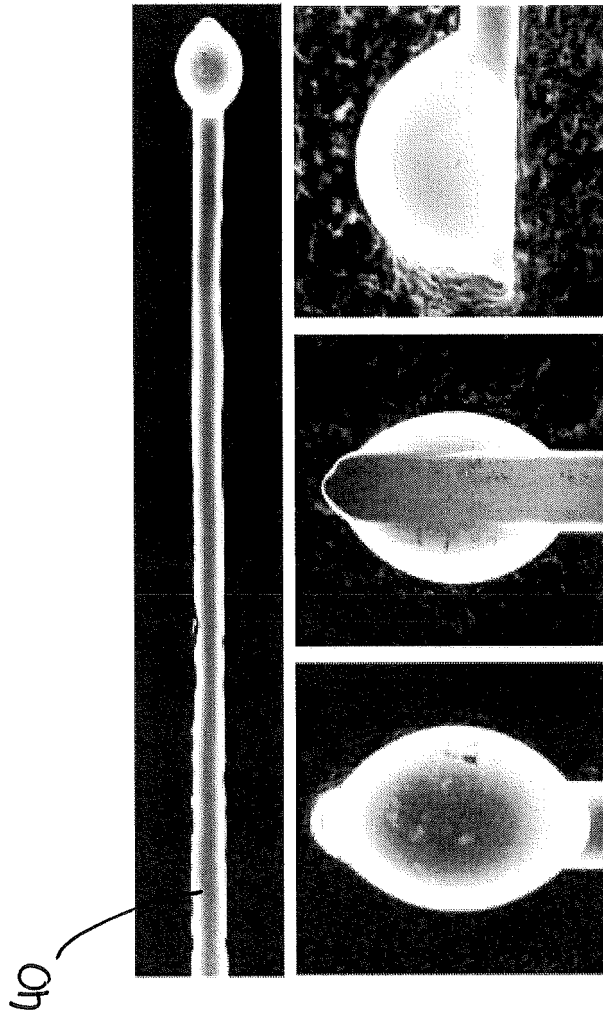


Fig. 6



Fig. 7

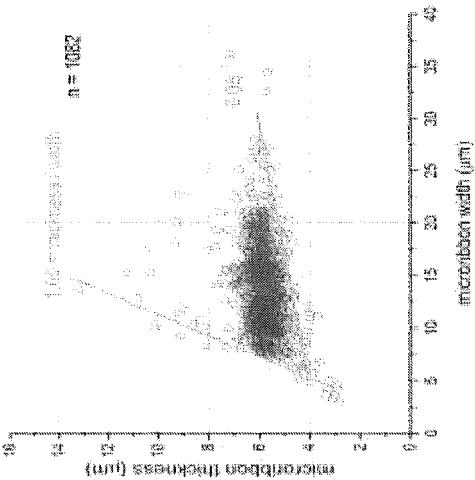


Fig. 8c

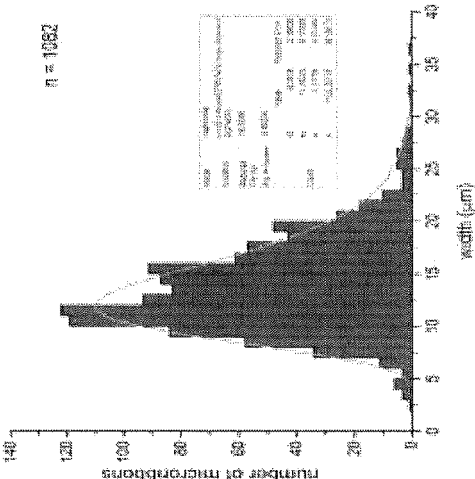


Fig. 8b

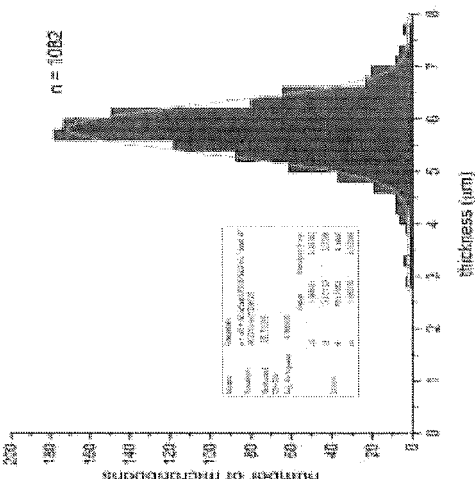


Fig. 8a

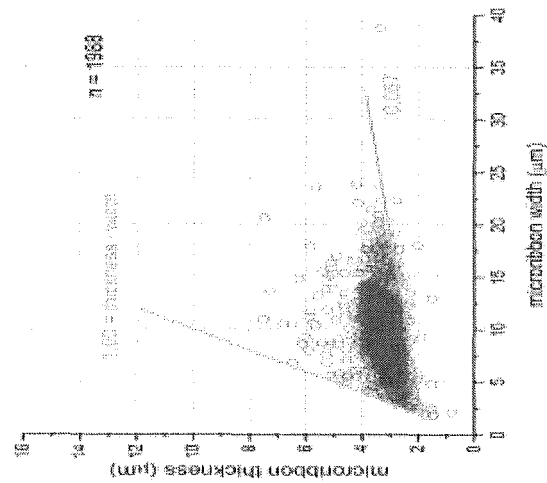


Fig. 9c

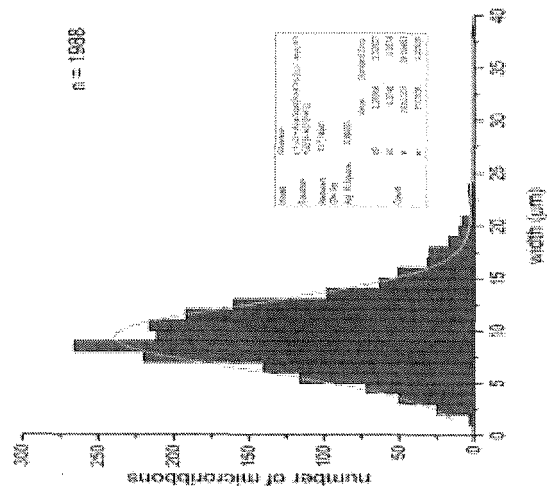


Fig. 9b

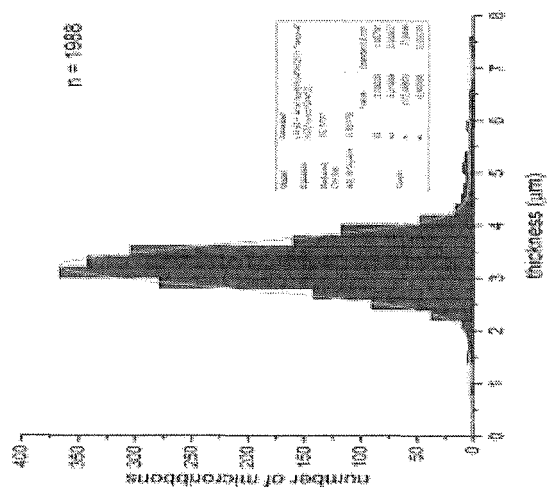


Fig. 9a

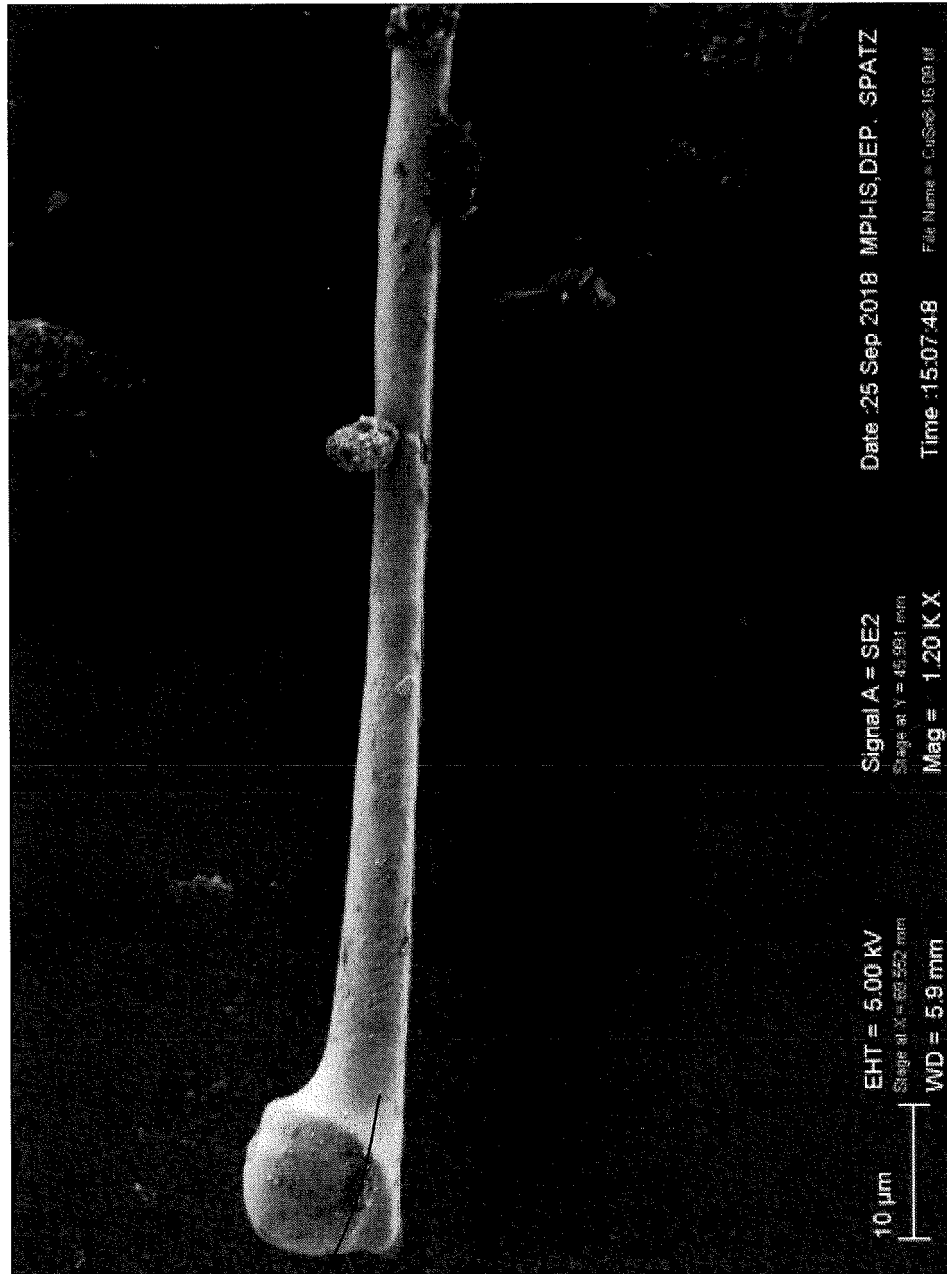


Fig. 10

110

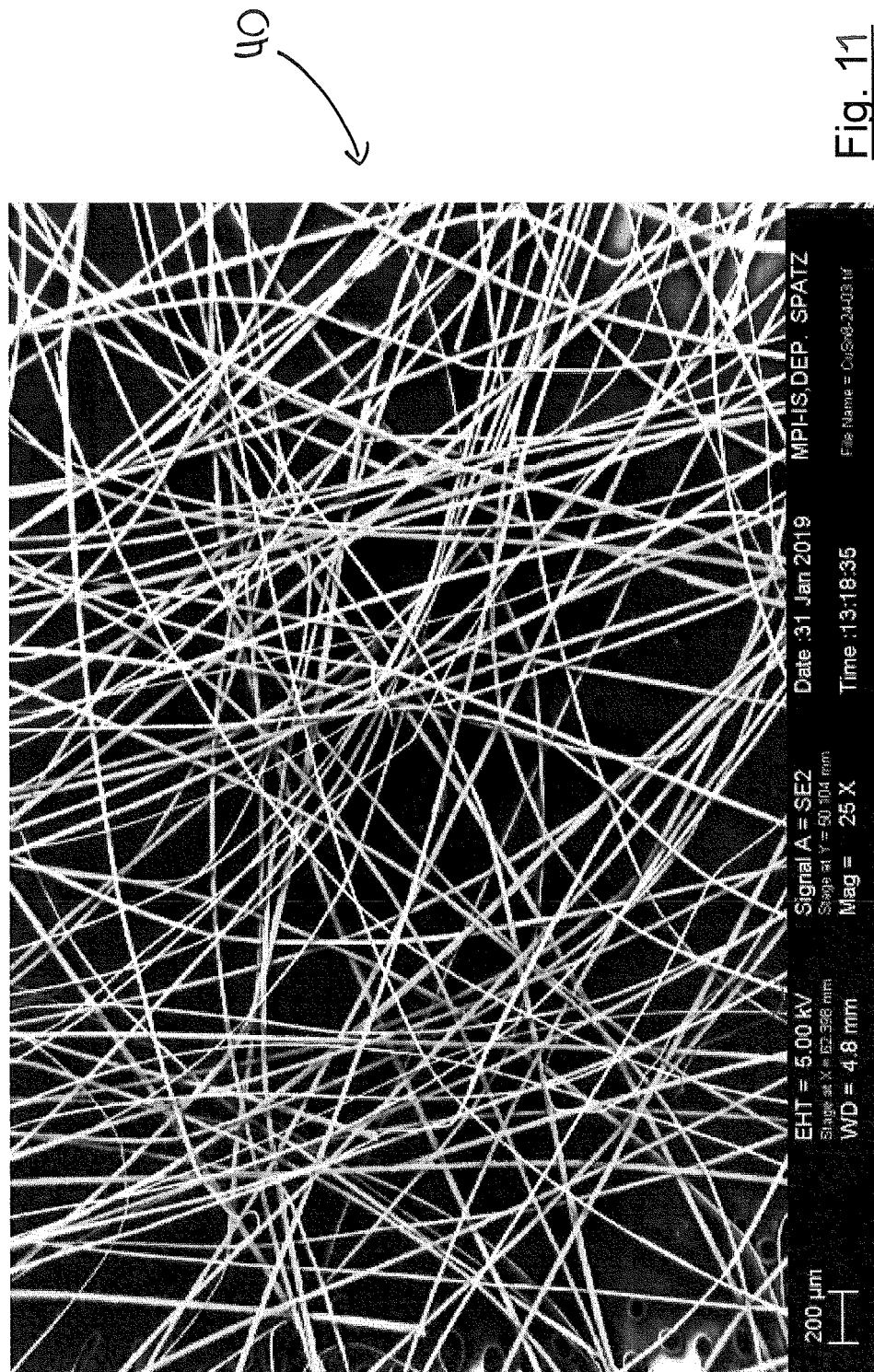


Fig. 11

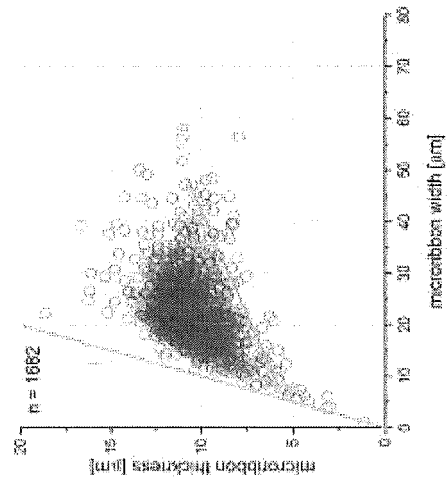


Fig. 12c

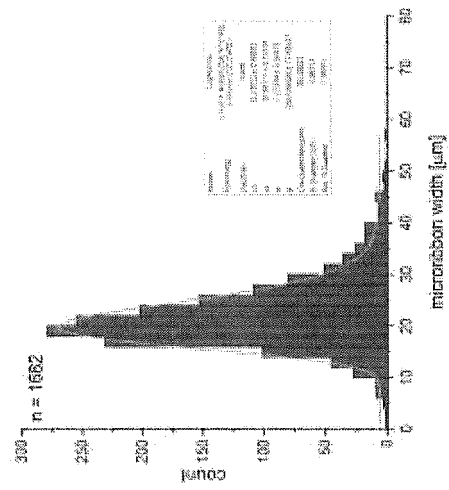


Fig. 12b

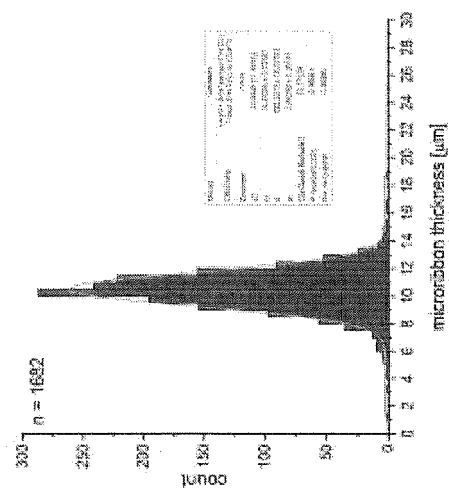


Fig. 12a

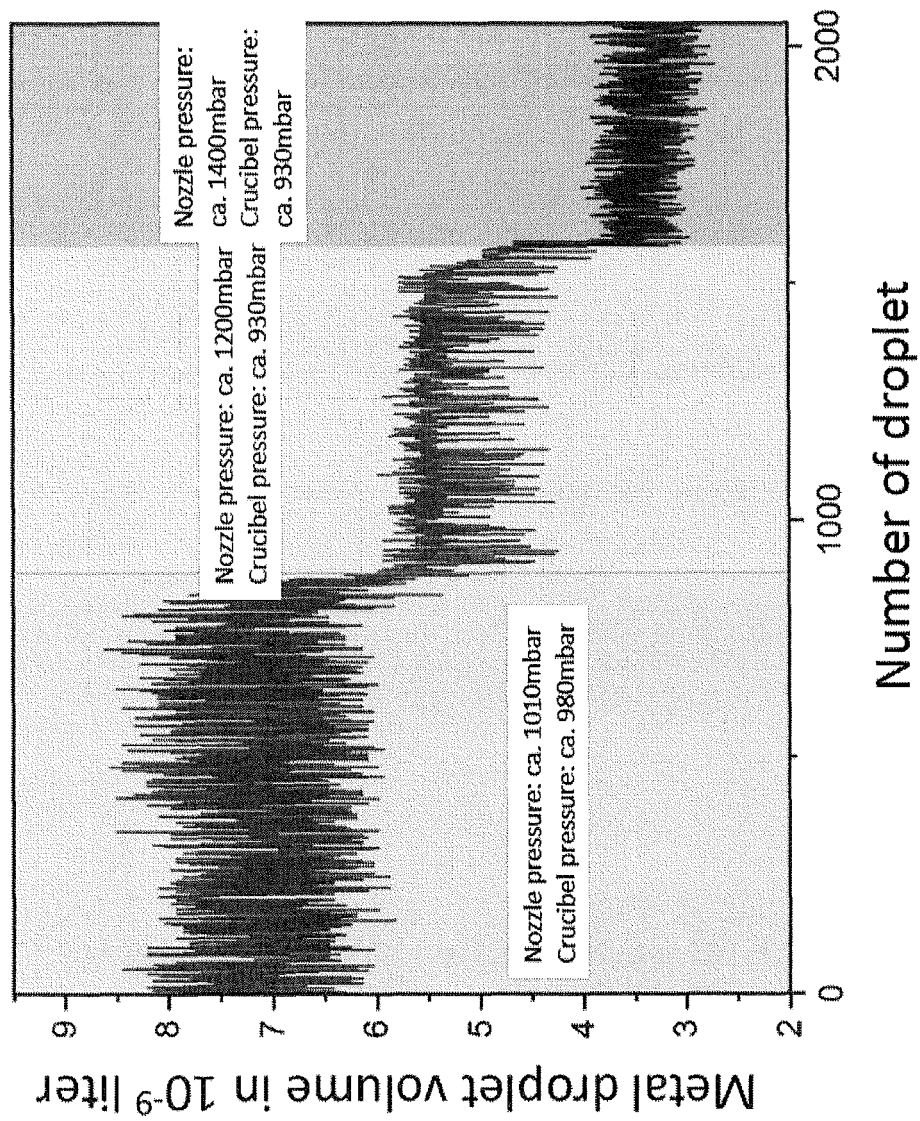


Fig. 13



EUROPEAN SEARCH REPORT

Application Number
EP 20 18 8662

5

10

15

20

25

30

35

40

45

50

55

1

EPO FORM 1503 03.82 (P04C01)

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 3 598 526 A1 (MAX PLANCK GESELLSCHAFT [DE]) 22 January 2020 (2020-01-22) * paragraph [0082]; figure 1a *	1-18	INV. B22F9/08 B22F9/10 B22F9/14 B22D11/06 B22D11/16
X	WO 2014/172152 A1 (SIEMENS HEALTHCARE DIAGNOSTICS [US]) 23 October 2014 (2014-10-23) * paragraphs [0040], [0045], [0059]; claim 1; figure 5 *	1-18	
X	US 4 264 641 A (MAHONEY JOHN F ET AL) 28 April 1981 (1981-04-28) * claim 1; figure 2 * * columns 8-9; lines 15-12 *	1-18	
X	JP 2002 087829 A (MINOLTA CO LTD) 27 March 2002 (2002-03-27) * paragraphs [0001], [0004], [0005], [0019]; figure 1 *	1-18	
X	WO 2020/063625 A1 (UNIV DALIAN TECH [CN]; WANG XIAOMING [CN] ET AL.) 2 April 2020 (2020-04-02) * paragraphs [0020], [0031]; figure 1 *	1-18	TECHNICAL FIELDS SEARCHED (IPC) D01D B22D C03B B22F C22C
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 10 December 2020	Examiner Momeni, Mohammad
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 20 18 8662

5

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

10-12-2020

10

15

20

25

30

35

40

45

50

55

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 3598526 A1	22-01-2020	EP 3598526 A1	22-01-2020
		WO 2020016240 A1	23-01-2020
-----		-----	
WO 2014172152 A1	23-10-2014	EP 2986704 A1	24-02-2016
		JP 6433982 B2	05-12-2018
		JP 2016524521 A	18-08-2016
		US 2016074857 A1	17-03-2016
		WO 2014172152 A1	23-10-2014
-----		-----	
US 4264641 A	28-04-1981	NONE	
-----		-----	
JP 2002087829 A	27-03-2002	NONE	
-----		-----	
WO 2020063625 A1	02-04-2020	CN 109014227 A	18-12-2018
		WO 2020063625 A1	02-04-2020
-----		-----	

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- WO 2017042155 A [0051]
- EP 2020063026 W [0051]