Method of producing an item with enhanced wetting properties by fast replication and replication tool used in the method

Poulsen, Carl Esben; Wolff, Anders; Andersen, Nis Korsgaard; Kistrup, Kasper; Taboryski, Rafael J.

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(71) Applicant: **DANMARKS TEKNISKE UNIVERSITET** [DK/DK]; Anker Engelunds Vej 101 A, 2800 Kgs. Lyngby (DK).

(72) Inventors: **POULSEN, Carl Esben**; Magistervej 64, 1. tv., 2400 Copenhagen NV (DK). **WOLFF, Anders**; Abildgaardsgade 35, 2100 Copenhagen Ø (DK). **ANDERSEN, Nis Korsgaard**; Stenvadpark 16, 3520 Farum (DK). **KISTRUP, Kasper**; Thorsgade 62, 3., 2200 Copenhagen N (DK). **TABORYSKI, Rafael**; Jordbærvænget 11, 2880 Bagsværd (DK).

(74) Agent: **GUARDIAN IP CONSULTING I/S**; Diplomvej, Building 381, 2800 Kgs. Lyngby (DK).

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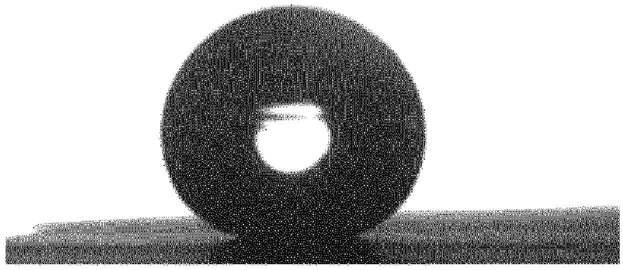

Fig. 5

(57) **Abstract**: The invention relates to a replication tool (1) for producing an item (4) with enhanced wetting properties by fast replication, such as injection moulding or extrusion coating. The replication tool (1) comprises a tool surface (2a, 2b) defining a general shape of the item (4). The tool surface (2a, 2b) comprises a microscale structured master surface (3a, 3b, 3c) having a lateral master pattern and a vertical master profile. The microscale structured master surface (3a, 3b, 3c) has been provided by localized pulsed laser treatment to generate microscale phase explosions. A method of producing an item with enhanced wetting properties uses the replication tool (1) to form an item (4) with a general shape as defined by the tool surface. The formed item (4) comprises a microscale textured replica surface (5a, 5b, 5c) with a lateral arrangement of polydisperse microscale protrusions.

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Method of Producing an Item with Enhanced Wetting Properties by Fast Replication and Replication Tool Used in the Method

The present invention relates in one aspect to a method of producing an item having a surface with an enhanced wetting property by fast replication. In a further aspect, the present invention relates to an item produced by that method. In yet a further aspect the invention relates to a replication tool for use in that method and a method of preparing the replication tool.

BACKGROUND OF THE INVENTION

Wetting properties of a surface may be modified by changing the finish of a surface on a microscale and/or on a nanoscale. For example, microscale structuring of hydrophobic surfaces is known to yield an enhanced hydrophobicity with water contact angles well above 120 degrees as compared to a flat surface of the same hydrophobic material. Micro- and nanoscale structures applied to the surface of a hydrophobic material may even result in superhydrophobic surfaces, i.e. surfaces with an apparent water contact angle of 150 degrees and above, e.g. when applying a hierarchical surface structuring with nano-structures on top of a micro-structured surface. In the context of this application, a material is referred to as hydrophobic, if a flat surface thereof is characterized by a water contact angle of above 90 degrees, such as above 95 degrees, such as about or above 100 degrees.

Applications for such superhydrophobic surfaces are numerous. They include, but are not limited to: packaging; medical devices; self-cleaning surfaces on e.g. wind turbine blades, helicopter blades, air plane wings, or solar energy panels; microfluidic devices; and biotechnical devices, such as assays, cell culture vessels, and lab-on-a-chip systems.

Accordingly, the hydrophilicity of a surface may be enhanced by microscale surface modifications. In the context of this application, a material is referred to as hydrophilic, if a flat surface thereof is characterized by a water contact angle of below 90 degrees, such as below 85 degrees, such as about or below 80 degrees. For example, a flat surface of the hydrophilic plastics material acrylonitrile butadiene styrene (ABS) may have a water contact angle of about 81 degrees.

Vast varieties of techniques for micro- and nano-structuring of surfaces exist, and may in principle serve to provide a surface structure enhancing the hydrophobicity of the surface of a hydrophobic material. One technique is based on the use of laser sources for machining a microscale finish into the surface of a work piece. In one approach, laser milling is used for directly micro-structuring the surface of an item that may be made of a metal, such as stainless steel. After applying the microstructure, the micro-structured surface of the stainless steel item may be coated with a hydrophobic substance to thereby generate a superhydrophobic surface. However, an approach based on micro-structuring by sequentially “writing” the micro-structure on the surface of each item is not suited for a large scale/high volume industrial production. In another approach described in US 2013/0189485 A1, femtosecond laser machining is used to generate microstructure cones on a metal or semiconductor surface, and faithfully replicating said microstructure in PDMS using a moulding or hot embossing technique to generate a superhydrophobic surface of the replicated part. The disclosed processes include time consuming heating and setting steps hampering a low-cost production on a large industrial scale. However, considerations of production cost and time are of the essence, if e.g. mass produced low-cost items are to be provided with such superhydrophobic surfaces on a broad basis in a commercially viable way.

Therefore, there is a need for a process for providing items with enhanced wetting properties, such as items with a superhydrophobic surface, wherein the process is suited for low-cost production on an industrial scale.

SUMMARY OF THE INVENTION

A first aspect of the invention relates to a method of providing a replication tool, the method comprising providing a forming tool having a tool surface adapted to define a general shape of an item to be formed; modifying at least portions of the tool surface by a pulsed laser treatment to obtain a microscale structured master surface with a lateral master pattern and a vertical master profile; wherein the pulsed laser treatment is adapted to generate microscale phase explosions on the tool surface, thereby forming the microscale structured master surface as a lateral arrangement of microscale crater-shaped depressions. The crater-shaped depressions obtained by the microscale phase explosions are irregular in shape and polydisperse, i.e. varying in size with a spread about a most prominent size. The size may e.g. be characterized by the area covered by the depression as seen in a vertical projection on a lateral plane.

The microscale structuring of the tool surface is provided by the localized application of laser pulses directly to selected portions of the tool surface. This post-treatment of the tool surface by means of localized laser treatment has the advantage that the replication tool with the shape defining tool surface may be designed and produced using existing techniques and equipment for tool making, thereby contributing to a relatively simple and cost effective implementation of the surface functionalization in an existing fabrication process.

At the targeted portion of the tool surface, the localized pulsed laser treatment is adapted to melt and evaporate material at the tool surface to generate microscale phase explosions, thereby producing a randomised surface structure of polydisperse microscale features. The microscale surface features are depressions, which are typically crater shaped with steeply sloped side walls. The process of provoking microscale phase explosions by locally applying laser energy to the tool surface so as to form the crater-shaped depressions is stochastic in nature, wherein upon appropriate exposure the microscale surface features are densely packed and may even partially overlap, thereby forming a microscale lateral pattern with a microscale porous appearance. The localized application of laser power may be scanning a laser spot along a predetermined scanning path at a pre-determined scan speed over the tool surface. The path may follow a single scan along the path over the tool surface, a repetitive scanning along the same linear path, or a combination of both. The path is adapted to cover the selected portions of the tool surface. The path may e.g. be straight, curved, meandering, segmented or a combination thereof and some sections of the path may overlap other sections of the path in order to achieve an even exposure of the selected portions of the tool surface with laser energy.

The pulsed laser radiation has to be of a wave length and pulse characteristics that is absorbed by the tool surface in order to be able to locally melt and evaporate material from the tool surface so as to produce microscale phase explosions creating the crater-shaped depressions. For example, the laser radiation may be from a picosecond-laser source with a wavelength in the near infrared, such as 1064 nm, but other wavelength ranges, e.g. in the visible part of the electromagnetic spectrum, and pulse characteristics that are suitable for locally heating the tool surface to generate microscale phase-explosions may be conceived, too. The finish of the targeted portions of the tool surface is controlled by adapting the exposure of these tool surface portions with the pulsed laser radiation. The exposure of the tool surface is controllable e.g. by adjusting the laser power/spot intensity and/or by varying the scan speed, wherein exposure of a given surface portion increases with increasing laser power, but decreases with increasing scan speed. The finish of the targeted portions of the tool in turn determines the finish of the replicated item in the corresponding regions on the item surface via the replication process. Furthermore, multiple exposures of the same surface portions, e.g. by repetitive and/or overlapping scanning of the laser spot over these surface portions, results in an exposure that is increased correspondingly.

Preferably, the lateral pattern of the microscale structured master surface has an area density of microscale master features of at least 5000/mm². Thereby, a reasonably densely packed lateral distribution of microscale features on the master surface is achieved, thereby allowing for a significant enhancement of wetting properties of items replicated using the replication tool as further detailed below.

Further preferably, the lateral pattern of the microscale structured master surface has an area density of microscale master features of at least 8000/mm², or even of at least 10000/mm². Thereby, a densely packed lateral distribution of microscale features on the master surface is achieved, thereby allowing for a particularly significant enhancement of wetting properties of items replicated using the replication tool as also detailed further below.

A further aspect of the invention relates to a method of producing an item with enhanced wetting properties by a replication process, the method comprising the steps of

- providing a replication tool with a microscale structured master surface by a method according to the above-mentioned embodiment;

- using the replication tool to form the item by the replication process, wherein the formed item has the general shape as defined by the tool surface, and wherein the formed item comprises a microscale textured replica surface with a lateral arrangement of microscale protrusions produced by the microscale structured master surface.

The method is useful for forming the item from a replication material replicating the microscale structured master surface onto the item to form a surface region with a lateral arrangement of polydisperse microscale protrusions thereon. A lateral replica pattern is defined by the lateral master pattern, and a vertical replica profile has a finite peak-to-peak amplitude to form a three-dimensional texture. Since the lateral replica pattern is defined by the lateral master pattern, it is equally irregular as seen in a projection onto a lateral plane, and the microscale protrusions are polydisperse. The method is for producing the item with enhanced hydrophobicity by a fast replication process using the replication tool, such as required by a commercially viable production of the item in large numbers.

According to some embodiments, the method comprises the steps of

a) providing a replication tool having a tool surface adapted to define a general shape of the item, wherein the tool surface comprises a microscale structured master surface obtained by localized pulsed laser treatment of the tool surface to generate microscale phase explosions, said microscale structured master surface having a lateral master pattern and a vertical master profile.

b) contacting the tool surface with a replication material in the melt phase, wherein the tool surface is maintained at a process temperature below the melt temperature of the replication material, thereby

c) cooling the thermoplastic replication material to a stabilized shape with a microscale textured replica surface, wherein the lateral master pattern defines a corresponding lateral replica pattern of the microscale textured replica surface and wherein the amplitude of a vertical profile of the microscale textured replica surface is in the microscale, and

d) releasing the shaped item from the tool surface.

The method is for the production of items by a fast replication process, thereby allowing for a low-cost and/or mass production of the item with a surface that is functionalized for enhanced hydrophobicity by providing the item with a microscale textured surface. A replication process may be considered fast, for example, if the replication period from contacting the tool surface with the molten replication material to releasing the shaped item is short, such as well below ten minutes, such as less than five minutes, such as less than 3 minutes, such as less than one minute, such as less than 30 seconds, or even less than 10 seconds. In particular, the suggested thermally controlled replication process using a thermoplastic replication material can be performed fast as compared to for example replication processes using thermosetting replication materials, or chemically setting replication materials.

The term microscale refers to dimensions of about 1 μm to 1000 μm that are generally measured in microns (micrometres), typically in the range of about 1 μm to 100 μm. Accordingly, the term nanoscale refers to dimensions of about 1 nm to 1000 nm that are generally measured in nanometres, typically in the range of about 1 nm to 100 nm.

The microscale structure of the master surface and, accordingly, the microscale texture of the replica surface have a three-dimensional topography of microscale elements arranged next to each other and may be decomposed in a lateral pattern and a vertical profile. The term “lateral pattern” refers to the arrangement in lateral directions of the (3D) microscale elements making up the microscale structure/texture, as seen in vertical projection on to a lateral plane. The term “vertical profile” refers to the variation of the location of the surface in a direction perpendicular to the lateral directions.

When a surface structuring/texturing is applied to an object having a general shape, such as a tool surface or an item, the surface structuring/texturing can be seen as a vertical variation of the surface, which is added to the general shape of the tool surface/item. Accordingly, on an object with a microscale structured/textured surface, an average surface that flattens out any vertical variations of the surface by averaging on a lateral scale larger than that of the microscale structuring/texturing essentially follows the general shape of the object. The general shape of the object is thus defined independent of any nano- or microscale surface roughness / finish / structuring. At a given point on the surface of the object, lateral directions are parallel / tangential to a surface defining the general shape of the object on a scale larger than the scale of the lateral pattern. Accordingly, the vertical direction at a given point on the surface of the object is the surface normal to the general shape in that point. In each given point, the vertical direction is perpendicular to the corresponding lateral directions.

The general shape of the replicated item is defined by the general shape of the tool surface. The replication process is for accurately replicating the general shape of the item as defined by the tool surface. The surface of the replicated item is functionalised by applying a surface finish with a microscale texture at least on selected regions of the item surface. The particular functionalization is to enhance the hydrophobic nature of the surface of the item by providing the hydrophobic material with a surface finish having a microscale texture in the selected regions. The micro-textured surface finish in selected regions of the item surface is achieved by providing a microscale structuring in corresponding portions of the tool surface from which the item is replicated.

As mentioned above, the laser treatment of the tool surface results in a porous surface appearance produced by a randomised arrangement of densely packed microscale depressions, which are typically shaped as relatively deep, steep-walled craters with a more or less pointed bottom. The sloped sidewalls facilitate an easy de-moulding of the replicated item in the step of releasing the item from the tool surface.

The term “wetting properties” refers to the interfacial interactions in a system comprised of three states of matter, a solid, a liquid, and a gas, and can be quantified by a contact angle. The line connecting all three interfaces, e.g. solid-liquid, solid-gas, liquid-solid, is denoted the three phase-contact line. The contact angle is defined as the angle between the tangents of the liquid-gas and the liquid-solid interphases perpendicular to the three-phase line at any intersection of the two tangents on the three phase line. The wetting properties between a solid and a liquid in a three phase system are considered enhanced with respect to the wetting properties of a flat surface if the apparent macroscopic contact angle is altered by the structure on the surface, wherein the wetting properties of a system with a solid-liquid contact angle smaller than 90° (philic behaviour) is considered enhanced if this contact angle is reduced by the modification (philic enhancement). Likewise, the wetting properties of a system with a solid-liquid contact angle greater than 90° (phobic behaviour) is considered enhanced if this contact angle is increased by the modification (phobic enhancement).

An important insight is that achieving the enhancement in wetting properties for the replicated item does not require controlling the exact 3D-shape of each of the microscale features on the tool surface and their exact arrangement with respect to each other. Also, the exact details of the individual microscale elements and of their arrangement making up the micro-texture on the surface of the replicated item are uncritical for achieving an enhanced wetting properties as compared to a flat untextured surface of the replication material.

The fast replication process thus yields proper items as long as the general shape is faithfully obtained reliably, the microscale lateral pattern is reliably reproduced in each reproduction process, and the peak-to-peak amplitude of the vertical profile of the replica surface is sufficient to provide enhanced wetting properties. As mentioned above, the enhanced wetting properties may be an enhancement of the hydrophobicity. Enhanced hydrophobicity is achieved when water droplets on the surface of the replicated item form a so-called Wenzel state or a so-called Cassie Baxter state. Relatively small amplitudes of the vertical profile of the texture of the replica surface may already enhance the hydrophobicity, such as amplitudes of at least 100nm, alternatively at least 200nm, alternatively at least 500nm, and preferably in the microscale, such as 1μm-100μm, such as 1μm-30μm, preferably in the range 1μm-10μm. For ensuring a good production yield it is therefore sufficient to control the lateral scale of the texture which is well controlled by the lateral scale of the pattern of the master surface – and ensuring that the amplitude of the profile of the texture on the replica surface is sufficient to enhance hydrophobicity, preferably in the microscale, as detailed above. To achieve super-hydrophobicity, the amplitude of the vertical profile of the texture of the replica surface has to be sufficiently large to support water droplets on the surface of the item in a so-called Cassie Baxter state.

A further important insight therefore relates to the nature of the fast replication process. Here, it is exploited that the lateral pattern of the microscale master structure on the tool surface is inherently reproduced with high fidelity on the replicated item. The fidelity of replication of the vertical profile on the other hand tends to be affected by standard parameters of processes for fast replication in thermoplastic materials, such as tool temperature, replication period, and temperature and/or pressure of the thermoplastic replication material in the melt phase. This is owing to the ability of the thermoplastic replication material to fill the depressions of the relatively deep steep-walled master structure before solidifying, which may be controlled by these parameters. Thereby, the fidelity of replication may be controlled. For example, fidelity of microstructure replication may be reduced by reducing the temperature at which the tool surface is maintained. When the replication material contacts the tool surface at the lower the melt is cooled more rapidly, thereby increasing the viscosity of the melt and impeding the filling of the microscale depressions/crevices/craters/pores of the master structure on the tool surface by the melt before it solidifies. A reduced fidelity is reflected by a reduced amplitude of the replicated profile as compared to the master profile: the replication is more shallow than the master. The fidelity of replication of the vertical profile may thus be characterised e.g. by comparing the peak-to-peak amplitudes of the vertical profiles of the replicated microscale texture and the microscale master structure to each other, wherein for a low fidelity replication the amplitude of the replicated profile as compared to the master profile is lower than for a higher fidelity replication. Typically, the low-fidelity replicated microscale textures exhibit a rounded top. Since the enhancement of the hydrophobicity is uncritical as to the exact shape and arrangement of the individual microstructures, another advantage of the method is that it facilitates a relatively simple and cost effective implementation of the surface functionalization in an existing fabrication process by merely modifying the tool surface of a replication tool in a post-treatment step.

A replication process, where the tool surface is maintained at a more or less constant temperature below the melt transition temperature throughout the production process is sometimes referred to as an “isothermal” type process. Isothermal processes may be performed at high throughput. As also mentioned above, the surprising insight resides in that the truthfulness of the replication of the vertical profile of the microscale master structure is uncritical for achieving the desired effect of enhanced hydrophobicity, or even superhydrophobicity, as long as the lateral pattern is faithfully transferred and the peak-to-peak amplitude of the vertical profile of the micro-texture on the replica surface is in the microscale.

Note that the item may be made entirely from replication material with a shape defined by the tool surface, or the replication material may be applied to/carried by a substrate material, e.g. in an additive moulding step or a coating step.

Further according to one embodiment of the method for producing an item with enhanced wetting properties, the replication process is injection moulding. In a particularly preferred embodiment, the fast replication process is injection moulding. Injection moulding is a cyclic replication process with a fast cycle time, i.e. using this embodiment a large number of separate items with a microscale textured replica surface may be produced at high throughput. The inner surface of the injection mould is the tool surface defining the general shape of the item. At least portions of the tool surface have a finish with a microscale structuring generated by localised treatment with a pulsed laser source. The thermoplastic replication material is in the melt phase injected into the closed mould, which is kept at a temperature below the melt temperature of the replication material. When the molten replication material contacts the cooled tool surface it solidifies, whereby it is shaped and textured, before the item is released from the mould. As mentioned above, a surprising insight is that the replica surface produced in a fast injection moulding process exhibits enhanced wetting properties, such as hydrophobicity or even superhydrophobicity, also if the vertical profile of the microscale texture on the replica surface is a low fidelity replication of the corresponding profile of the microscale structure on the master surface, as long as the lateral pattern is faithfully transferred and the peak-to-peak amplitude of the vertical profile of the micro-texture on the replica surface is in the microscale. Thereby, a robust low-cost mass-production process for items with an enhanced hydrophobic or even superhydrophobic replica surface is achieved.

Further according to one embodiment of the method for producing an item with enhanced wetting properties, the replication process is extrusion coating.

In another particularly advantageous embodiment, the fast replication process is extrusion coating. Extrusion coating is a process for roll-to-roll processing, i.e. using this embodiment the item may be produced in a continuous process as a layered web with a microscale textured replica surface. To that end, a substrate web may be passed between a nib roll and a cooling roll, in a conventional manner, wherein the rotary surface of the cooling roll is the tool surface defining the general shape of the item. The tool surface has a finish with a microscale structuring generated by treatment with a pulsed laser source. The thermoplastic replication material is heated to above the melt transition temperature and in the melt phase supplied between the substrate web and the cooling roll, which is kept at a temperature between the glass transition temperature and the melt transition temperature. When the molten replication material contacts the cooled tool surface it solidifies, whereby it is shaped and textured, before the item is released from the replication tool.

Further according to one embodiment of the method for producing an item with enhanced hydrophobicity, a replication period from contacting the tool surface with the molten replication material to releasing the shaped item is less than 3 minutes, such as less than one minute, such as less than 30 seconds, or even less than 10 seconds. Typically, in an injection moulding process, the replication time may be less than one minute, i.e. a few tens of seconds, such as about 30 seconds. Extrusion coating is a continuous roll-to-roll process. Typically, an extrusion coating process is therefore even faster with replication times of less than 10 seconds, less than 5 seconds, or even less than 1 second.

Further according to one embodiment of the method for producing an item with enhanced wetting properties, the vertical replica profile predominantly has rounded tops with a radius of curvature in the microscale. As described above, the replication process may be controlled to influence the fidelity of replication to provide a vertical replica profile that predominantly has rounded tops with a radius of curvature in the microscale. In fact, a less faithful replication of the crater-like microscale features on the master surface yields a structure with rounded tops, which has a positive effect on reducing the roll-off angle at which water droplets forming on the superhydrophobic replica surface easily roll off as compared to sharp-edged structures. A process goal/constraint of a faithful replication of the vertical profile of the master structure, on the other hand may entail long settling or curing times incompatible with a fast replication process.

Advantageously, the radius of curvature of the rounded tops is of the same order as the lateral distance between adjacent structures/features of the lateral pattern, such as predominantly above 1μm, above 5μm, or even above 10μm, and predominantly less than 300 μm, less than 100μm or even less than 50μm. Further advantageously, the vertical amplitude of the replica profile is about equal or less than the lateral distance between adjacent microscale features.

According to some embodiments, the method may further comprise the additional step, after releasing the replicated item from the tool surface, of modifying the replica micro-texture surface by applying a further surface layer capping the surface of the replication material. The additional layer may, for example, be a surface layer modifying the wetting properties of the replication surface, such as a molecular coating. Alternatively or in addition thereto, the additional layer may be brought about by a post treatment of the replica surface.

Wetting properties are determined by the contact angle of a droplet formed on the surface. An enhancement of the wetting properties is reflected by a change in contact angle, wherein, for example, an enhancement of the hydrophobicity of a surface increases the contact angle, and an enhancement of the hydrophilicity decreases the contact angle. Contact angles are understood as static contact angles measured in a commonly known way using an optical tensiometer. Roll-off angle is determined using a base-tilt method by observing the tilt-angle with respect to horizontal at which a droplet rolls off the surface of the base.

The replica material may be hydrophobic, wherein a flat surface of a bulk sample thereof exhibits a contact angle larger than 90 degrees.

Further according to one embodiment of the method for producing an item with enhanced hydrophobicity, the replica material is hydrophobic with a flat surface contact angle larger than 95 degrees, preferably larger than 100 degrees, and less than 120 degrees, preferably less than 110 degrees. The microscale texture on the replica surface enhances the hydrophobicity of the unstructured replica material. Achieving a higher contact angle is therefore easier when starting out with a material that is more hydrophobic, i.e. a material that is characterised by a higher contact angle on the unstructured surface. However, many materials with the highest contact angles may comprise components that are toxic or hazardous to the health or the environment. The recited selection of materials provides a good compromise of hydrophobic response against health and/or environmental impact considerations. A particularly preferred range in that respect is for thermoplastic polymers a flat surface bulk sample water contact angle of 100 degrees – 110 degrees.

Advantageously according to one embodiment of the method for producing an item with enhanced hydrophobicity the thermoplastic replica material is polypropylene.

Further according to some embodiments, the microscale textured replica surface is superhydrophobic.

Further according to one embodiment of the method for producing an item with enhanced hydrophobicity, the replica surface has, upon release from the tool surface, a contact angle of more than 150 degrees, preferably more than 155 degrees or about 160 degrees, and/or a sliding angle less than 10 degrees, preferably less than 8 degrees, about 5 degrees, or even less than 5 degrees.

Further according to some embodiments, the replica material is hydrophilic with a flat surface contact angle below and including 85 degrees, below and including 80 degrees, or preferably below and including 75 degrees, and at least 50 degrees, at least 60 degrees, or at least 70 degrees.

Further according to some embodiments, the microscale textured replica surface is superhydrophilic.

Further according to one embodiment of the method for producing an item with enhanced wetting properties, the replica material is lipophobic with a flat surface water contact angle larger than 95 degrees, preferably larger than 100 degrees, and less than 120 degrees, preferably less than 110 degrees.

Further according to some embodiments, the microscale textured replica surface is superlipophobic.

Further according to some embodiments, the replica material is lipophilic with a flat surface contact angle below and including 85 degrees, below and including 80 degrees, or preferably below and including 75 degrees, and at least 50 degrees, at least 60 degrees, or at least 70 degrees.

Further according to some embodiments, the microscale textured replica surface is superlipophilic.

A further aspect of the invention relates to a method of preparing a replication tool for producing items with enhanced wetting properties by a fast replication method according to any of the above-mentioned embodiments, wherein the method of preparing a replication tool for producing items with enhanced wetting properties comprises the steps of

- providing a forming tool having a tool surface corresponding to a general shape of the items to be formed
- applying a microscale surface structuring to the tool surface using localized laser treatment to generate microscale phase explosions over a predefined portion of the tool surface,

thereby obtaining a replication tool having a tool surface with a microscale structured master surface on at least portions of the tool surface.

The step of providing a forming tool may be producing a tool for the replication process in question, e.g. a mould for injection moulding or a roller for extrusion coating, in a conventional manner and using conventional tooling materials as known in the art, such as tool steel or 2017 aluminium. The step of applying a microscale surface structuring is performed as a post treatment of the tool surface by means of a pulsed laser directly scanned over the tool surface. A suitable pulsed laser may be, but not limited to, an industrial picosecond-laser operating in the near infrared, such as at 1064nm. The exposure of the surface to the pulsed laser radiation is adapted to generate microscale phase explosions. This includes localised melting of tool material on the tool surface, evaporating molten tool material, and ejecting molten and evaporated material in microscale eruptions from the melt surface, thereby forming a densely packed arrangement of microscale crater-shaped depressions. The obtained microscale structured master surface has a lateral master pattern and a vertical master profile as described above.

Since the post-treatment applied here does not require the precise micro-milling of a specific pre-determined shape of the master structure, such as a regular array of micro-cones, the post-treatment may be applied using cheaper equipment. Furthermore, this post-treatment adapted to generate a microscale porous surface from microscale phase explosions is faster to apply than e.g. micro-milling of microscale features. Furthermore, as also mentioned above, the microscale phase explosions generate microscale crater-shaped depressions with sloped sidewalls that are well suited for fast replication processes, such as injection moulding and extrusion coating. Amongst others, the crater shape with sloped sidewalls facilitates easy releasing of the shaped items from the tool surface at the end of the moulding process (de-moulding).

In a further aspect, a method of producing a plurality of items with enhanced wetting properties comprises preparing a replication tool using the above-mentioned method, and repeatedly performing the method of producing an item with enhanced wetting properties by a fast replication process according to any one of the above-mentioned embodiments. Large numbers of items exhibiting enhanced wetting properties, such as enhanced hydrophobicity or super-hydrophobicity, may thus be produced cheaply.

According to a further aspect, the invention relates to an item with enhanced wetting properties produced by fast replication according to any of the above-mentioned methods.

A further aspect of the invention relates to a replication tool for producing an item with enhanced wetting properties by fast replication, the tool comprising a tool surface defining a general shape of the item, the tool surface comprising at least on portions thereof a microscale structured master surface having a lateral master pattern and a vertical master profile, wherein said microscale structured master surface has been provided by localized pulsed laser treatment of the tool surface, the pulsed laser treatment being adapted to generate microscale phase explosions. Thereby, the localized pulsed laser treatment is adapted to provide a micro-porous structure of the master surface, wherein the micro-porous structure is formed by a densely packed arrangement of crater-shaped microscale depressions with outwardly sloped side walls with the advantages as described above with reference to the method of producing a replicated item as well as with reference to the method of preparing a replication tool for use in a fast replication process, such as isothermal injection moulding, or roll-to-roll processing in e.g. an extrusion coating process.

Further according to one embodiment of the replication tool, the tool surface is made of a metal, such as aluminium or steel. The tool surface has to be suited for the fast replication processes for which the method is intended. The tool surface comprising the microscale master structure can be directly on a mould surface for contacting the replication material and/or on a insert attached to the inside of a mould. It is understood that the tool surface may be broken up in sub-surfaces that form part of the mould as is customary in tool design for fast replication processes, such as injection moulding or extrusion coating. Examples of commonly used metals that are also suitable for the present invention include, but are not limited to, aluminium alloys of the types 2017, 1050 or 5754, or tool steel, such as “Sandvik Corona C60”, orvar 2343 or similar.

Further according to one embodiment of the replication tool, the microscale structured master surface is a lateral arrangement of polydisperse microscale master features. The term polydisperse refers to microscale features having varying transverse dimensions as seen in a vertical projection. Typically, the polydisperse dimensions are characterized by a statistical distribution having a centre value and a spread. The transverse dimensions may be specified as transverse linear dimensions characteristic of the lumen defined by the crater-shaped depression. Given the irregular nature of a polydisperse arrangement, transverse dimensions can also be defined in combination by specifying an area covered by the crater-shaped depression. An equivalent linear dimension characterizing of a given crater-shaped depression may then be defined as the diameter of a circle with the same area. In order to be able to achieve an enhanced hydrophobicity on the surface of the replicated item, the microscale master features on the master surface are preferably densely packed, with neighbouring crater shaped depressions only being separated from each other by a ridge having a width that is comparable to or preferably less than the transverse linear dimension characterizing the crater-shaped depression.

Further according to one embodiment of the replication tool the microscale master features are crater-shaped depressions. Typically the crater-shaped depressions appear more or less circular as seen in a vertical projection. Furthermore, the crater-shape implies an outwardly sloped sidewall providing a positive release angle facilitates de-moulding of the shaped item.

Further according to one embodiment of the replication tool, the vertical profile of the microscale structured master surface has a peak-to-peak amplitude of at least 0,3μm, or at least 0,5μm or at least 1μm and below 30μm, below 20μm, or preferably below 10μm.

Further according to one embodiment of the replication tool, the lateral pattern of the microscale structured master surface has an area density of microscale master features of at least 8000/mm², or at least 10000/mm². Thereby, the replication tool is particularly useful for producing items with enhanced wetting properties, since the formed items comprise a microscale textured replica surface with a densely packed lateral arrangement of microscale protrusions produced replicated from the microscale structured master surface.

It should be noted, however, that the process according to the present invention will not exceed an inherent upper limit for the area density of the microscale lateral structuring. Such an inherent limit is due to the fact that the microscale features produced by the microscale phase explosions according to the present invention require a minimum footprint in order to be resolved. While the present invention produces polydisperse features with a distribution that may include submicron elements, their average (most prominent) lateral dimensions are in the microscale. Increasing the area density of the microscale features results in an increasing probability for the occurrence of overlap between adjacent microscale features. Above a critical overlap, the microscale features are overlapping to such an extent that they appear merged and effectively have a much larger lateral extension than a targeted feature size of individual, unmerged microscale features. As a consequence, above a critical area density such merged features increasingly dominate the actual feature size produced on the replication tool.

In a characterization of the microscale surface structure of the master surface, e.g. by commonly known image analysis techniques applied to micrographs thereof, the merged features are then counted as a single feature with a larger lateral dimension or foot print. This effect is best seen in a graph showing the area density of microscale features, e.g. counted in a given surface portion by means of image analysis, as a function of the laser energy exposure applied to that surface portion. By way of example, such a graph is shown in Fig.21. The data shown has been obtained by an analysis of the microscale structuring applied to more than 70 replication tool blanks (tool grade aluminium as specified elsewhere in this application) using the method according to the invention. The ordinate shows the exposure dose expressed in terms of the number of repetitions divided by the scan speed; the coordinate shows the area density of holes detected by an image analysis performed on micrographs of the processed surface; and the marker size indicates the size of the detected feature determined by the same image analysis algorithm. In an initial regime at low exposure, the individual microscale features are resolved and all have essentially the same size. The initial regime covers a low density regime up to about 5000/mm^2 where the distribution of the microscale features may be considered as sparse. In an intermediate exposure regime above about 5000/mm^2, the microscale features may be considered as more and more densely packed, reaching a critical density of about 12000/mm^2, where overlap of adjacent microscale features begins to become significant. The critical density is the maximum achievable density for a given system, which in the example of Fig.21 is about 12000/mm^2. Other material systems and laser processing set-ups may have a different maximum achievable area density, such as about 100000/mm^2, or about 50000/mm^2, or 20000/mm^2, or about 15000/mm^2. An inherent limit to the maximum achievable area density is given by the requirement of microscale dimensions of the lateral structuring as achieved by the present invention. Increasing the exposure beyond the critical value then only results in merging of the microscale features and in a deterioration of the desired patterning. In the example of Fig.21, a significant decrease of the area density of microscale features to below 5000/mm^2, accompanied by a corresponding increase of the average feature size is observed. When the microscale structure of the replication tool master surface is transferred onto a replicated item to form a microscale surface texture for the enhancement of a wetting behaviour, a sparse distribution of microscale features may prove insufficient to provide a significant wetting behaviour enhancement – if any at all. In a preferred exposure regime around the maximum achievable area density of about 100000/mm^2, or about 50000/mm^2, or 20000/mm^2, or about 15000/mm^2, or about 12000/mm^2, the microscale features are adequately dimensioned in their lateral extend, yet are packed sufficiently dense so as to achieve a significant wetting behaviour enhancement. An adequate range may be determined by an exposure experiment as outlined in Fig.21, wherein preferably the area density is at least 60%, at least 70%, at least 80%, or at least 90% of the maximum achievable area density of microscale features. Above a critical exposure, in the regime where merging becomes more and more dominant, the wetting behaviour enhancement of the replicated item also deteriorates more and more.

Further according to one embodiment of the replication tool, the microscale master features have an aspect ratio of a vertical dimension to a lateral dimension of at least 1:2, or about 1:1, wherein the vertical dimension is the peak-to-peak amplitude and the lateral dimension is the square root of the average footprint area per microscale master feature, which for a given microscale structured surface area is calculated as the inverse of the area density of microscale master features per area, i.e. the area of the given surface in lateral projection divided by the count of microscale features in that area.

BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the invention will be described in more detail in connection with the appended drawings, which show in

FIG. 1a–c, SEM micrographs of a microscale structured master surface at different magnifications,

FIG. 2 a SEM micrograph of another microscale structured master surface,

FIG. 3 a microscope image of a droplet of water on an unstructured polypropylene surface,

FIG. 4 a SEM micrograph of the microscale textured surface of an injection moulded item (polypropylene) using an isotherm process,

FIG. 5 a microscope image of a droplet of water on a polypropylene surface of the type as shown in Fig.4,

FIG. 6 a SEM micrograph of the microscale textured surface of an injection moulded item (polypropylene) using a variotherm process,

FIG. 7 a microscope image of a droplet on a polypropylene surface of the type as shown in Fig.6,

FIG. 8 schematically, the surface modification of a tool surface by pulsed laser treatment to generate microscale phase explosions,

FIG. 9 schematically, an injection moulding process according to one embodiment of the invention,

FIG. 10 schematically, an extrusion coating process according to a further embodiment of the invention,

FIGS.11–14 four graphs plotting hole size and hole density on a microscale structured master surface for different parameter settings of the pulsed laser treatment of the tool surface,

FIGS.15–18 four graphs plotting hole density on a number of microscale structured master surfaces against the scan speed used during the pulsed laser treatment of the respective tool surfaces, FIGS.19 (a) a microscope image and (b) a photographic top view of a droplet of mineral oil on an unstructured polypropylene surface,

FIGS.20 (a) a microscope image and (b) a photographic top view of a droplet of mineral oil on a microscale textured replica surface as the one shown in Fig.4, and in

FIG. 21 a graph plotting hole density on a number of microscale structured master surfaces against the exposure in terms of repetitions divided by scan speed used during the pulsed laser treatment of the respective tool surfaces.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Super-hydrophobic surfaces are ubiquitous in the plant kingdom. Super-hydrophobic plant leaves possess the so-called lotus-effect, which causes rain drops falling on the leaves to roll off while capturing any dust particles. This way, the surfaces are passively self-cleaning. The super-hydrophobic properties are achieved by a combination of the chemical properties of the surface (molecular level) and its roughness (micro-level). In nature, this is realised as rough leaves covered with a wax layer.

When a water droplet interacts with a hydrophobic surface, several different possible “interaction-states” are possible. However, the one where the droplet is the most mobile is the Cassie-Baxter state. In this state, the droplet is only partially wetting the surface, and air is trapped in the trenches of the surface. Without going into the mathematics of super-hydrophobicity, surface roughness and the hydrophobicity can be understood as a scaling factor. This means that a hydrophobic surface will be more hydrophobic when surface roughness is increased, and a hydrophilic surface will be more hydrophilic when surface roughness is increased. This explains why tissue paper is good for wiping up water, and why lotus leaves are super-hydrophobic. Man-made super-hydrophobic surfaces are typically realised using a Teflon coating, which contains hydrophobic fluor-saturated molecules. This is non-ideal from a mass-production perspective and from a health safety perspective. If the surface roughness is increased, the intrinsic hydrophobicity of the polymer may be exploited to achieve super-hydrophobicity. Alternatively, Teflon coated pieces will also benefit from the increased roughness. Super-hydrophobic injection-moulded plastic parts have many applications in food packaging, pharmaceuticals, medical equipment, consumer plastic products and electronics. How the steps of the invention may be implemented is illustrated by way of example in the following. The examples given are not to be considered as limiting for the scope of the invention.

Replication Tool

Examples of suitable materials are materials commonly used as inlays/ or mould materials in e.g. injection moulding or extrusion coating processes. These materials of the tool surface suited to be modified by pulsed laser treatment to generate microscale phase explosions include Aluminium alloys, such as so-called 1050 aluminium, 5754 aluminium, or 2017 aluminium, as well as tool steel, such as Sandvik corona C60 and orvar 2343.

Figs.1a-c show micrographs taken by scanning electron microscopy (SEM) of an aluminium tool surface, more particular a tool surface made of 2017 aluminium, which has been modified by pulsed laser treatment using a picosecond laser with a maximum power output of 50 W operating at a pulse frequency of 200 kHz and at a wavelength of 1064 nm. The surface was scanned repetitively at a given power setting in per cent of the maximum power output and with a given speed. The laser beam was incident on the tool surface in a vertical direction, wherein the laser was slightly defocused by shifting the focal point by 1,3mm in a vertical direction with respect to the tool surface to be modified. While the apparent spot size was about 50μm on the surface, a line scan of the laser produced a modified trace width of about 10μm ± 5μm. A broader trace as the one shown in Fig.1a and 1b was obtained by a meander line scan with adjacent legs of the meander shifted in a direction perpendicular to the scanning direction. Thereby an arbitrary area can be covered by a microscale surface structure. As best seen in Fig. 1a, the laser treatment results in an ablation of some of the tool surface material. The parameters of the pulsed laser treatment are, however, adjusted such the bottom of the trace exhibits a lateral arrangement of polydisperse microscale master features, see e.g. Fig.1b. The microscale master features obtained by this pulsed laser treatment are crater-shaped depressions. The crater-shaped depressions at the bottom of the trace are a consequence of the localized pulsed laser treatment generating microscale phase explosions.

Figs.2 shows a SEM micrograph of tool surface made of tool steel, more particular Sandvik corona C60 tool steel, which has been modified by pulsed laser treatment using the same picosecond laser with a maximum power output of 50 W operating at a pulse frequency of 200 kHz and at a wavelength of 1064 nm. Again, the surface was scanned repetitively at a given power setting in per cent of the maximum power output and with a given speed. The laser beam was incident on the tool surface in a vertical direction, wherein the laser was slightly defocused. Also here, the localized pulsed laser treatment generates microscale phase explosions resulting in a lateral arrangement of polydisperse microscale master features, wherein the microscale master features are crater-shaped depressions.

Replicated Item

The laser structured aluminium insert was installed in a Victory 80/45 Tech injection moulder (Engel). The polymer substrate used for injection moulding polypropylene HD120MO (Borealis) with a Heat Deflection Temperature (0.45 N/mm²) of 88 °C. Injection temperature of the polymer was 255 °C with an injection pressure of 1200 bar. Both variotherm and isotherm injection moulding processes were tested.

Parameters specific for isotherm injection moulding:

- Temperature of microscale structured aluminium insert face = 80 °C. (constant)
- Temperature of “backside” mould = 60 °C. (constant)

Parameters specific for variotherm injection moulding:

- Temperature of structured aluminium insert face = 120 °C. (injection)
- Temperature of “backside” mould = 100 °C. (injection)
- Active cooling was applied immediately after polymer injection for the duration of the holding time (60 seconds) followed by and additional cooling time (60 seconds). This resulted in a final mould temperature of 40-50 degrees.

The respective surfaces have been characterised with respect to the shape of the microscale features on the microscale textured surface of the replicated item, see

Fig.4 and Fig.6. The isothermal process results in a surface texture with rounded tops, see Fig.4, and the variothermal process results in a surface texture with a hairy appearance ("pulled polypropylene"). Both surfaces faithfully replicate the lateral pattern of the master, but only provide a low fidelity replication of the vertical profile of the master. Nevertheless, both processes result in a fast replication of items with a super-hydrophobic surface. The isothermal process is preferable for high through-put or high volume production, because the isothermal moulding process is not time limited by any process step(s) involving temperature adjustments of mould and/or mould inserts, whereas the variotherm moulding process is partially time limited by one or more process step(s) involving temperature adjustments of mould and/or mould inserts.

Enhancement of Wetting Properties

The wetting properties of the obtained surfaces of the replicated items where characterized by performing contact angle measurements. Drop roll-off experiments for determining contact angles were conducted on an Attension Theta optical tensiometer (Biolin Scientific) by applying a 10 µl droplet of water and slowly tilting the stage until roll-off was observed.

Table 1: Results of contact angle measurements

	Variotherm	Isotherm	Unstructured
Contact angle	160°	160°	104°
Contact angle hysteresis	<5°	<5°	21°
Stage tilt angle (@ roll-off)	<5°	<5°	NA*

*Droplet is sticking to the surface.

Fig.3, Fig.5 and Fig.7 show microscope images as obtained during the contact angle measurements performed with water droplets on replicated items, where Fig.3 is for the unstructured material, Fig.5 is for the isotherm process, and Fig.7 is for the variotherm process. A very pronounced hydrophobic enhancement is observed for both types of microscale textured replica surfaces. More particularly, both microscale textured replica surfaces exhibit superhydrophobic behaviour.

Figs.19a/b and 20a/b show in a further example the lipophilic enhancement of a polypropylene surface with a microscale textured replica surface (Fig.20a/b) as compared to a flat, unstructured surface (Fig.19a/b). In these figures, the droplet is a PCR reactant grade mineral oil (Sigma-Aldrich; CAS Number 8042-47-5) with a volume of 5µl. Figure 19a shows a microscopic side view of the droplet of the mineral oil on flat, unstructured polypropylene, from which a contact angle of 14 degrees can be measured (lipophilic behaviour). The lateral spreading of this droplet on the unstructured surface is outlined by the circle in the top view in Fig.19b. The polypropylene substrate has a diameter of 5cm. Fig.20a shows a microscopic side view of the droplet of the mineral oil on a microscale textured surface of the same material as in Fig.19. A contact angle below 1 degree is now observed, which may be characterised as complete wetting of the substrate surface. Accordingly, a large increase in the spreading of the droplet over the surface of the substrate is observed as in Fig.20b, where the circle outlines the droplet border. The substrate has a diameter of 5cm. Note that the droplets in Fig.19 and Fig.20 both have the same volume of 5µl. A very pronounced lipophilic enhancement is thus observed for the microscale textured replica surface. More particularly, the microscale textured replica surface exhibits superlipophilic behaviour.

Replication Process

Fig.9 shows schematically an injection moulding process for producing a replicated item 4. The process uses a mould having mould parts 1a and 6, wherein mould part 6 has an insert 1b. Tool surfaces 2a, 2b, 7 define a general shape of the replicated item 4. Tool surfaces 2a, 2b are provided with microscale structured master surfaces 3a, 3b, 3c, which are replicated on the item 4 as microscale textures 5a, 5b, 5c, respectively.

Fig. 10 shows schematically an extrusion coating process for coating a substrate web S, with a coating 14. The process uses a roll 11, 11a with a tool surface 12, 12a defining a general shape of the coating. The tool surface comprises microscale structured master surfaces 13, 13a, which are replicated as microscale surface texture 15 on the coating 14. A microscale structured master surface 13 may be applied directly to the tool surface 12 of the roll 11 and/or a microscale structured master surface 13a may be applied to the tool surface 12a of a replication tool insert 11a for attachment to the roll 11.

Localized Pulsed Laser Treatment Generating Microscale Phase Explosions

Fig.8 shows schematically the configuration of the set-up for localized pulsed laser treatment of a tool surface 2 on a replication tool 1 to generate a microscale structured master surface 3 by scanning a pulsed laser beam 99 over the tool surface.

EXAMPLE

The example illustrates different ways of identifying suitable laser processing parameters for modifying a given tool surface to obtain a microscale structured master surface.

Aluminium 2017 (available from “Metalcenteret” Glostrup, Denmark) was surface structured using a 1064nm, 200kHz, 50W picosecond laser (FUEGO, Time Bandwidth) mounted in a microSTRUCT vario (3D-Micromac AG). To perform the surface structuring, the area intended for structuring was irradiated by the laser in parallel lines separated by 20 µm. Every second layer was perpendicular to the previous, and so one set of perpendicular planes of lines is referred to as one “cross repetition”. The laser power was set to 25% and 10 repetitions was conducted with focus offset +1.3 mm above the surface.

As illustrated in 11-18, the average dimension and standard deviation of the hole sizes may be adjusted by varying parameters such as laser power in percent of maximum power output, scanning speed, number of cross repetitions and z offset of the focus plane. To identify the optimal parameter settings for achieving a desired hole size population and hole density in the alloy in question, one may map the parameter space of the laser settings. When replicated in polymer, the hole size population and hole density will determine the surface structure and roughness and hence the final wetting properties of the polymer piece.

In the example below, the parameter space was for the

- Laser power in percent of the maximum power of 50W: from 10 to 100 (both included), in increments of 5;

- Scan Speed in mm/s: from 150 to 1950 (both included), in increments of 100; and from 600 to 4200 (both included), in increments of 200;
- Number of cross repetitions: from 3 to 39 (both included), in increments of 2;

It may be noted that similar surface characteristics may be achieved using different parameter combinations. However, to minimise time consumption for the laser process, the parameter coordinate with the highest (scan speed / cross repetition) value, and hence lowest process time, is preferred.

Additional information:

- Alloy: 2017, aluminium
- Wavelength = 1064 nm
- Pulse frequency = 200kHz
- Focus plane = z + 1.3 mm
- Max laser power = 50 W

A recommended method to reduce the number of parameters and experiments is by locking parameter pairs in a fixed ratio, such as keeping (laser power / scan speed) constant, see Fig.11 and Fig.12, where the numerical value of the ratio of (laser power (in percent of the max power of 50W) divided by the scan speed (in mm/s) is kept constant at 25E-5 (= 0,00025) or 50E-5 (= 0,0005) and allows for identification of the desired modification characteristics: both figures show peaks in hole density X. Likewise, the numerical value of the ratio of the number of repetitions divided by the scan speed (in mm/s) can be kept constant, see Fig.13 and Fig.14, where this ratio is kept constant at 1E-2 (= 0.01) or 2E-2 (= 0.02) and allows for identifying desired modification characteristics. As can be seen in Fig. 14, the high intensity (slow speed) results in few but large holes, whereas Fig. 13 shows that for the numerical value of the ratio of repetitions over scan speed (in mm/s) equal to 0.01 a more densely packed and uniform hole formation is achieved.

Figs.15-18 show four graphs plotting hole density against the scan speed used during the pulsed laser treatment of the respective tool surfaces. At speeds ≤ 1250 mm/s, the hole density is consistent regardless of other parameters than speed, and it is concluded that writing speed is the main determining factor in this regime. At speeds ≥ 1250 mm/s, the hole density varies with the number of cross repetitions. This is true, even when the product (power X repetitions) is kept constant, (see Fig. 16). Marker size represents cross repetitions in Fig.15 and (cross repetitions X power) in Fig.16. Regardless of the parameter settings used to achieve a desired hole density, the coefficient of variance (CV) of hole size is observed to be stable in the regime where (speed ≥ 1250 mm/s), see Fig.17, and accordingly for the standard deviation (STD), see Fig.18. Marker size represents hole size CV in Fig.17 and hole size STD in Fig.18. Similarly, the laser focus parameter space may be mapped to identify applicable laser settings.

CLAIMS

1. Method of producing an item with enhanced wetting properties by a replication process, the method comprising the steps of
   - providing a forming tool having a tool surface adapted to define a general shape of an item to be formed;
   - modifying at least portions of the tool surface by a pulsed laser treatment to obtain a replication tool with a microscale structured master surface with a lateral master pattern and a vertical master profile, wherein the pulsed laser treatment is adapted to generate microscale phase explosions on the tool surface, thereby forming the microscale structured master surface as a lateral arrangement of microscale crater-shaped depressions, wherein the lateral pattern of the microscale structured master surface has an area density of microscale master features of at least 5000/mm²;
   - using the replication tool to form the item by the replication process, wherein the formed item has the general shape defined by the tool surface, and wherein the formed item comprises a microscale textured replica surface with a lateral arrangement of microscale protrusions produced by the microscale structured master surface.

2. Method according to claim 1, wherein the replication process is injection moulding or extrusion coating.

3. Method according to claim 1 or claim 2, wherein a replication period from contacting the tool surface with the molten replication material to releasing the shaped item is less than three minutes, such as less than two minutes, such as less than one minute, such as less than 30 seconds, or even less than 10 seconds.

4. Method according to any of the preceding claims, wherein the vertical replica profile predominantly has rounded tops with a radius of curvature in the microscale.

5. Method according to any of the preceding claims, wherein the replica material is hydrophobic with a flat surface contact angle of at least 95 degrees, preferably at least 100 degrees, and up to 120 degrees, preferably up to 110 degrees.

6. Method according to claim5, wherein the microscale textured replica surface is superhydrophobic.

7. Method according to any one of claims 1-4, wherein the replica material is hydrophilic with a flat surface contact angle below and including 85 degrees, below and including 80 degrees, or preferably below and including 75 degrees, and at least 50 degrees, at least 60 degrees, or at least 70 degrees.

8. Method according to claim 7, wherein the microscale textured replica surface is superhydrophilic.

9. Replication tool for producing an item with enhanced wetting properties by fast replication, the replication tool comprising
- a tool surface defining a general shape of the item,
- the tool surface comprising a microscale structured master surface having a lateral master pattern and a vertical master profile
wherein said microscale structured master surface has been provided by localized pulsed laser treatment to generate microscale phase explosions, wherein the lateral pattern of the microscale structured master surface has an area density of microscale master features of at least 5000/mm²,.

10. Replication tool according to claim 9, wherein the tool surface is made of a metal, such as alloys of aluminium or steel.

11. Replication tool according to any one of claims 9-10, wherein the microscale structured master surface is a lateral arrangement of polydisperse microscale master features.

12. Replication tool according to claim 11, wherein the microscale master features are crater-shaped depressions.

13. Replication tool according to any one of claims 9-12, wherein the vertical profile of the microscale structured master surface has a peak-to-peak amplitude of at least 0,3µm, or at least 0,5µm or at least 1µm and below 30µm, below 20µm, or preferably below 10µm.

14. Replication tool according to any one of claims 11-13, wherein the lateral pattern of the microscale structured master surface has an area density of microscale master features of at least 8000/mm², or at least 10000/mm².

Fig. 1a

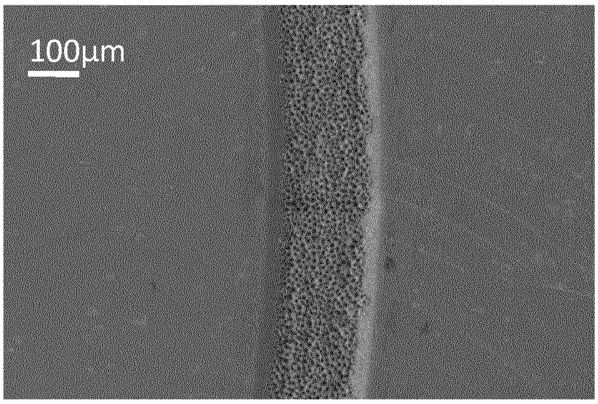


Fig. 1b

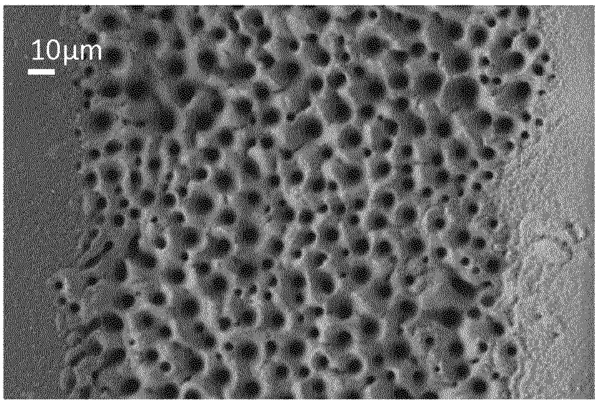


Fig. 1c

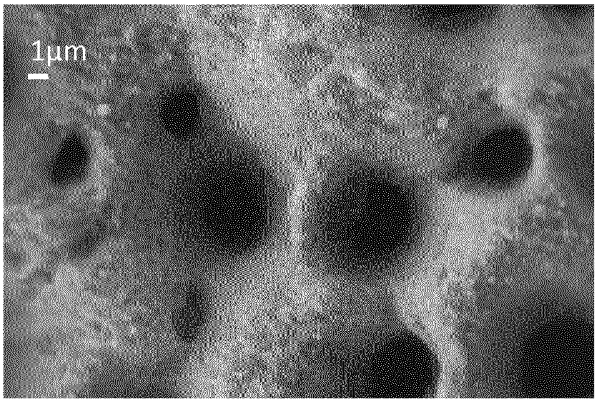
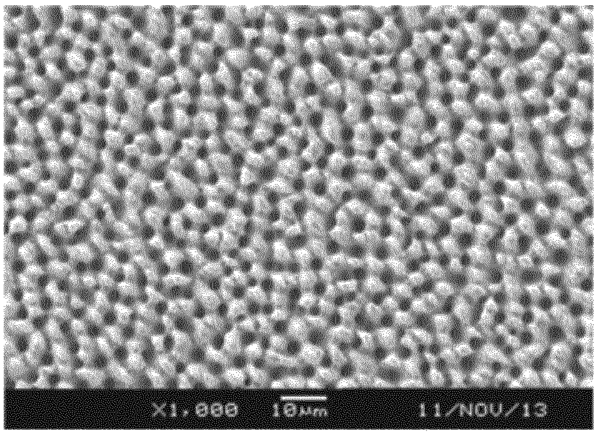


Fig. 2



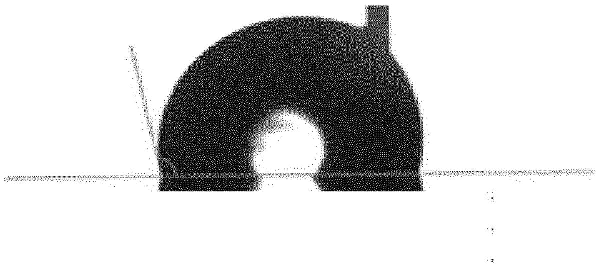


Fig. 3

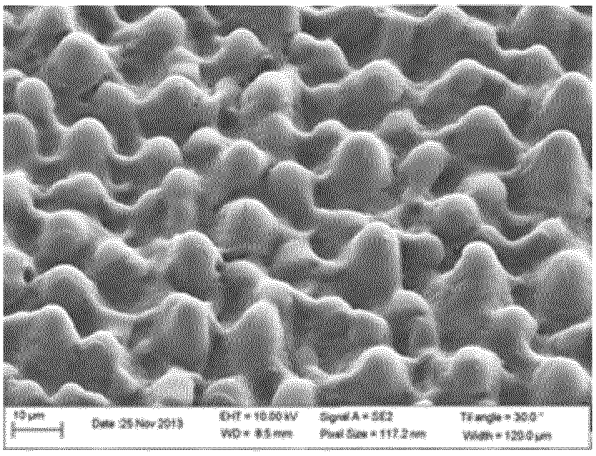


Fig. 4

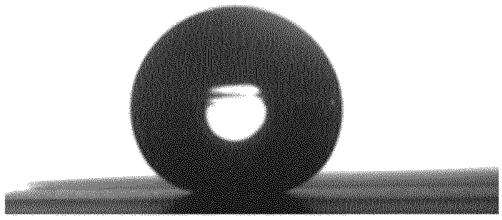


Fig. 5

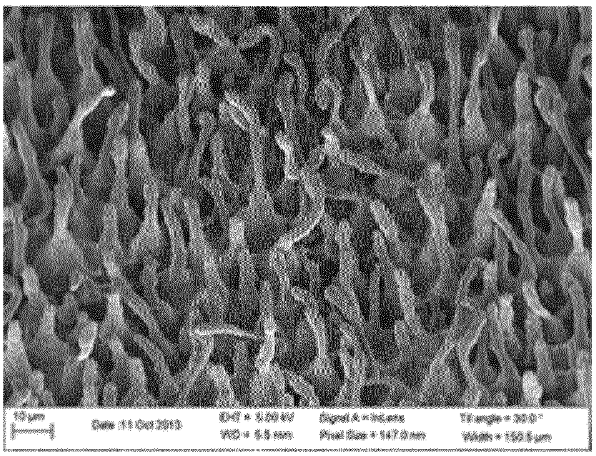


Fig. 6

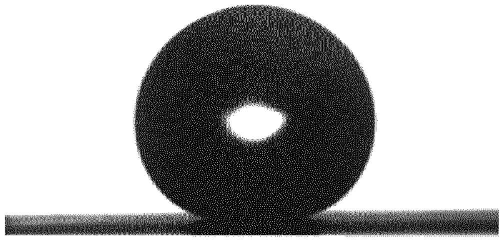


Fig. 7

Fig. 8

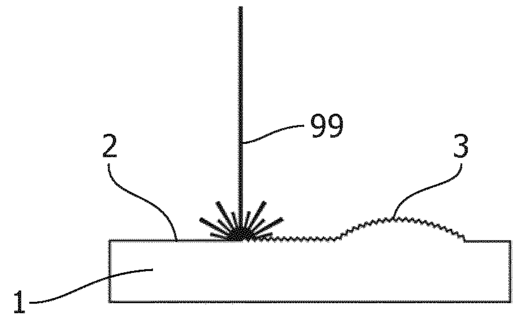


Fig. 9

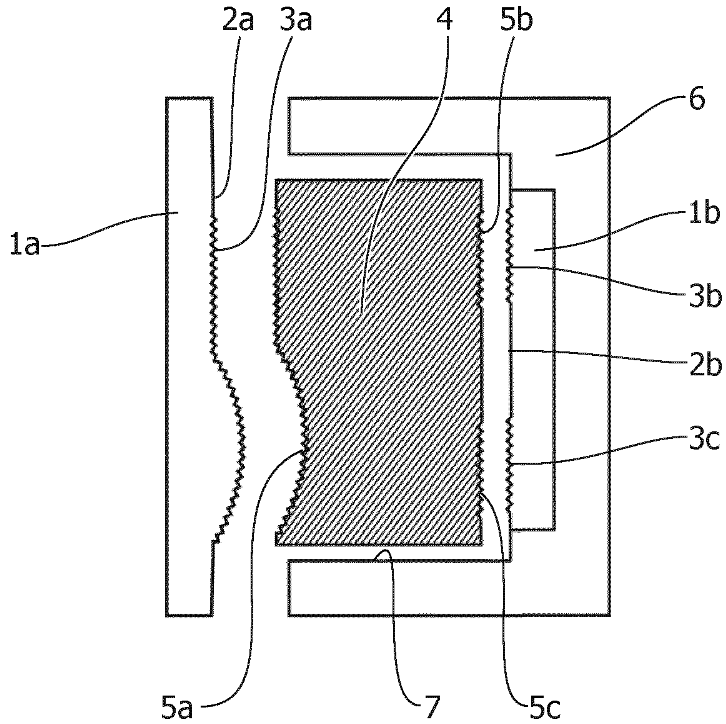


Fig. 10

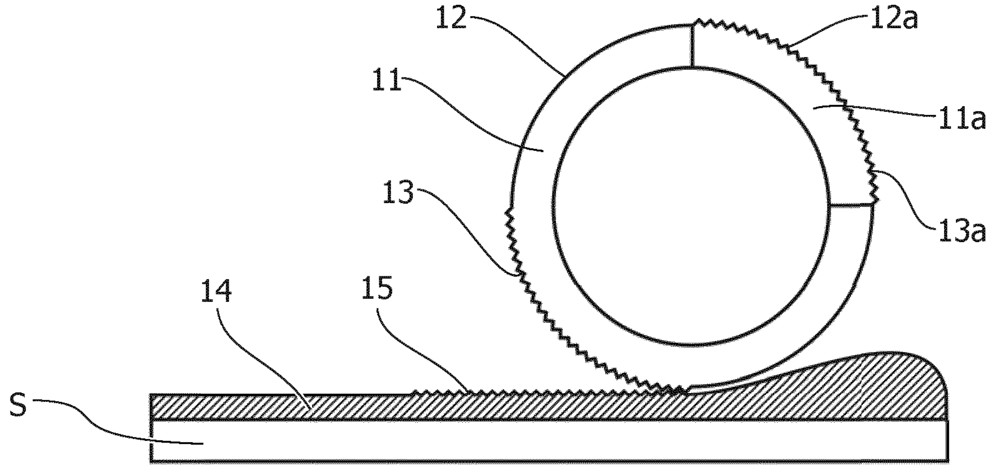
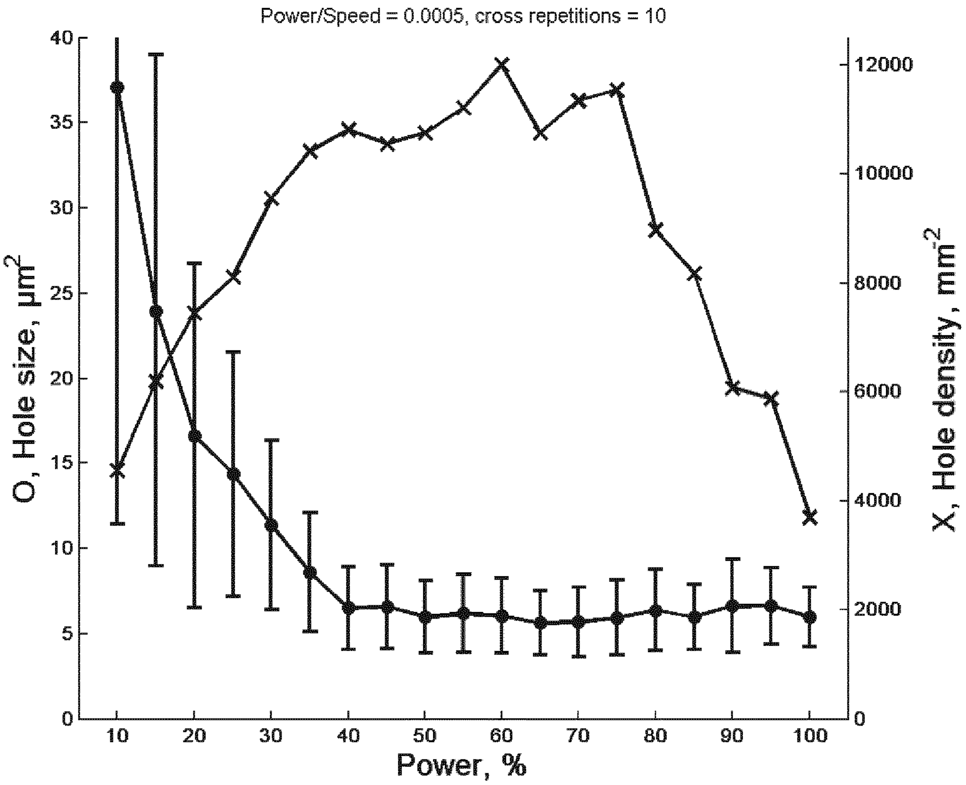


Fig. 11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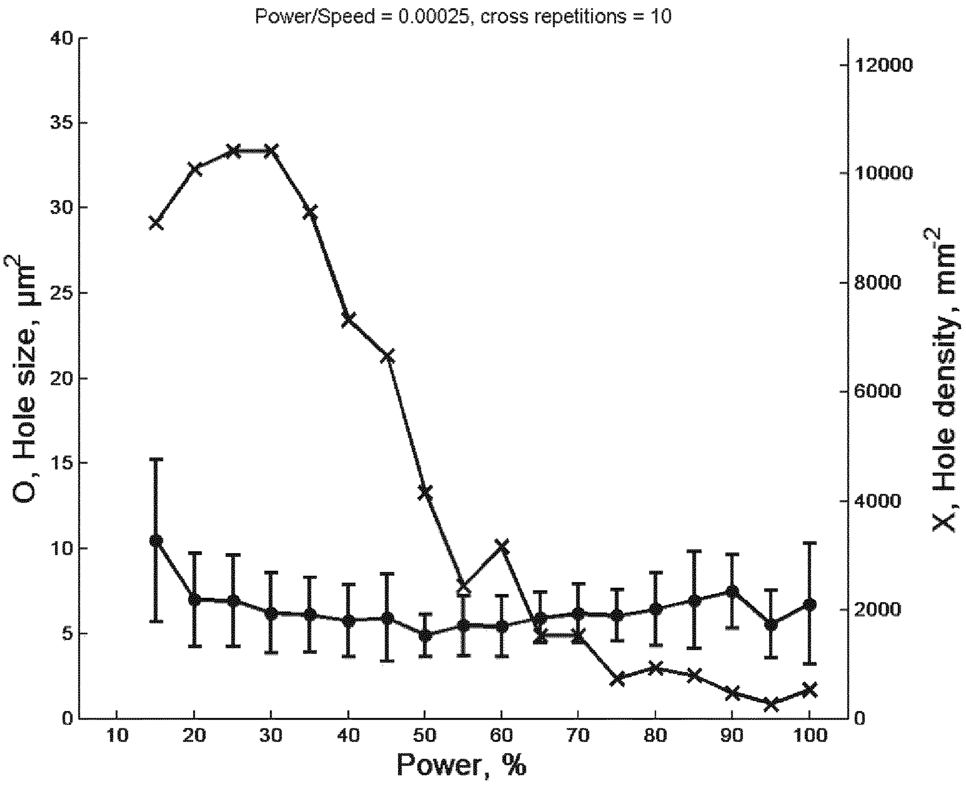
O, Hole size, µm2
X, Hole density, mm-2
Power, %
40
35
30
25
20
15
10
5
0
10
20
30
40
50
60
70
80
90
100
12000
10000
8000
6000
4000
2000
0

Fig. 12


Power/Speed = 0.00025, cross repetitions = 10
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X, Hole density, mm-2
Power, %
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35
30
25
20
15
10
5
0
10
20
30
40
50
60
70
80
90
100
12000
10000
8000
6000
4000
2000
0

Fig. 13

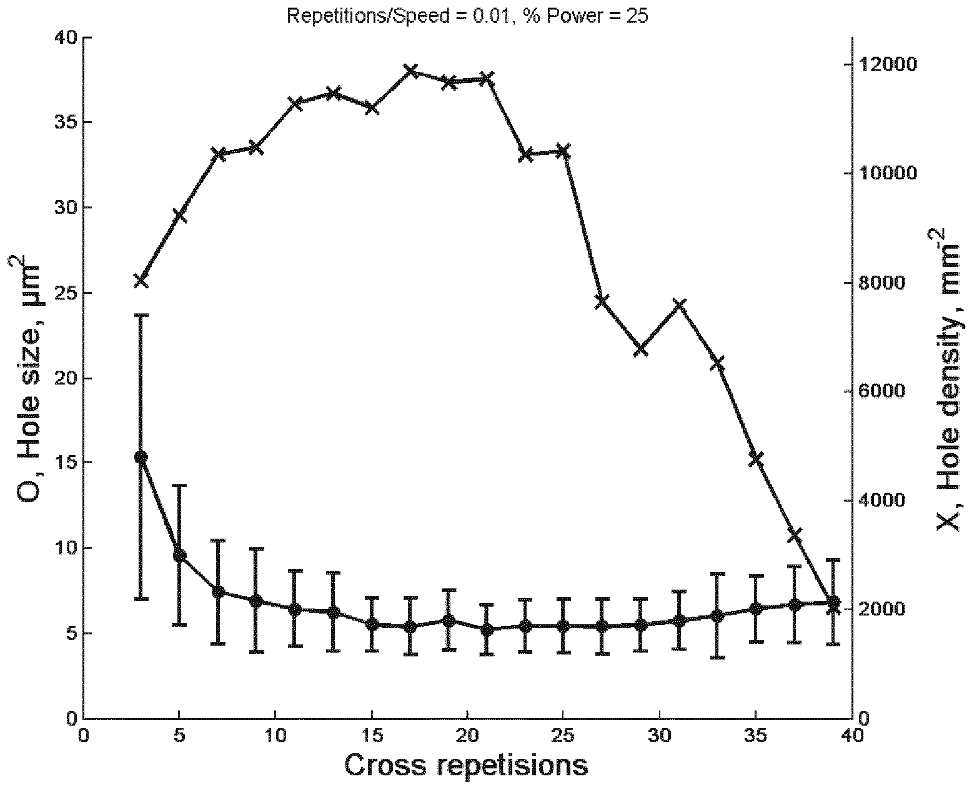
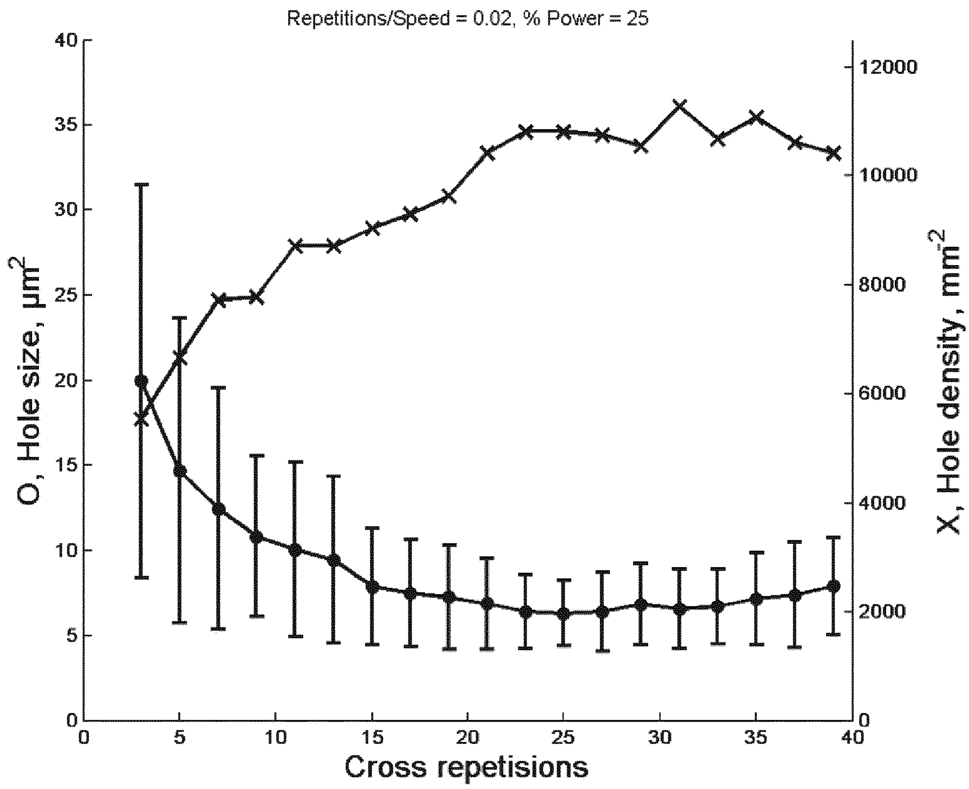

Repetitions/Speed = 0.01, % Power = 25
O, Hole size, μm^2
X, Hole density, mm^-2
Cross repetisions
0
5
10
15
20
25
30
35
40
2000
4000
6000
8000
10000
12000

Fig. 14


Repetitions/Speed = 0.02, % Power = 25
O, Hole size, μm^2
X, Hole density, mm^-2
Cross repetisions
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5
10
15
20
25
30
35
40
2000
4000
6000
8000
10000
12000

Fig. 15

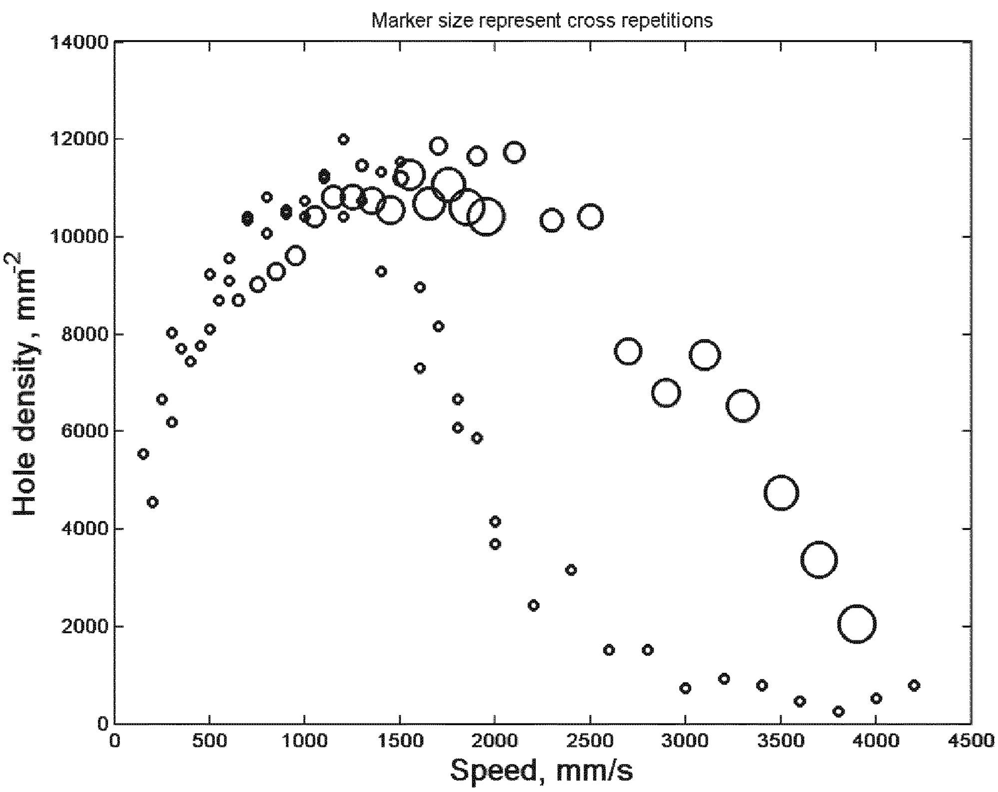

Marker size represent cross repetitions
Hole density, mm-2
Speed, mm/s
14000
12000
10000
8000
6000
4000
2000
0
0
500
1000
1500
2000
2500
3000
3500
4000
4500

Fig. 16

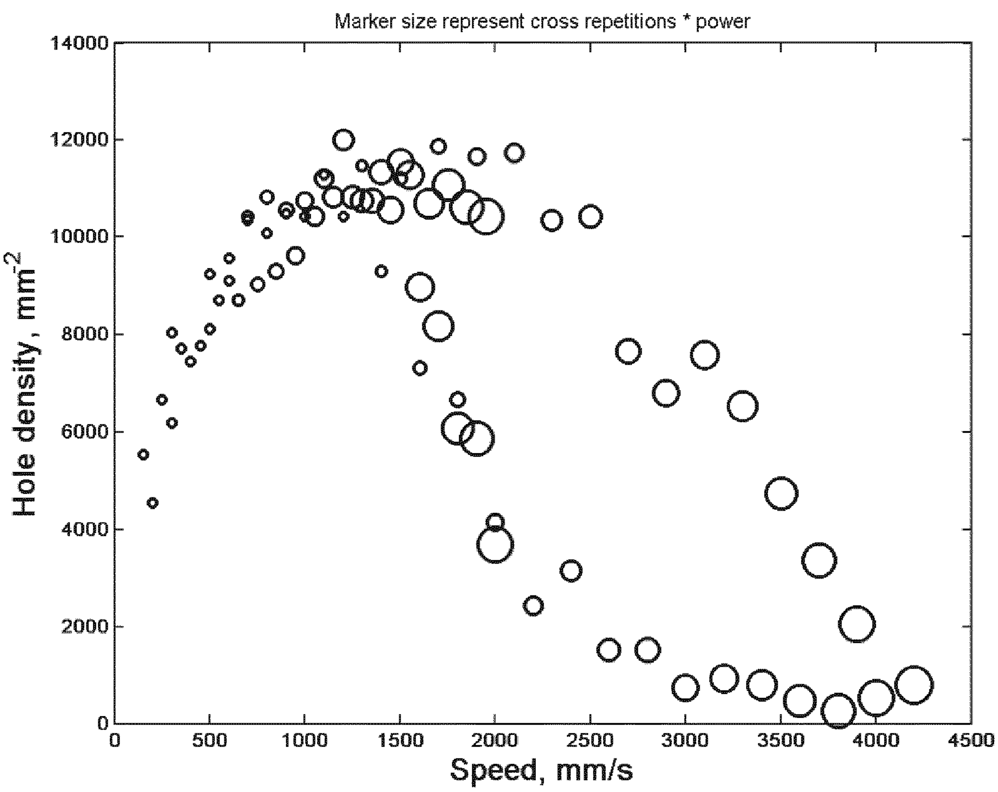

Marker size represent cross repetitions * power
Hole density, mm-2
Speed, mm/s
14000
12000
10000
8000
6000
4000
2000
0
0
500
1000
1500
2000
2500
3000
3500
4000
4500

Fig. 17

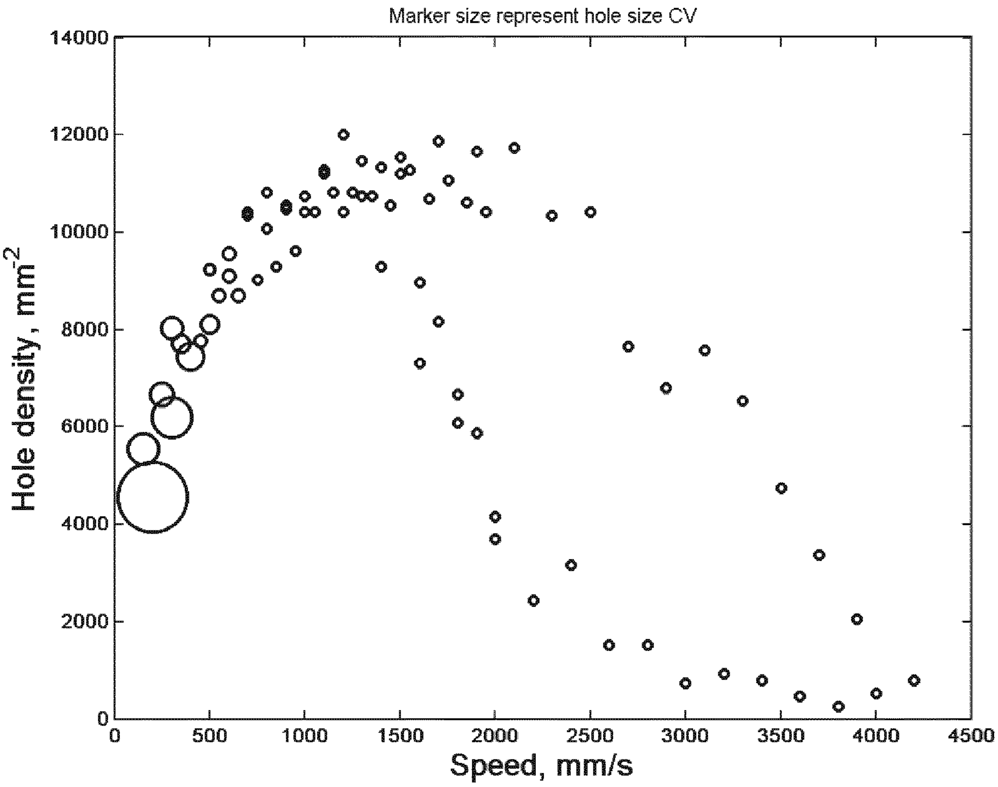
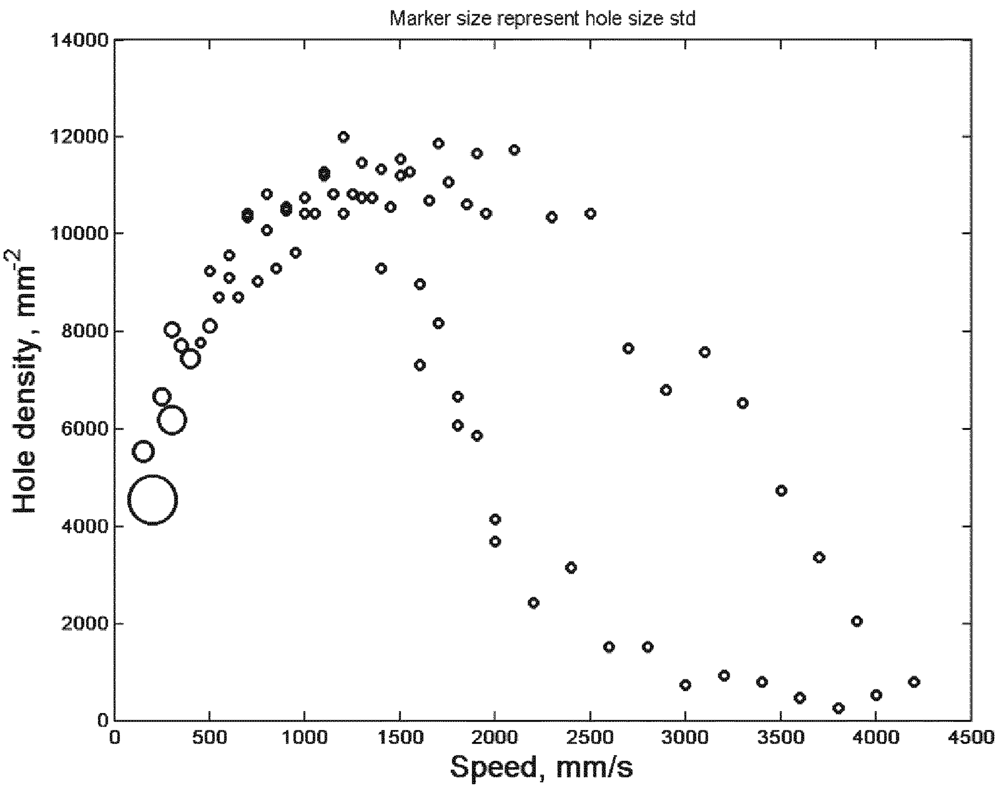

Marker size represent hole size CV
Hole density, mm-2
Speed, mm/s
14000
12000
10000
8000
6000
4000
2000
0
0
500
1000
1500
2000
2500
3000
3500
4000
4500

Fig. 18


Marker size represent hole size std
Hole density, mm-2
Speed, mm/s
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12000
10000
8000
6000
4000
2000
0
0
500
1000
1500
2000
2500
3000
3500
4000
4500

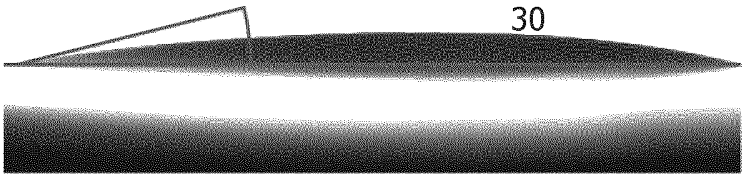

Fig. 19a

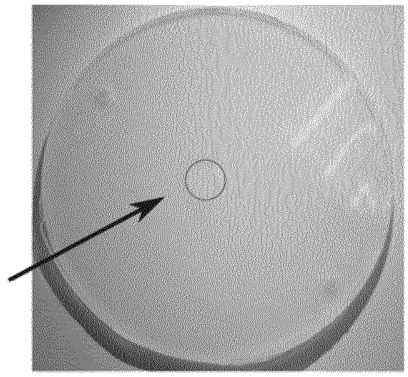

Fig. 19b

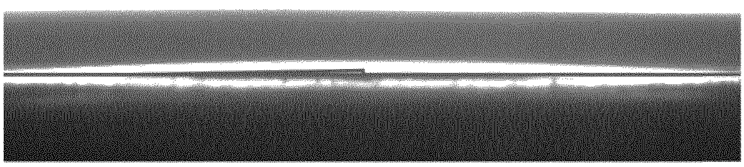

Fig. 20a

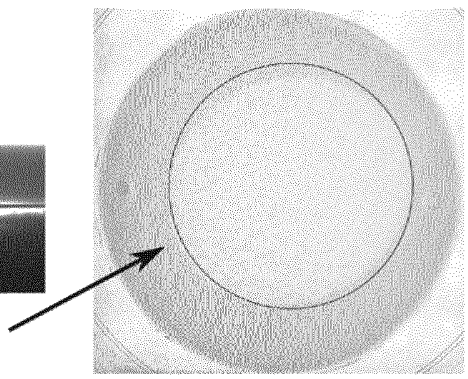

Fig. 20b

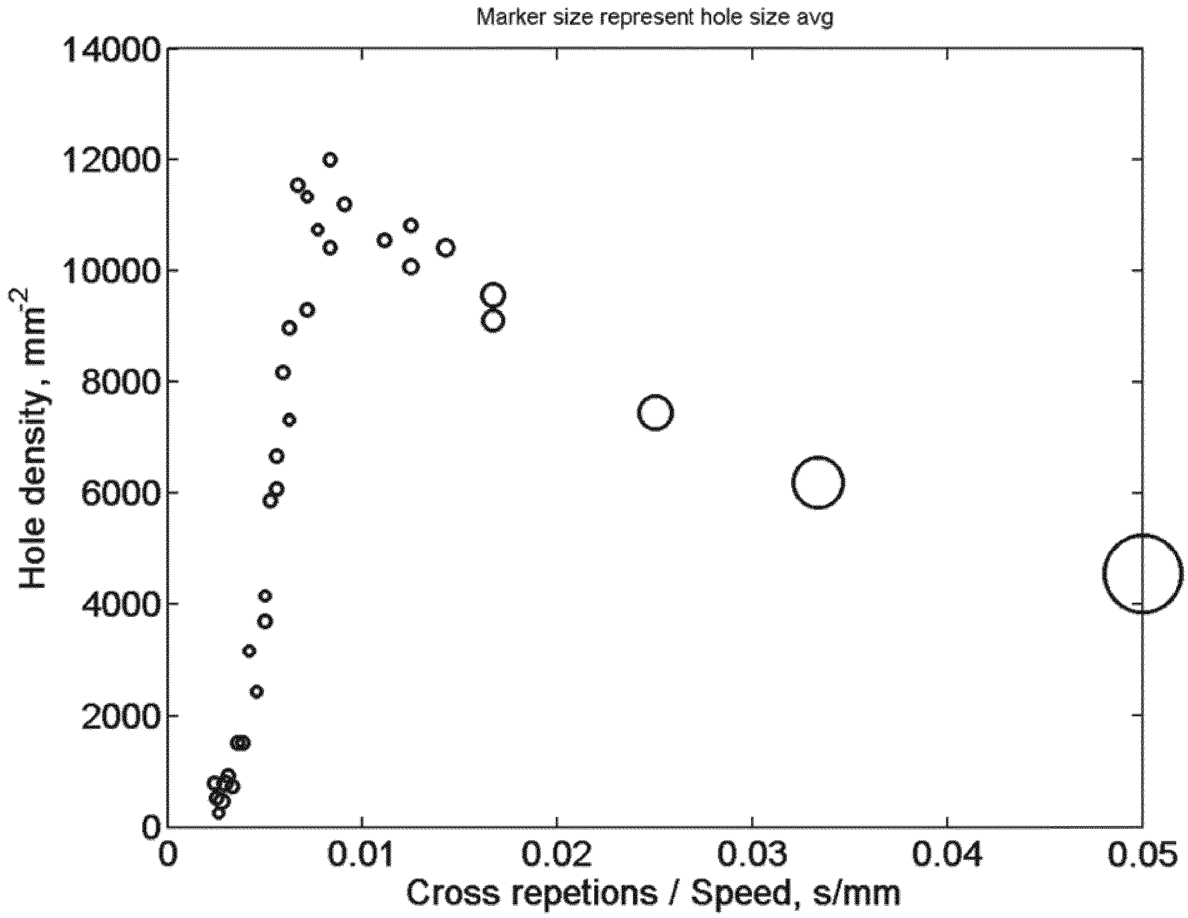
Marker size represent hole size avg
14000
12000
10000
8000
6000
4000
2000
0
Hole density, mm^{-2}
0
0.01
0.02
0.03
0.04
0.05
Cross repetions / Speed, s/mm

Fig. 21

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/076520

A. CLASSIFICATION OF SUBJECT MATTER

INV. B23K26/00 B29C33/42 B29C37/00 B29C65/08 B29C65/00
ADD. B29C59/02

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)

B29K B29C B23K

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	US 2011/287203 A1 (VICTOR JARED J [CA] ET AL) 24 November 2011 (2011-11-24)	1-14
Y	paragraph [0001] - paragraph [0003] paragraph [0043] - paragraph [0045] paragraph [0081] - paragraph [0083] paragraph [0085] paragraph [0097] paragraph [0124] - paragraph [0127] figure 1 -----	1-14
X	US 2014/205801 A1 (IWATA RYOSUKE [JP] ET AL) 24 July 2014 (2014-07-24) paragraph [0001] paragraph [0220] - paragraph [0243] paragraph [0260] - paragraph [0274] figures paragraph [0172] paragraph [0279] - paragraph [0285] -----	1-14
	-/--	

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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"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
16 February 2016	24/02/2016

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	Fageot, Philippe

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Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2012/227879 A1 (MUHLHOFF OLIVIER [FR] ET AL) 13 September 2012 (2012-09-13) paragraph [0001] paragraph [0015] - paragraph [0019] paragraph [0033] paragraph [0042] paragraph [0045] - paragraph [0050] paragraph [0054] - paragraph [0061] figures 4-9 -----	1-14

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2015/076520

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		EP 2576171 A1	10-04-2013
		US 2011287203 A1	24-11-2011
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		JP 5642795 B2	17-12-2014
		JP 2013505872 A	21-02-2013
		US 2012227879 A1	13-09-2012
		WO 2011036061 A1	31-03-2011