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REPLICATION TOOL AND METHOD OF PROVIDING A REPLICATION TOOL

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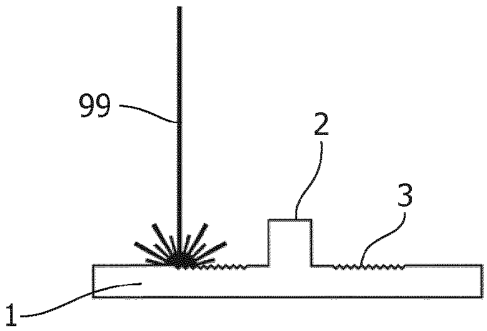
Fig. 6



(57) Abstract: The invention relates to a replication tool (1, 1a, 1b) for producing a part (4) with a microscale textured replica surface (5a, 5b, 5c, 5d). The replication tool (1, 1a, 1b) comprises a tool surface (2a, 2b) defining a general shape of the item. The tool surface (2a, 2b) comprises a microscale structured master surface (3a, 3b, 3c, 3d) having a lateral master pattern and a vertical master profile. The microscale structured master surface (3a, 3b, 3c, 3d) has been provided by localized pulsed laser treatment to generate microscale phase explosions. A method for producing a part with microscale energy directors on flange portions thereof uses the replication tool (1, 1a, 1b) to form an item (4) with a general shape as defined by the tool surface (2a, 2b). The formed item (4) comprises a microscale textured replica surface (5a, 5b, 5c, 5d) with a lateral arrangement of polydisperse microscale protrusions. The microscale protrusions may be provided on a flange portion of a first part and are configured to act as energy directors when forming an ultrasonic joint with a cooperating flange portion of a second part.

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Replication Tool and Method of Providing a Replication Tool

The present invention relates in one aspect to a replication tool and in a further aspect to a method of providing the replication tool. In a yet further aspect, the present invention relates to a method of producing a part by replication, using the replication tool.

BACKGROUND OF THE INVENTION

Producing items at industrial scales often involves replicating such items by replication techniques involving the transfer of a shape from a master tool to a mouldable material. Examples for such replication techniques include e.g. moulding techniques for producing large numbers of discrete items, or roll-to-roll techniques for high volume processing of material into continuous webs. The tools used for replication techniques have to have highly wear resistant and precise tool surfaces, and are therefore costly to produce. In return, the high volume production allows for a very low unit price of the produced items.

While such items can be produced at low cost, high value may be added by adapting these items for innovative uses. Such innovative uses typically involve or even inevitably require a functionalization of the surface One kind of functionalization involves providing the surface of the replicated items or produced materials with a particular finish, for example a microscale texture roughening.

However, known technologies for adding a microscale roughening typically involve expensive additional processing of the item after the replication step, thereby adding to the cost of the item, which in some cases is prohibitive to the commercial exploitation of such innovative improvements.

Therefore, there is a need for improved techniques for the cost-effective fabrication of replicated items with functionalized surfaces, more particular for the cost-effective production of replicated items with a microscale roughened surface. Furthermore, there is a need for suitable tooling for use in the fabrication of replicated items with microscale roughened surfaces. Furthermore, there is a need for a fast and reliable process for providing such suitable tooling.

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 a part 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 modification 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 part in the corresponding regions on the surface of the part 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.

As mentioned above, the formation of crater-shaped microscale features by the microscale phase explosions of the laser-based modification process according to the present invention is random in nature and may best be described as a Poisson-process where the microscale phase explosions occur in a stochastic manner. The stochastic nature of the structure formation is best seen in the resulting surface structure, where a spatial distribution of the microscale structures over the surface follows a Poisson distribution function.

As a further consequence of the stochastic nature of the laser-modification process, a surprisingly evenly distributed random appearance is observed. The porous appearance best resembles a roughness, rather than a periodic patterning, as would be the case e.g. in prior art techniques of sequential ablation of individual features using so-called femtosecond lasers with a pulse-length of 1ps or below. Instead, the surface finish according to the present invention is formed by stochastically distributed polydisperse microscale features (crater-shaped depressions) with no apparent trace of individual lines or stitching effects, despite the exposure by scanning along a path and/or along repetitive path segments. The surprising uniformity of the randomized micro-structuring makes this technique particularly well suited for preparing a tool with a microscale structured master surface adapted for replicating items with a microscale roughened surface finish applied to a larger surface area. In addition thereto, the present technique is considerably faster than any sequential writing technique where nano and microscale features are formed one by one, and therefore allows for modifying relatively large tool surface areas in an efficient manner.

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.

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, an even more densely packed lateral distribution of microscale features on the master surface is achieved.

It should be noted, however, that an upper limit for the area density resulting from the microscale of the surface structuring exists, which is discussed in detail further below.

An important advantage of the laser-based tool-modification technique according to the invention is that it facilitates the commercially viable implementation of microscale roughened surfaces for innovative uses. One innovative use of microscale roughening of the surface of replicated items includes the formation of ultrasonic welding flanges with integrated energy directors. The ultrasonic welding flanges are shaped as regions covered with densely packed polydisperse microscale cone-like projections. As disclosed in a parallel application by the same inventors, when using such micro-textured flanges, ultrasonic welding seams with astonishing precision and surprising bonding strength can be obtained. Another innovative use of a microscale surface roughening on replicated items is the enhancement of wetting properties, such as rendering a surface of a hydrophobic material super-hydrophobic, or enhancing a hydrophilic surface so it becomes super-hydrophilic. As also disclosed in a parallel application by the same inventors, this can be achieved in the same step as the shaping/forming of the replicated item by using a laser modified replication tool.

As mentioned above, the laser treatment of the tool surface results in a porous surface appearance produced by a randomised lateral arrangement of, preferably 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 a replicated item in the step of releasing the item from the tool surface.

Since the method is useful for the production of items by a fast replication process, it allows for a low-cost and/or mass production of the items. 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 formed part 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. However, the method is also useful for the production of items with a microscale surface texturing thereon by other replication techniques, such as the mentioned slower methods using thermosetting or chemically setting replication materials, or for replication techniques like compression moulding and hot embossing.

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 part is defined by the general shape of the tool surface. The replication process is for accurately replicating the general shape of the part as defined by the tool surface. The surface of the replicated part is functionalised by applying a surface finish with a microscale texture at least on selected regions of the surface of the part. For example, the particular functionalization may be to make a flange portion of the replicated part susceptible to concentrate ultrasonic energy so as to act as a distributed energy director when forming an ultrasonic joint with a cooperating flange portion of a counterpart. To concentrate the ultrasonic energy applied across the interface between the first and second flange portions, the area of contact is reduced to point contacts where the tops of the protrusions meet the surface of the counterpart when the first flange portion is brought in contact with the cooperating second flange portion.

An important advantage of the present method is that the laser treatment of the tool surface is only limited by the requirement of an optical access to the surface to be modified. Consequently, a microscale structured master surface may be applied to virtually any surface topology, including very narrow and deep trenches or holes, as long as a laser beam can be guided to the tool surface to be modified. This allows for an improved freedom for designing the parts to be replicated. Furthermore, at the choice of the designer, the microscale protrusions of the replicated item may be distributed over the entire surface of the replicated parts or only to selected regions thereof. Also, the exposed portion may be arbitrarily shaped as seen in the lateral direction, e.g. the exposed portion may easily be adapted to cover larger surfaces. The microscale features may even be arranged on curved and/or oblique surfaces following a more complex general shape of the replicated part, thereby adding to the above-mentioned improved freedom of design.

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 first part, 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 a melt temperature of the replication material, thereby (c) cooling the 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.

A replication process, where the tool surface is maintained at a more or less constant temperature below the melt 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 truthfulness of the replication of the vertical profile of the microscale master structure is uncritical as long as the peak-to-peak amplitude of the vertical profile of the micro-texture on the replica surface is sufficient, and further preferably the lateral pattern is faithfully transferred.

Alternatively, e.g. in a so-called variothermal injection moulding process, the microscale structured master surface is prior to contact with the replication material heated to an injection temperature above the melting temperature of the replication material, but immediately upon injection of the replication material rapidly cooled to a temperature below the melting temperature of the replication material, at which the first part is finally released from the mould.

Further according to some embodiments the replication process is one of injection moulding, hot embossing, compression moulding, and extrusion coating.

Further according to one embodiment of the method, the microscale textured replica surface has a peak-to-peak amplitude of at least 0.1μm, or at least 0.3μm, or at least 0.5μm, or at least 1μm and up to 5μm, or up to 10μm, or even up to 30μm.
Note that the part/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, the replication process used for producing the part 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 part. 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 heated to above the melt transition temperature and in the melt phase injected into the closed mould, which is kept at a temperature between the glass transition temperature and the melt transition 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.

In another particularly advantageous embodiment of the method, the replication process is extrusion coating. Extrusion coating is a process for roll-to-roll processing, i.e. using this embodiment the part 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. A thermoplastic replication material is heated to above the melting temperature and in the melt phase supplied between the substrate web and the cooling roll, which is kept at a temperature below the melting 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 replication tool.

Further according to one embodiment of the method for producing a part with microscale energy directors on flange portions thereof, 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. Typically, an extrusion coating process is even faster with replication times of less than 10 seconds.

In a further aspect, a method for producing a part with microscale energy directors on flange portions thereof comprises preparing a replication tool using the above-mentioned method, and repeatedly performing the method of producing an item with a microscale textured replica surface by a replication process according to any one of the above-mentioned embodiments. Large numbers of items exhibiting enhanced hydrophobicity or super-hydrophobicity may thus be produced cheaply.

According to a further aspect, the invention relates to a part with a microscale textured replica surface produced by replication according to any of the above-mentioned methods.

A further aspect of the invention relates to a replication tool for producing a part with a microscale textured replica surface by replication, the replication tool comprising a tool surface defining a general shape of the part, 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 adapted to generate microscale phase explosions.

Preferably, the vertical master profile has a peak-to-peak amplitude of at least 0.5μm

Preferably, the lateral master pattern has an area density of microscale master features of at least 5000/mm².

The replication tool for the replication process in question, e.g. a mould for injection moulding or a roller for extrusion coating, has a tool surface defining the general shape of the part to be formed and may be provided in a conventional manner and using conventional tooling materials as known in the art, such as tool steel or 2017 aluminium. The microscale surface structuring is applied 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 is 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 localized pulsed laser treatment is adapted to produce a micro-porous structure, wherein the micro-porous structure is formed by a densely packed, randomly distributed arrangement of crater-shaped microscale depressions with outwardly sloped side walls. The obtained microscale structured master surface has a lateral master pattern and a vertical master profile as described above. The occurrence of the microscale phase explosions on the surface under the laser processing according to the invention is stochastic (random and uncorrelated) and may be described by a Poisson process. The microscale crater-shaped depressions resulting from that process are randomly distributed over the processed surface. By randomly distributed it is understood that the lateral location of the of the microscale features as they occur in the lateral master pattern on the tool surface is a random (and accordingly the replicated microscale features produced from that master), wherein the occurrence of observed spacing between adjacent microscale features follows a distribution function that is exponentially decaying for increasing distances. 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).

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 produced on a mould surface for contacting the replication material and/or on an inlay 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 a given crater-shaped depression may then be defined as the diameter of a circle with the same area. 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 some embodiments 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 5000/mm², at least 8000/mm², or at least 10000/mm². Thereby, the replication tool is particularly useful for producing parts comprising a microscale textured surface with a reasonably densely packed lateral distribution of microscale features.

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.19. 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.19 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.19, 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.19, 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. 2a-c	SEM micrographs of a microscale textured replica surface at different magnifications,
FIG. 3	a SEM micrograph of another microscale structured master surface,
FIG. 4	a SEM micrograph of the microscale textured surface of an injection moulded item (polypropylene) using an isotherm process,
FIG. 5	a SEM micrograph of the microscale textured surface of an injection moulded item (polypropylene) using a variotherm process,
FIG. 6	schematically, the surface modification of a tool surface by pulsed laser treatment to generate microscale phase explosions,
FIG. 7	schematically, an injection moulding process according to one embodiment of the invention,
FIG. 8	schematically, an extrusion coating process according to a further embodiment of the invention,

FIG. 9	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;
FIG. 10	a graph analysing the random distribution of microscale features over the exposed region for an ensemble of 76 samples;
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, and in
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. 19a-d	SEM micrographs of (a) cone like protrusions in an al2017 mould at a 30° view angle, (b) cone like protrusions in an al2017 mould at a 0° view angle, (c) replication of the al2017 mould in cyclic olefin copolymer, and (d) an orvar2343 steel surface modified using the presented technology as seen at an 0° view angle;
Figs. 20a-d	SEM micrographs of (a), (c) a laser modified mould on indicated length scales, (b), (d) the corresponding injection moulded piece seen at 30° tilt,

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

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 that 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.

Fig. 3 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

Figs. 2a-c show an example of a microscale textured replica surface on a mould insert for injection moulding, as observed in a scanning electron microscope at different magnifications, wherein the width of the image corresponds to 1.2mm in Fig.2a, 0.23mm in Fig.2b, and 0.03mm in Fig.2c. The mould insert for injection moulding was designed and fabricated in 2017 aluminium alloy (MetalCentret, Denmark) by micro milling using conventional techniques to provide a tool surface defining the general shape of the part to be fabricated. To create the microscale structured master surface on the tool surface, a 1064nm, 200kHz, 50W (max power) picosecond laser (FUEGO, Time Bandwidth) mounted in a microSTRUCT vario (3D-Micromac AG) was used to generate microscale phase explosions on the tool surface, thereby producing a densely packed lateral arrangement of microscale crater-shaped depressions. The area intended for structuring was irradiated by the laser in parallel lines separated by 20 µm. In the example shown in Figs.2a-c, this pattern was repeated 20 times, and the laser power was set to 25% of the max power. Focus was offset by +1.3 mm above the surface. The microscale structured master surface produced in this example consisted of 10 lines (200 µm wide) and was 305.5 mm long. The part with the microscale textured replica surface thereon was replicated from this replication tool with the microscale structured master surface on its tool surface using a Victory 80/45 Tech injection moulder (Engel, Schwertberg, Austria). The polymer substrate used for injection moulding was cyclic olefin copolymer (COC) TOPAS grade 5013L-10 (TOPAS Advanced Polymers, Düsseldorf, Germany) with a glass transition temperature (Tg) of 135 C. Injection temperature of the polymer was 270 C and the mould temperature was kept stable at 120 C. The injection moulding was performed in isothermal mode. The resulting microscale surface texturing is depicted in Figs.2a-c. The microscale textured replica surface on this first part is adapted to act as microscale energy directors for forming an ultrasonic welding joint with a cooperating second part.

Further examples for the microscale textured replica surface on replicated parts are given in Figs.4 and 5. To produce these replica surfaces, 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.5. 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”), see Fig.5. 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 parts with microscale energy directors on flange portions thereof. The isothermal process is preferable for high throughput 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.

Replication Process

Fig.7 shows schematically an injection moulding process for producing a replicated part 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, 3d, which are replicated on the item 4 as microscale textures 5a, 5b, 5c, 5d respectively.

Fig. 8 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.6 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.

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.

Microscale Crater-Shaped Depressions

EXAMPLE

Referring to Figs.19-20 in the following, an example is given for forming crater-shaped depressions in mould materials, and their subsequent replication.

Figures 19a and 19b show scanning electron microscopy (SEM) images of the microscale crater-shaped depressions written in an al2017 mould. It is noteworthy that although the laser scanning is conducted in bundles of parallel lines, the formed crater-shaped depressions are stochastically formed within the laser ablated area without any apparent traces of the propagation path or any indications for stitching effects. This may be ascribed to the fact that the microphase explosions causing the crater-shaped depressions are caused by a combination of metal impurities (alloy) picking up the energy, the pulsing nature of the laser beam and non-uniformity of the laser fluence distribution. The crater-shaped depressions have a typical depth and spacing of 10 µm and 10 µm, respectively. On average, the area with the crater-shaped depressions is about 47 µm lower than the untreated plane of the tool. Note that the crater-shaped depressions are locally convex depressions in the mould that hence facilitate easy demoulding during replication. Fig. 19c shows a SEM image of a COC replica of the mould. The replicated structures are observed to have rounded tops due to imperfect filling during replication. Operating at conditions yielding higher fidelity replication may result in more difficult demoulding, due to stronger adhesion between the mould and its replica. Fig. 19d shows tool steel Orvar2343 ablated to produce crater-shaped depressions similar to those demonstrated in al2017.

Figures 20a and 20b show SEM images of crater-shaped depressions in the al2017 mould for fabrication of a high-aspect ratio microfluidic system. The images clearly show the feasibility of writing crater-shaped depressions structures at the bottom of deep trenches in the mould. Note that the separation and joining of bundles of laser lines do not alter the pattern and formation of crater-shaped depressions. Thus, crater-shaped depressions can be formed in any pattern or geometry. Corresponding SEM images of the injection moulded COC replica (Figs. 20c, 20d) clearly show that micropillar structures (cone-like projections) are well reproduced on the top of the high-aspect ratio wall.

The laser processing method has further been demonstrated to work in high endurance tool steel used for making high performance injection moulding tools. Furthermore, the method of the invention supports a modification rate of 200 seconds/cm^2 and post processing capabilities on full three-dimensional mould surface shapes, as long as these are optically accessible.

A statistical analysis shows that the process for producing microstructures by microscale phase explosions with the method according to the invention is indeed random. The statistical analysis shows that the one-dimensional spacings between holes are exponentially distributed, proving that the process is indeed a Poisson process, i.e. the holes are formed randomly and uncorrelated. The x-axis spacings are found by sorting the x-coordinates of the center of mass of the microstructures by size, and calculating the increment. The y-spacings may be determined in the same manner, and since the sum of two independent identical distributed exponential distributions is also an exponential distribution, we may add the populations of x and y spacings. Plotting the histogram of the spacings reveals that they are indeed exponentially distributed for the samples, proving that the presented process is a random. Fig.10 shows such histogram plot obtained from an ensemble average of 76 samples (Sample average). An average exponential probability distribution (Average exp PDF) and error-bars representing standard deviation of the samples in the ensemble have been added. Individual probability density functions have also been fitted to the histogram data for the individual samples. These are marked in the background (Sample exp PDF).

The exponential probability density function is given as $f(x;\lambda) = \lambda e^{-\lambda x}$ (support is $x \geq 0$). Typical values for the rate parameter, λ, is 0.16±0.04 (with maximum and minimum of 0.22 and 0.06, respectively), which is reasonable, since the expected value of $x = 1/\lambda = 6.774 \pm 2.36$µm (with maximum and minimum of 15.57 µm and 4.475 µm, respectively).

CLAIMS

1. Method of providing a replication tool, the method comprising

   - providing a forming tool having a tool surface adapted to define a general shape of a part 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 randomly generate microscale phase explosions on the tool surface, thereby forming the microscale structured master surface as a lateral arrangement of randomly distributed microscale crater-shaped depressions.

2. Method according to claim 1, wherein random generation of the microscale phase explosions is a stochastic Poisson process.

3. Method according to any of the preceding claims, wherein the occurrence of spacings between the randomly distributed microscale crater-shaped depressions projected on one dimension x follows an exponentially decaying distribution function $f = \lambda e^{-\lambda x}$.

4. Method according to any of the preceding claims, wherein the lateral pattern of the microscale structured master surface has an area density of microscale crater-shaped depressions of at least 5000/mm², at least 8000/mm², or at least 10000/mm².

5. Method according to any of the preceding claims, wherein the forming tool is a forming tool adapted for use in a replication process, wherein the replication process is one of injection moulding, hot embossing, compression moulding, and extrusion coating.

6. Replication tool for producing a part with a microscale textured replica surface by replication, the replication tool comprising a tool surface defining a general shape of the part, 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 adapted to randomly generate microscale phase explosions.

7. Replication tool according to claim 6, wherein random generation of the microscale phase explosions is a stochastic Poisson process.

8. Replication tool according to claim 6 or claim 7, wherein the occurrence of spacings between the randomly distributed microscale crater-shaped depressions projected on one dimension x follows an exponentially decaying distribution function $f = \lambda\, e^{-\lambda x}$.

9. Replication tool according to any one of claims 6-8, wherein the replication tool is adapted for use in a replication process, wherein the replication process is one of injection moulding, hot embossing, compression moulding, and extrusion coating.

10. Replication tool according to any one of claims 6-9, wherein the microscale structured master surface is a lateral arrangement of polydisperse microscale master features.

11. Replication tool according to any one of claims 6-10, wherein the microscale master features are crater-shaped depressions.

12. Replication tool according to any one of claims 6-11, wherein the vertical master profile has a peak-to-peak amplitude of at least 0.3μm, or at least 0.5μm, or at least 0.8μm, or at least 1μm, or at least 2μm.

13. Replication tool according to any one of claims 6-12, wherein the vertical master profile has a peak-to-peak amplitude of up to 5µm, or up to 10µm, or up to 20µm, or even up to 30µm.

14. Replication tool according to any one of claims 6-13, wherein the lateral master pattern has an area density of microscale master features of at least 5000/mm², or at least 8000/mm², or at least 10000/mm².

15. Replication tool according to any one of claims 6-14, wherein 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.

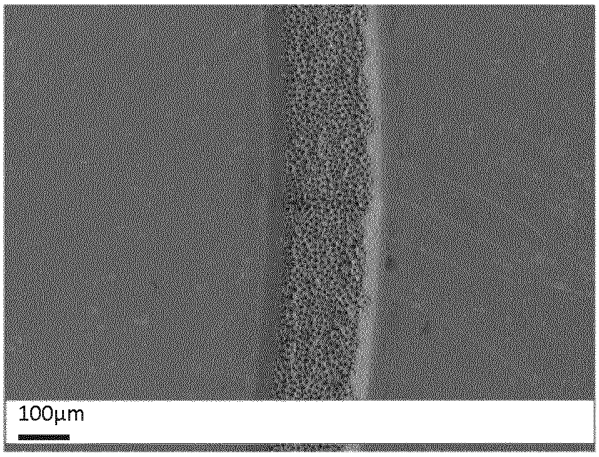


Fig. 1a

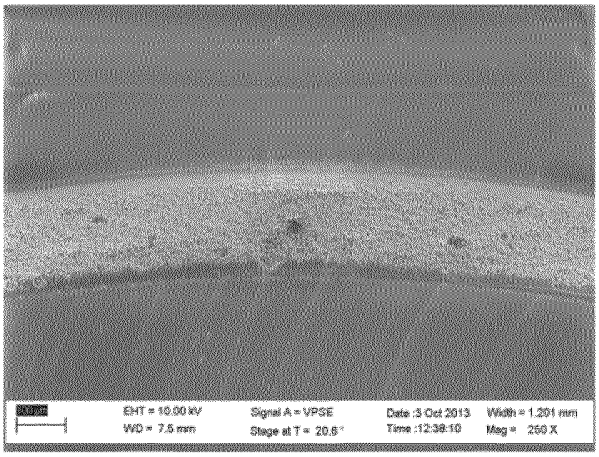


Fig. 2a

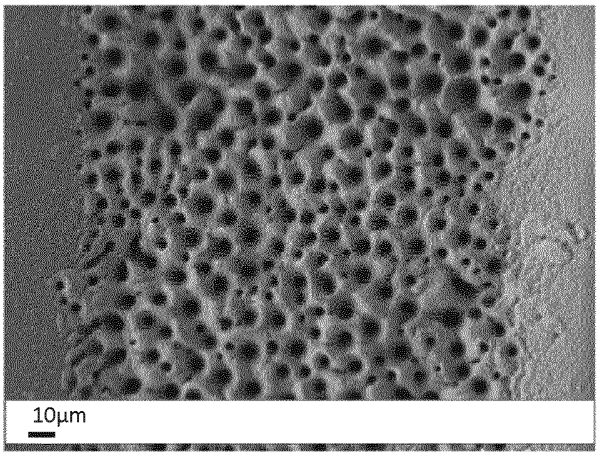


Fig. 1b

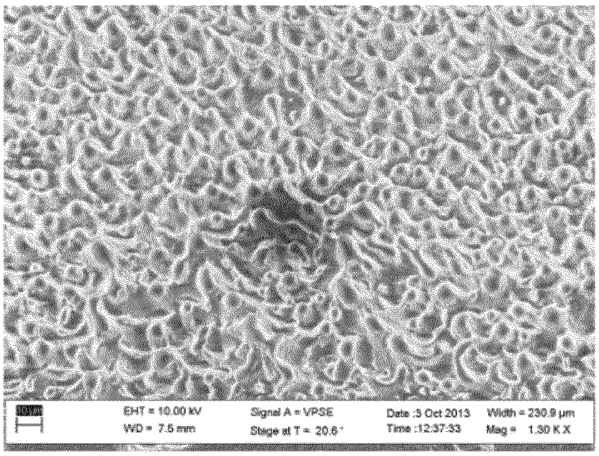


Fig. 2b

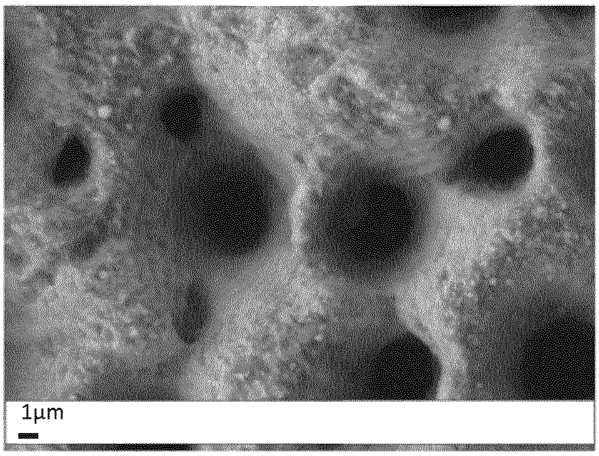


Fig. 1c

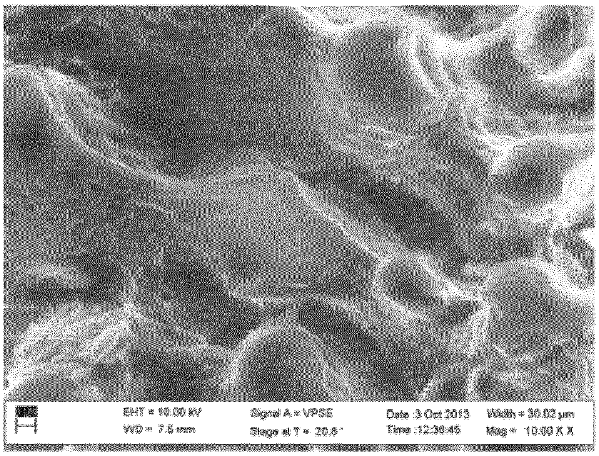


Fig. 2c

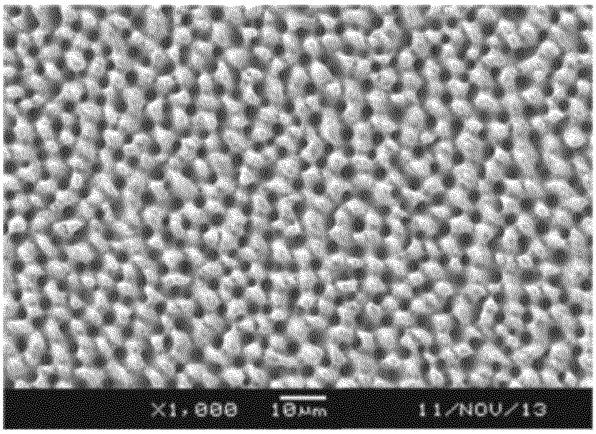


Fig. 3

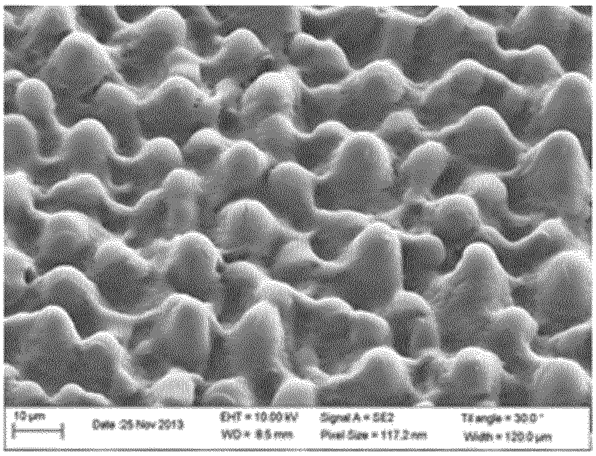


Fig. 4

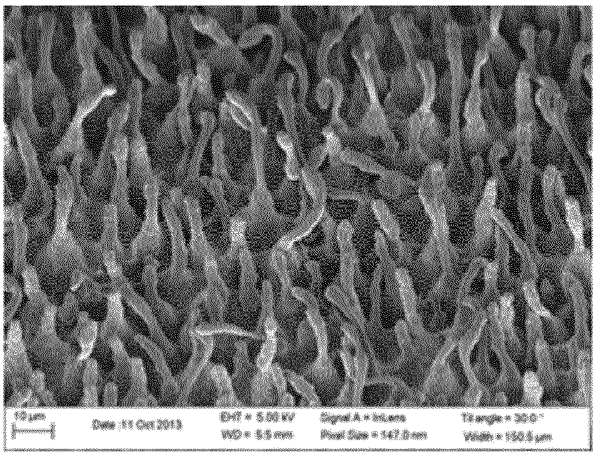


Fig. 5

Fig. 6

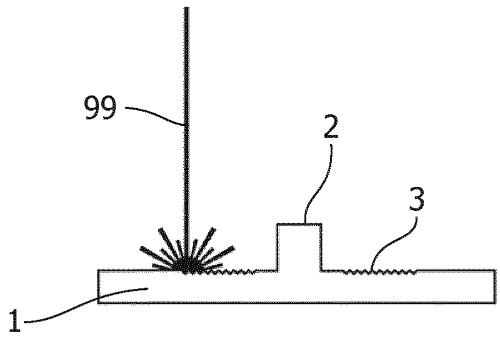


Fig. 7

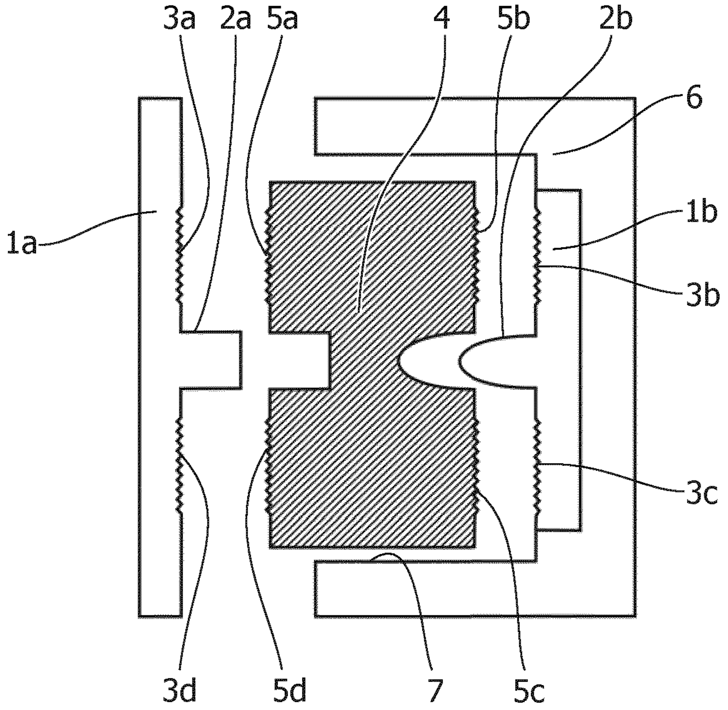
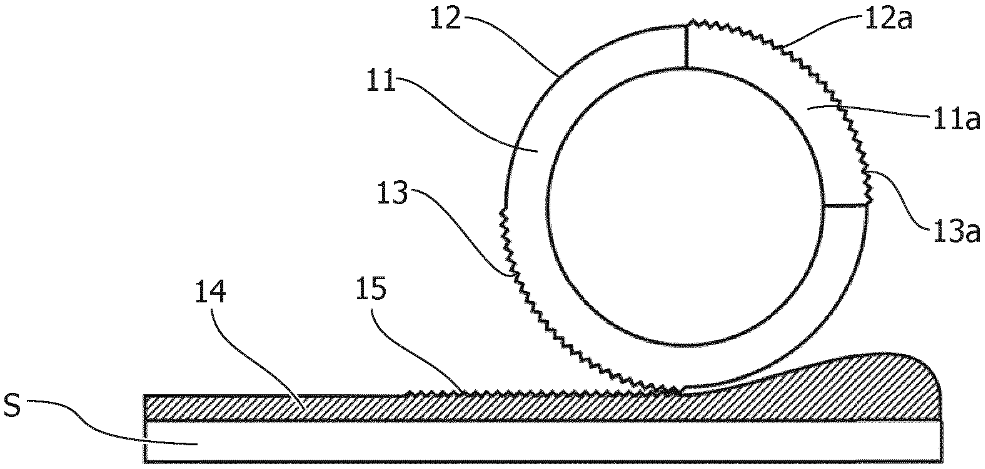
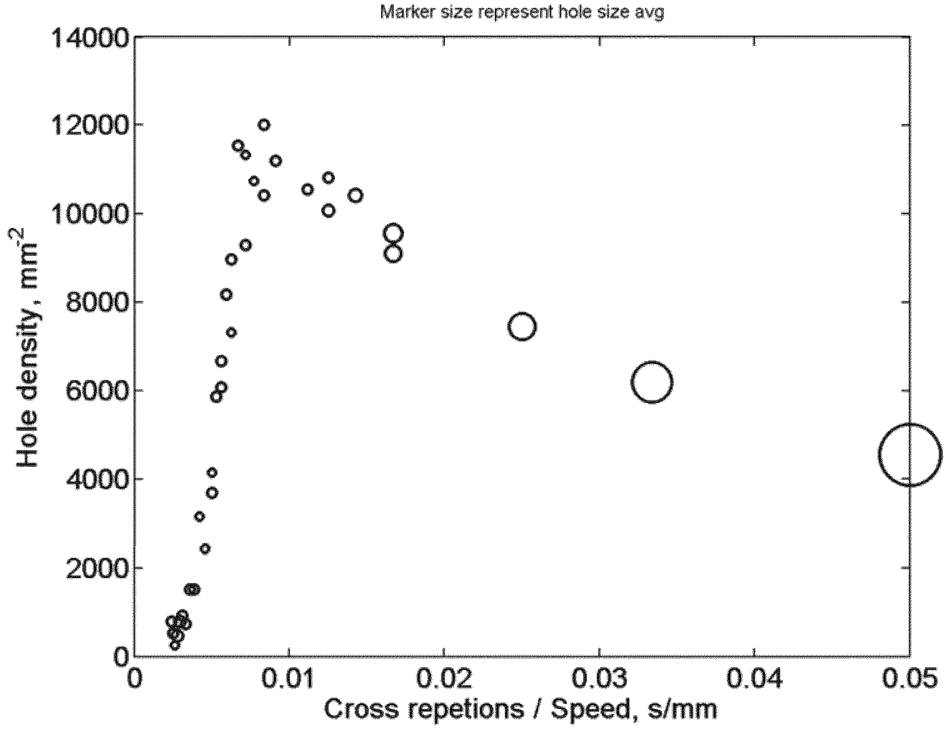


Fig. 8

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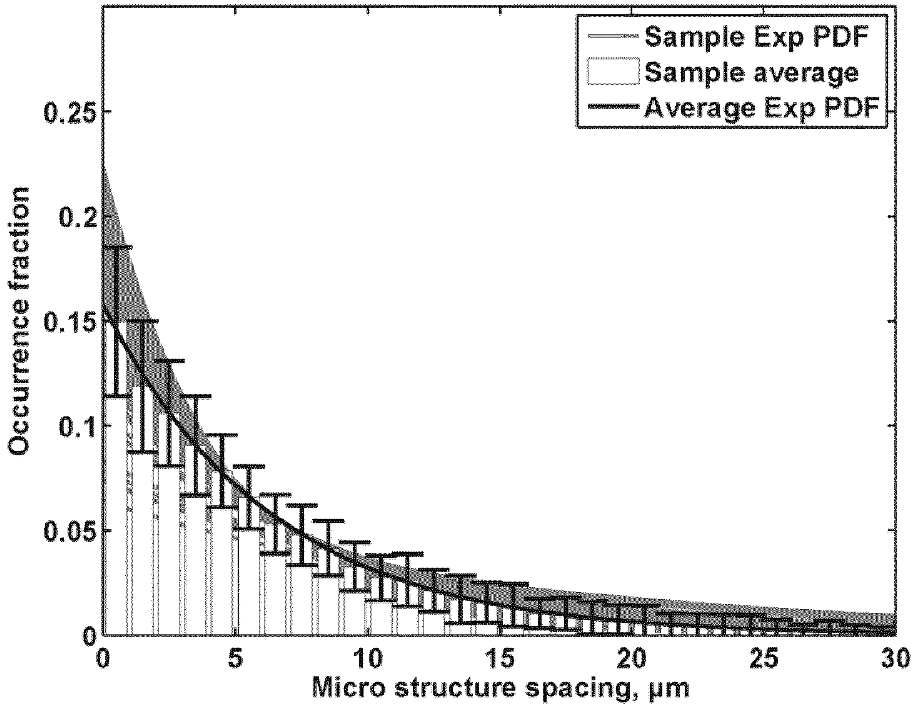
Hole density, mm^{-2}
0
2000
4000
6000
8000
10000
12000
14000
0
0.01
0.02
0.03
0.04
0.05
Cross repetions / Speed, s/mm

Fig. 9


Sample Exp PDF
Sample average
Average Exp PDF
Occurrence fraction
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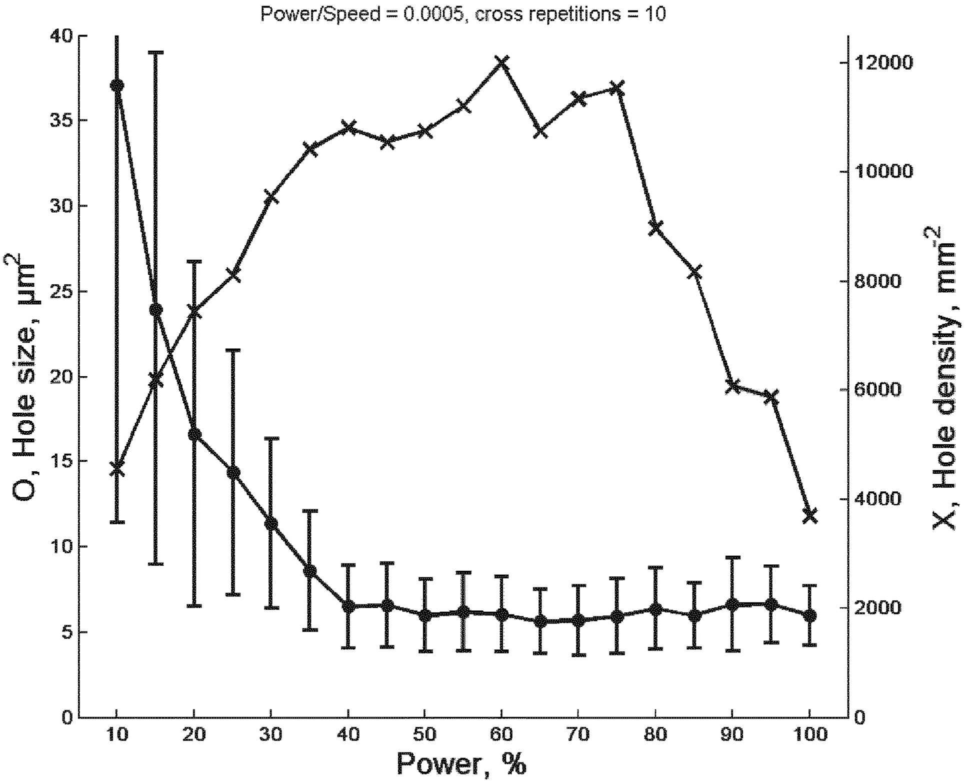
0.2
0.25
0
5
10
15
20
25
30
Micro structure spacing, μm

Fig. 10

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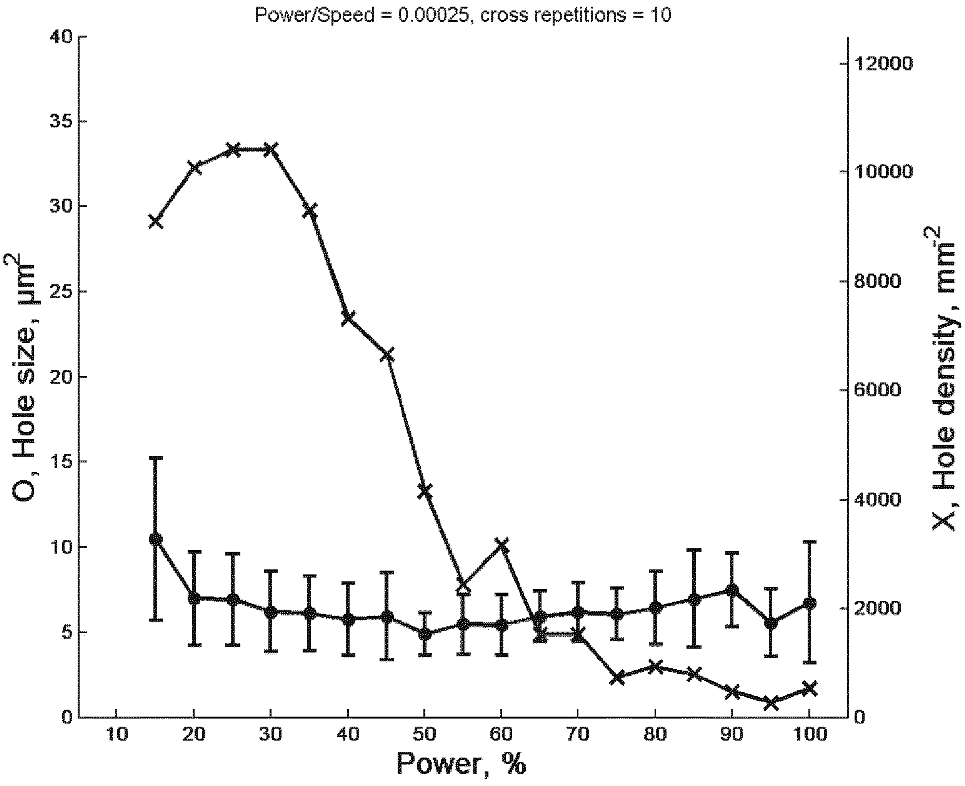
5
10
15
20
25
30
35
40
0
2000
4000
6000
8000
10000
12000
10
20
30
40
50
60
70
80
90
100

Fig. 12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O, Hole size, μm^2
X, Hole density, mm^{-2}
Power, %
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10
15
20
25
30
35
40
0
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4000
6000
8000
10000
12000
10
20
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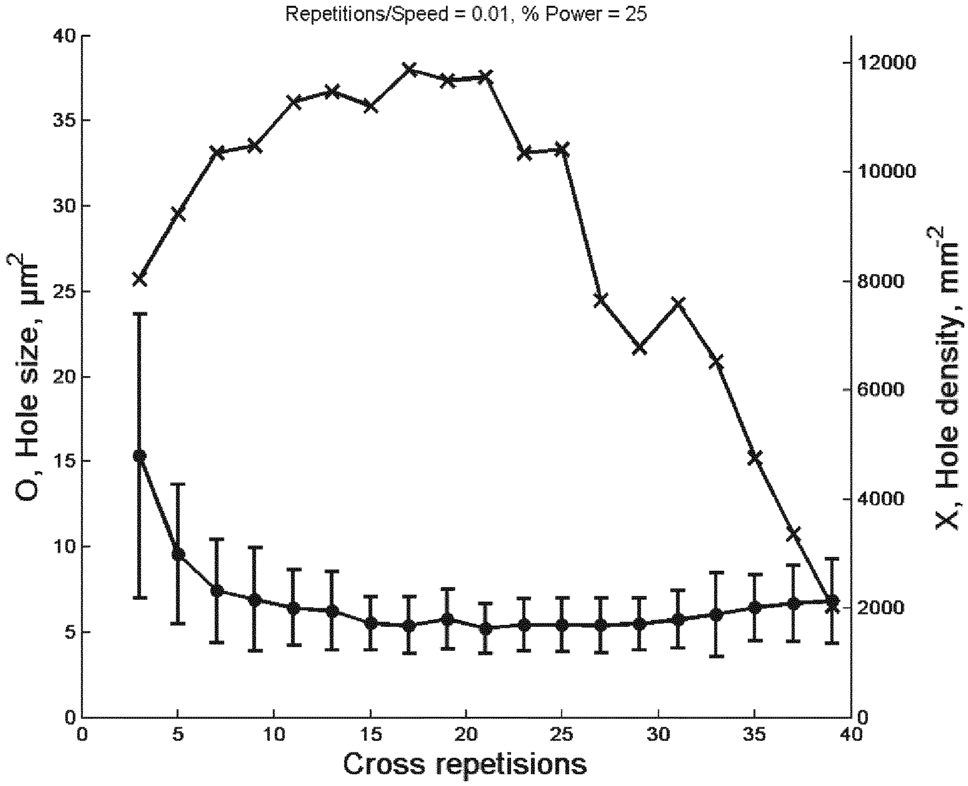
40
50
60
70
80
90
100

Fig. 13


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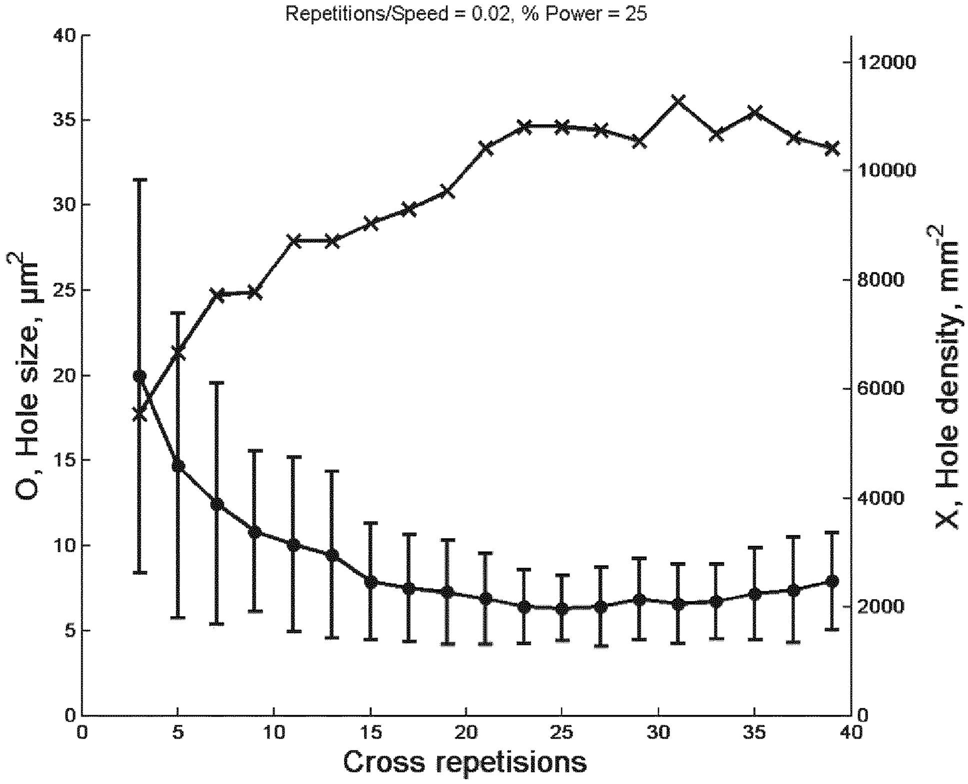
5
10
15
20
25
30
35
40
0
2000
4000
6000
8000
10000
12000

Fig. 14


Repetitions/Speed = 0.02, % Power = 25
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X, Hole density, mm^{-2}
Cross repetisions
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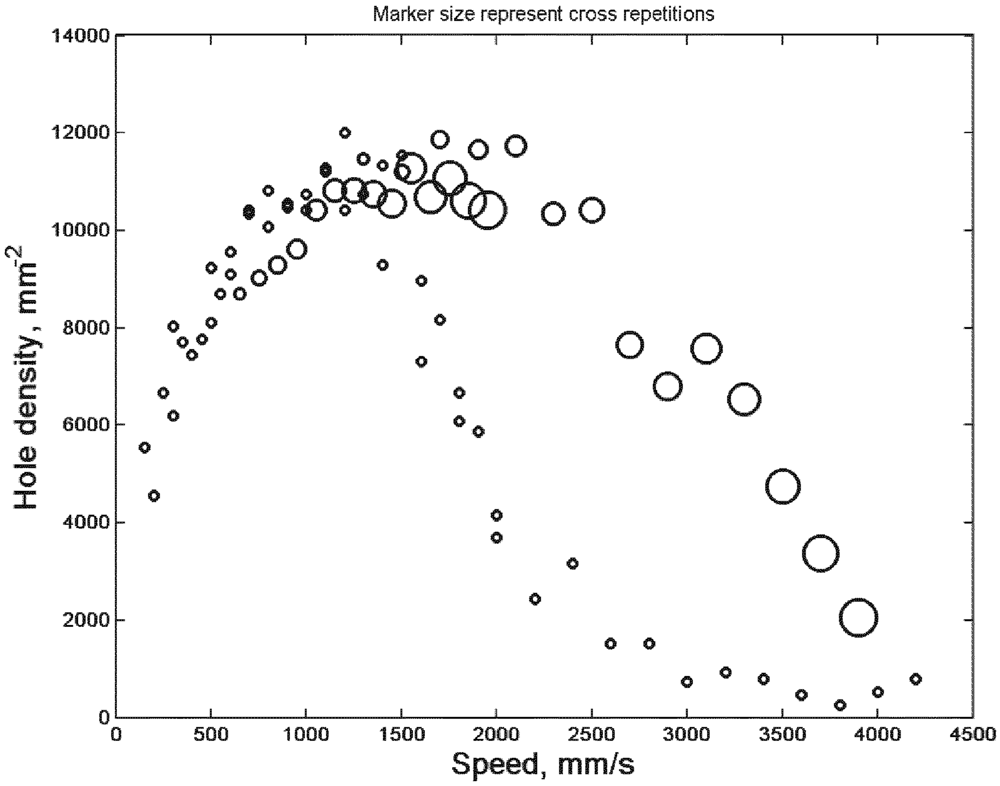
5
10
15
20
25
30
35
40
0
2000
4000
6000
8000
10000
12000

Fig. 15


Marker size represent cross repetitions
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. 16

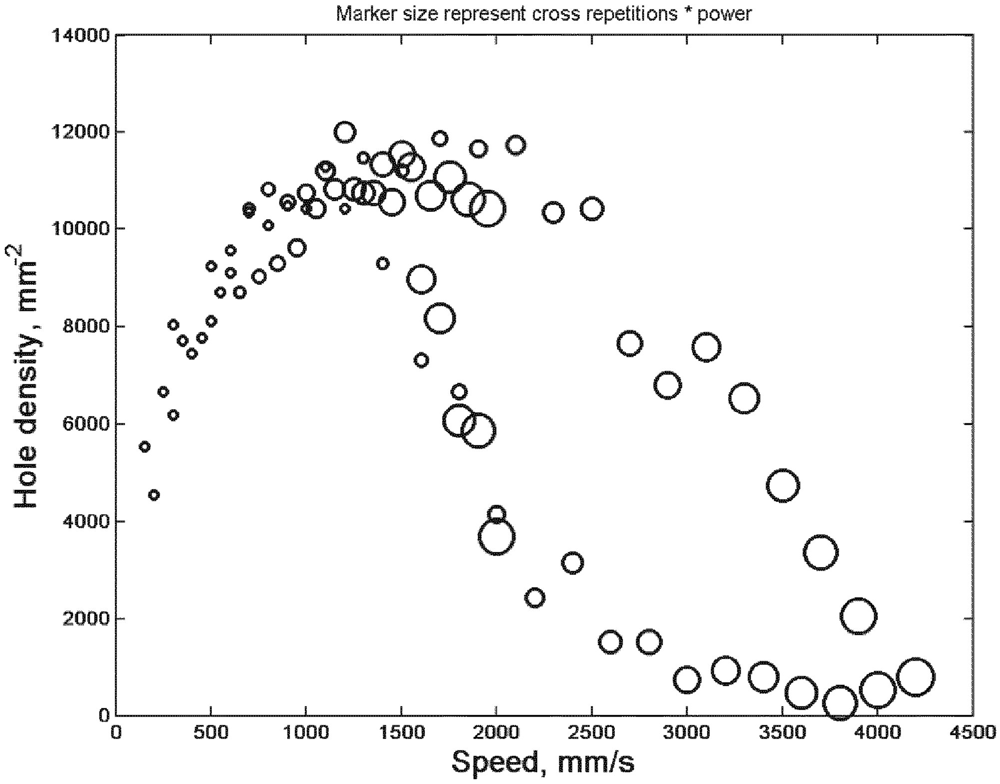

Marker size represent cross repetitions * power
Hole density, mm^{-2}
Speed, mm/s
14000
12000
10000
8000
6000
4000
2000
0
0
500
1000
1500
2000
2500
3000
3500
4000
4500

Fig. 17

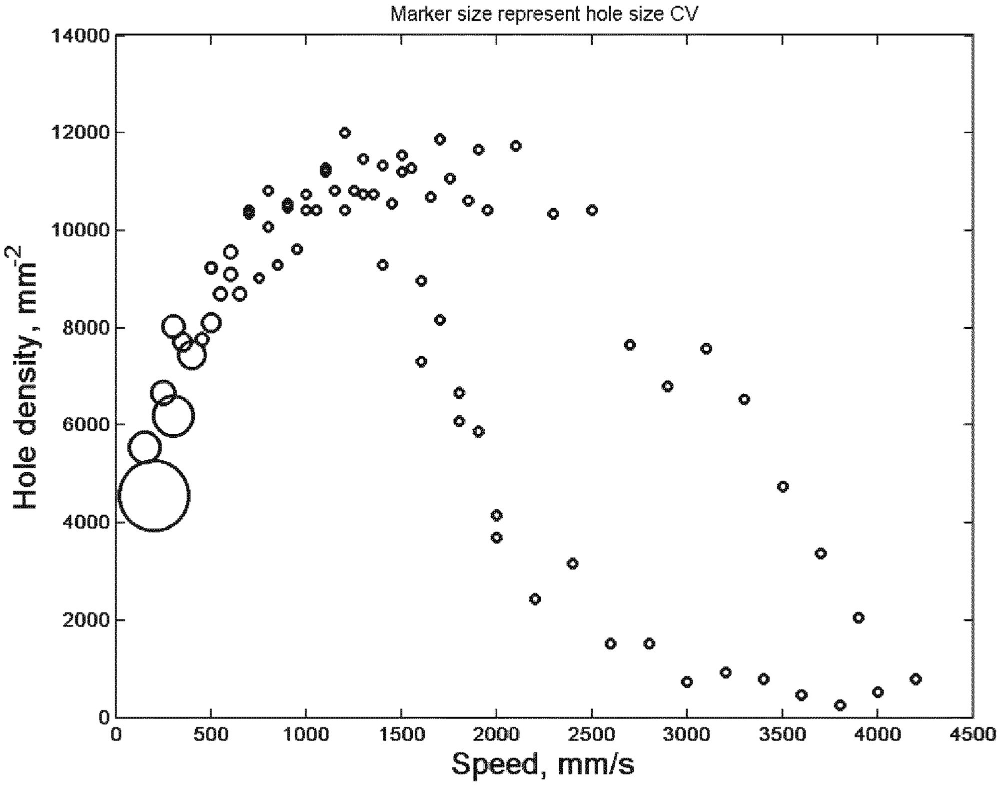
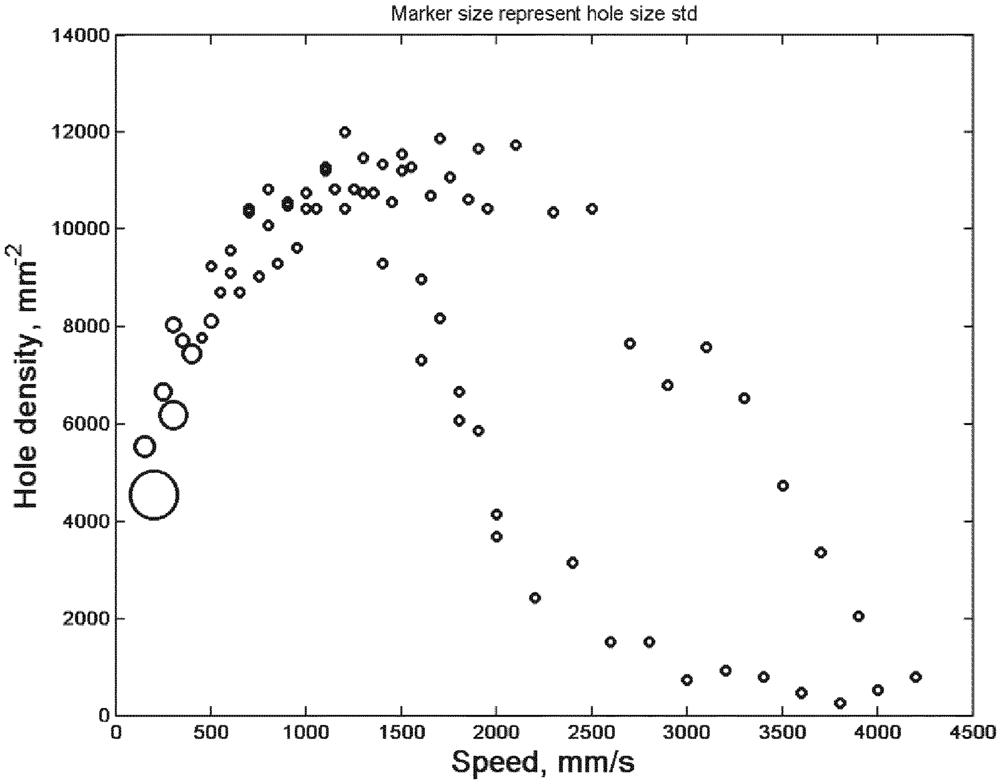

Marker size represent hole size CV
Hole density, mm^{-2}
Speed, mm/s
0
2000
4000
6000
8000
10000
12000
14000
0
500
1000
1500
2000
2500
3000
3500
4000
4500

Fig. 18


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

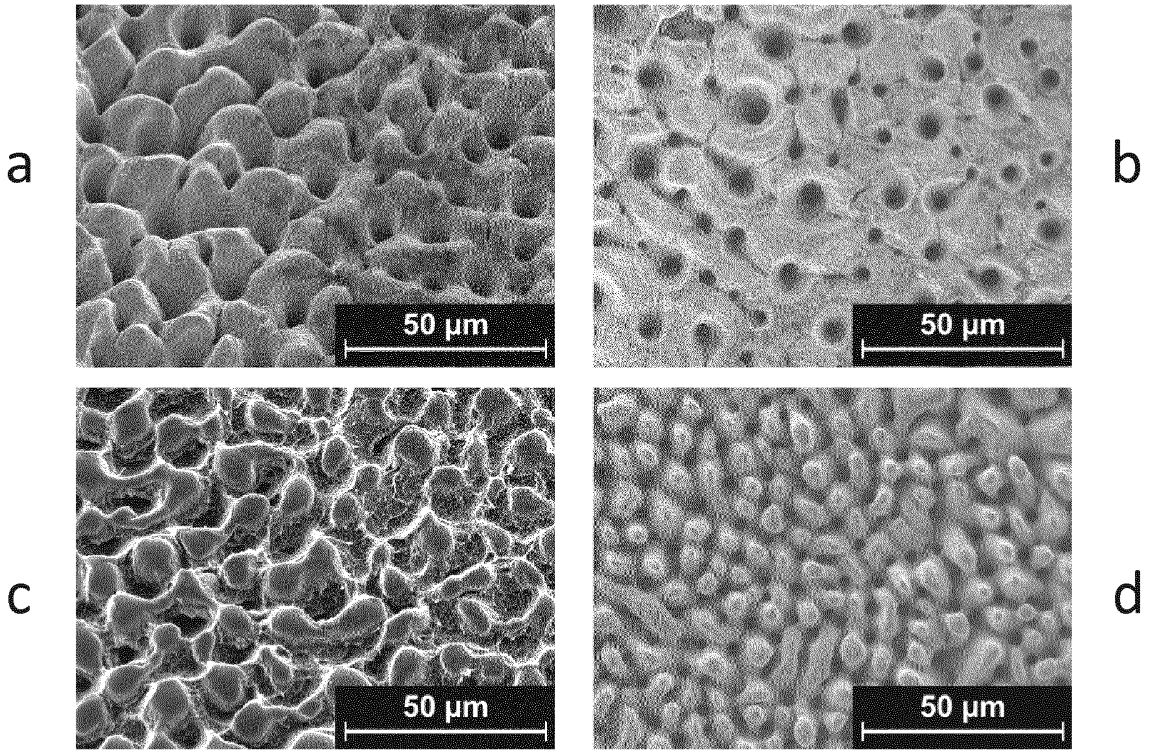


Fig. 19

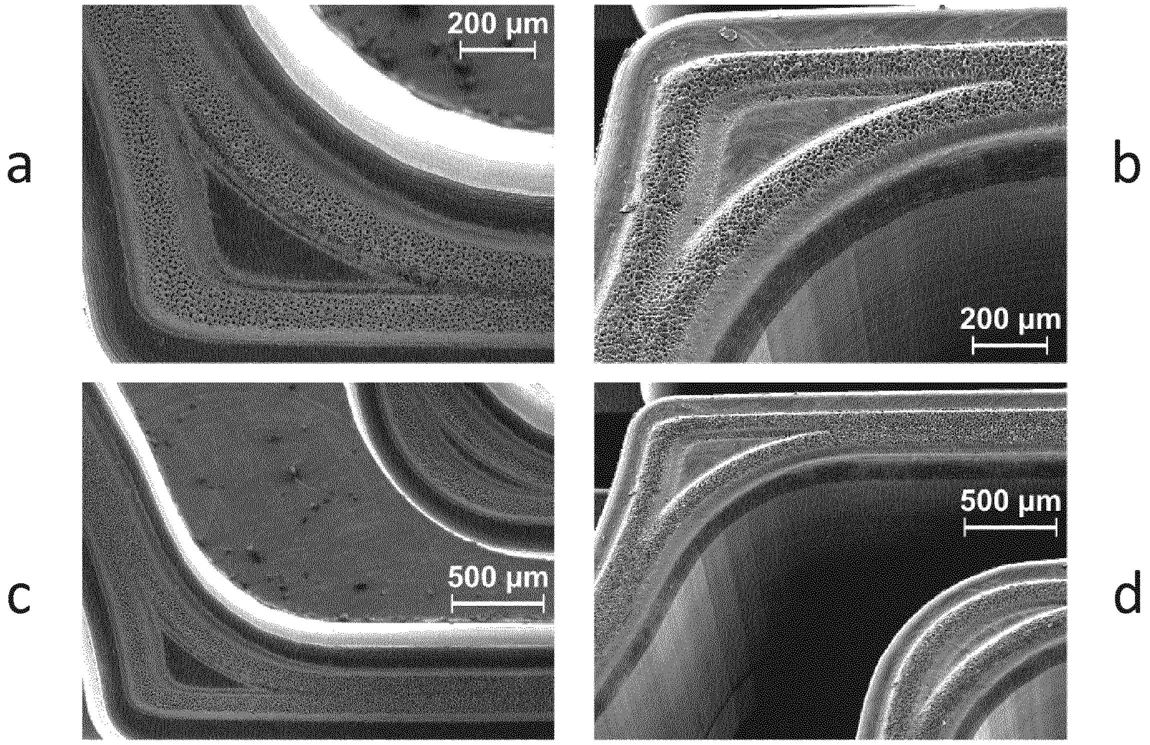


Fig. 20

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/076525

A. CLASSIFICATION OF SUBJECT MATTER
INV. B23K26/00 B29C33/42 B29C37/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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 2014/205801 A1 (IWATA RYOSUKE [JP] ET AL) 24 July 2014 (2014-07-24) paragraph [0001] paragraph [0094] - paragraph [0103] paragraph [0220] - paragraph [0243] paragraph [0260] - paragraph [0274] figures 3A-8,17A-20B -----	1-15
Y	US 2012/227879 A1 (MUHLHOFF OLIVIER [FR] ET AL) 13 September 2012 (2012-09-13) paragraph [0001] paragraph [0015] - paragraph [0019] paragraph [0042] paragraph [0045] - paragraph [0050] paragraph [0054] - paragraph [0061] figures 4-9 ----- -/--	1-15

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search 12 February 2016	Date of mailing of the international search report 23/02/2016
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Fageot, Philippe

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/076525

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 2011/287203 A1 (VICTOR JARED J [CA] ET AL) 24 November 2011 (2011-11-24) paragraph [0001] - paragraph [0003] paragraph [0043] - paragraph [0045] paragraph [0073] paragraph [0081] - paragraph [0083] paragraph [0085] paragraph [0097] paragraph [0124] - paragraph [0127] figures claim 14 -----	1-15

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2015/076525

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