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(54) Title: COATING ON A METAL SUBSTRATE AND A COATED METAL PRODUCT

(57) Abstract: The invention relates in general level to a method for coating metal products comprising large surface areas. The invention also relates to coat metal products manufactured by the method. The coating is carried out by employing ultra short pulsed laser deposition wherein pulsed laser beam is scanned with a rotating optical scanner comprising at least one mirror for reflecting said laser beam. The invention has several both industrially and qualitatively advantageous effects such as high coating production rate, excellent coating properties and overall low manufacturing costs.



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Coating on a metal substrate and a coated metal product

Field of invention

The invention relates generally to a method for coating metal products comprising large surface areas by ultra short pulsed laser ablation. The invention also relates to products manufactured by the method. The invention has many advantageous effects such as high coating production rate, excellent coating properties and low manufacturing costs.

Background

Metal products

Ever since bronze-age, the metals and different products derived thereof have played very significant role for mankind. Even though metals possess excellent wear, chemical and physical properties, there are still many problems associated with said products. Part of those have been solved by developing the physical and chemical properties of the metal product by altering the metal material construction (alloys and composites), attempts to solve the problems associated with surface properties being not so successful.

Taking the ferrous products into account, original iron has been derived to steel, carbon steel, alloy steel, stainless steel, heat-resistant steel, tool steel and for example cast iron.

The problems with metal product surfaces deal especially with their corrosion resistance, their wear- and tribological properties, heat-resistance, but also with properties associated the use of various metal products both in construction and interior/exterior use. Typically, metal products are designed for extremely long use, and their technical, mechanical and visual properties should preferably accomplish life-times exceeding decades.

Due to continuously increasing use of metal products not only in visible construction but direct interior use, special emphasis is also put on their cleaning properties.

Metal products comprise typically large surface areas, thin sheets for example for construction and interior products being produced for example in sizes like 1200 mm x 1500 mm, being then delivered to customer as plain or rolled sheets. To protect the product and increase the life-time, the problems have typically been addressed by simple coating by painting or in some cases, by electrolytic coating. For example aluminum products are typically subjected to eloxation, i.e. electrolytic oxidation by either oxalic acid or nowadays – sulfuric acid. Copper and many other metal products such as bras are oxidized due to their chemical nature, the interior effect being the desired one. Being environmentally hazardous, the leakage of copper and several other metal oxides or other derivatives is not desirable, and the problem should be solved by another protective coating simultaneously saving the interior effect of said product.

Nowadays, there is also increasing demand for products comprising the metallic look, i.e. the oxidation of the metal product surface should be prevented without loosing the original metallic decorative effect, especially on copper, bras and stainless steel. Thus, the protection

In visible construction and interior use, the cleaning problems have been recently addressed by means of nanotechnology. Nano-scale titan dioxide particles being activated by UV-radiation possess self-cleaning properties by degrading the organic material in a UV-catalytic reaction together with water. Due to simultaneous cleaning effect and transparency, said technology is commonly applied on glass, especially on windows and to somewhat on concrete products. Due to their poor adhesion on metal, the technology is not commonly applied on metal products. Furthermore, particle distribution can not create uniform layers of self-cleaning surfaces.

As it is difficult to coat for example chemical reactors and tubes as well as all the metallic products that are in contact with corrosive chemicals or are otherwise subjected to hazardous or wearing environments, those components must typically be manufactured from expensive special metals such as titan and its different alloys.

There have been several approaches to tackle some of the present problems associated with coating of metal products, the most recent and technically advanced methods comprising both CVD (Chemical Vapor Deposition) and PLD (Physical Vapor Deposition). One of the most recent coating/thin-film producing methods is laser assisted ablation and therein, especially cold ablation, the techniques being

available only for coating very small surfaces in high vacuums, long coating times and batch-wise coating set-ups.

Laser-ablation

In the recent years, considerable development of the laser technology has provided means to produce very high-efficiency laser systems that are based on semiconductor fibres, thus supporting advance in so called cold ablation methods.

At the priority date of the current application, solely fibrous diode-pumped semiconductor laser is competing with light-bulb pumped one, which both have the feature according to which the laser beam is lead first into a fibre, and then forwarded to the working target. These fibrous laser systems are the only ones to be applied in to the laser ablation applications in an industrial scale.

The recent fibres of the fibre lasers, as well as the consequent low radiation power seem to limit the materials to be used in the vaporization/ablation as the vaporization/ablation targets. Vaporizing/ablating aluminium can be facilitated by a small-pulsed power, whereas the more difficult substances to be vaporized/ablated as Copper, Tungsten, etc. need more pulsed power. The same applies into situation in which new compounds were in the interest to be brought up with the same conventional techniques. Examples to be mentioned are for instance manufacturing diamond directly from carbon (graphite) or alumina production straight from aluminium and oxygen via the appropriate reaction in the vapour-phase in post-laser-ablation conditions.

On one hand, one of the most significant obstacles to the forwarding progress of fibre-laser technology seems to be the fibre capability of the fibre to tolerate the high power laser pulses without break-up of the fibre or without diminished quality of the laser beam.

When employing novel cold-ablation, both qualitative and production rate related problems associated with coating, thin film production as well as cutting/grooving/carving etc. has been approached by focusing on increasing laser power and reducing the spot size of the laser beam on the target. However, most of the power increase was consumed to noise. The qualitative and production rate related problems were still remaining although some laser manufacturers resolved the laser power related problem. Representative samples for both coating/thin film

as well as cutting/grooving/carving etc. could be produced only with low repetition rates, narrow scanning widths and with long working time beyond industrial feasibility as such, highlighted especially for large bodies.

If the energy content of a pulse is kept constant, the power of the pulse increases in the decrease of the pulse duration, the problem with significance increases with the decreasing laser-pulse duration. The problems are significant even with the nano-second-pulse lasers, although they are not applied as such in cold ablation methods.

The pulse duration decrease further to femto or even to atto-second scale makes the problem almost irresolvable. For example, in a pico-second laser system with a pulse duration of 10-15 ps the pulse energy should be 5 μ J for a 10-30 μ m spot, when the total power of the laser is 100 W and the repetition rate 20 MHz. Such a fibre to tolerate such a pulse is not available at the priority date of the current application according to the knowledge of the writer at the very date.

The production rate is directly proportional to the repetition rate or repetition frequency. On one hand the known mirror-film scanners (galvano-scanners or back and forth wobbling type of scanners), which do their duty cycle in way characterized by their back and forth movement, the stopping of the mirror at the both ends of the duty cycle is somewhat problematic as well as the accelerating and decelerating related to the turning point and the related momentary stop, which all limit the utilizability of the mirror as scanner, but especially also to the scanning width. If the production rate were tried to be scaled up, by increasing the repetition rate, the acceleration and deceleration cause either a narrow scanning range, or uneven distribution of the radiation and thus the plasma at the target when radiation hit the target via accelerating and/or decelerating mirror.

If trying to increase the coating/thin film production rate by simply increasing the pulse repetition rate, the present above mentioned known scanners direct the pulses to overlapping spot of the target area already at the low pulse repetition rates in kHz-range, in an uncontrolled way. At worst, such an approach results in release of particles from the target material, instead of plasma but at least in particle formation into plasma. Once several successive laser pulses are directed into the same location of target surface, the cumulative effect seems to erode the target material unevenly and can lead to heating of the target material, the advantages of cold ablation being thus lost.

The same problems apply to nano-second range lasers, the problem being naturally even more severe because of the long lasting pulse with high energy. Here, the target material heating occurs always, the target material temperature being elevated to approximately 5000 K. Thus, even one single nano-second range pulse erodes the target material drastically, with aforesaid problems.

In the known techniques, the target may not only wear out unevenly but may also fragment easily and degrade the plasma quality. Thus, the surface to be coated with such plasma also suffers the detrimental effects of the plasma. The surface may comprise fragments, plasma may be not evenly distributed to form such a coating etc. which are problematic in accuracy demanding application, but may be not problematic, with paint or pigment for instance, provided that the defects keep below the detection limit of the very application.

The present methods wear out the target in a single use so that same target is not available for a further use from the same surface again. The problem has been tackled by utilising only a virgin surface of the target, by moving target material and/or the beam spot accordingly.

In machining or work-related applications the left-overs or the debris comprising some fragments also can make the cut-line uneven and thus inappropriate, as the case could for instance in flow-control drillings. Also the surface could be formed to have a random bumpy appearance caused by the released fragments, which may be not appropriate in certain semiconductor manufacturing, for instance.

In addition, the mirror-film scanners moving back and forth generate inertial forces that load the structure itself, but also to the bearings to which the mirror is attached and/or which cause the mirror movement. Such inertia little by little may loosen the attachment of the mirror, especially if such mirror were working nearly at the extreme range of the possible operational settings, and may lead to roaming of the settings in long time scale, which may be seen from uneven repeatability of the product quality. Because of the stoppings, as well as the direction and the related velocity changes of the movement, such a mirror-film scanner has a very limited scanning width so to be used for ablation and plasma production. The effective duty cycle is relatively short compared the whole cycle, although the operation is anyway quite slow. In the point of view of increasing the productivity of a system utilising mirror-film scanners, the plasma production rate is in prerequisite slow, scanning width narrow, operation unstable for long time period scales, but yield

also a very high probability to get involved with unwanted particle emission in to the plasma, and consequently to the products that are involved with the plasma via the machinery and/or coating.

Summary of the invention

The maintenance cost for metal products is huge and steadily increasing and there is a great need for coating technologies for especially metal products comprising large surface areas. The product lifetime should be increased and the maintenance costs should be lowered, sustainable development being a prerequisite. The coating and especially uniform coating of large metal surfaces with one or several of the following properties: excellent optical properties, chemical and/or wear resistance, thermal resistance, coating adhesion, self-cleaning properties and possibly, tribological properties has remained an unsolved problem.

Neither recent high-technological coating methods, nor present coating techniques related to laser ablation either in nanosecond or cold ablation range (pico-, femto-second lasers) can provide any feasible method for industrial scale coating of metal products comprising larger surfaces. The present CVD- and PVD-coating technologies require high-vacuum conditions making the coating process batch wise, thus non-feasible for industrial scale coating of most of the present metal products. Moreover, the distance between the metal material to be coated and the coating material to be ablated is long, typically over 50 cm, making the coating chambers large and vacuum pumping periods time- and energy-consuming. Such high-volume vacuumed chambers are also easily contaminated with coating materials in the coating process itself, requiring continuous and time-consuming cleaning processes.

While trying to increase the coating production rate in present laser-assisted coating methods, various defects such as pinholes, increased surface roughness, decreased or disappearing optical properties, particulates on coating surface, particulates in surface structure affecting corrosion pathways, decreased surface uniformity, decreased adhesion, unsatisfactory surface thickness and tribological properties etc. take place.

The present coating methods also drastically restrict the materials employable for coating purposes in general and thus, limit the scope of different coated metal

products available on market today. If applicable, the target material surface is eroded in a manner that only the outmost layer of the target material can be employed for coating purposes. The rest of the material is either wasted or must be subjected to reprocessing before reuse. An aim of the current invention is to solve or at least to mitigate the problems of the known techniques.

A first object of this invention is to provide a new method how to solve a problem to coat a certain surface of a metal product by pulsed laser deposition that so that the uniform surface area to be coated comprises at least 0.2 dm^2 .

A second object of this invention is to provide new metal products being coated by pulsed laser deposition so that the coated uniform surface area comprises at least 0.2 dm^2 .

A third object of this invention is to provide at least a new method and/or related means to solve a problem how to provide available such fine plasma practically from any target to be used in coating of metal products, so that the target material do not form into the plasma any particulate fragments either at all, i.e. the plasma is pure plasma, or the fragments, if exist, are rare and at least smaller in size than the ablation depth to which the plasma is generated by ablation from said target.

A fourth object of the invention is to provide at least a new method and/or related means to solve how to coat the uniform surface area of a metal product with the fine plasma without particulate fragments larger in size than the ablation depth to which the plasma is generated by ablation from said target, i.e. to coat substrates with pure plasma originating to practically any material.

A fifth object of this invention is to provide a good adhesion of the coating to the uniform surface area of a metal product by said pure plasma, so that wasting the kinetic energy to particulate fragments is suppressed by limiting the existence of the particulate fragments or their size smaller than said ablation depth. Simultaneously, the particulate fragments because of their lacking existence in significant manner, they do not form cool surfaces that could influence on the homogeneity of the plasma plume via nucleation and condensation related phenomena.

A sixth object of the invention is to provide at least a new method and/or related means to solve a problem how to provide a broad scanning width simultaneously

with fine plasma quality and broad coating width even for large metal bodies in industrial manner.

A seventh object of the invention is to provide at least a new method and/or related means to solve a problem how to provide a high repetition rate to be used to provide industrial scale applications in accordance with the objects of the invention mentioned above.

An eighth object of the invention is to provide at least a new method and/or related means to solve a problem how to provide fine plasma for coating of uniform metal surfaces to manufacture products according to the first to seven objects, but still save target material to be used in the coating phases producing same quality coatings/thin films where needed.

A further object of the invention is to use such method and means according previous objects to solve a problem how to cold-work and/or coat surfaces for coated products.

The present invention is based on the surprising discovery that metal products comprising large surfaces can be coated with industrial production rates and excellent qualities regarding one or more of technical features such as optical transparency, chemical and/or wear resistance, scratch-free –properties, thermal resistance and/or conductivity, coating adhesion, self-cleaning properties and possibly, tribological properties, particulate-free coatings, pinhole-free coatings and electronic conductivity by employing ultra short pulsed laser deposition in a manner wherein pulsed laser beam is scanned with a rotating optical scanner comprising at least one mirror for reflecting said laser beam. Moreover, the present method accomplishes the economical use of target materials, because they are ablated in a manner accomplishing the reuse of already subjected material with retained high coating results. The present invention further accomplishes the coating of metal products in low vacuum conditions with simultaneously high coating properties. Moreover, the required coating chamber volumes are dramatically smaller than in competing methods. Such features decrease dramatically the overall equipment cost and increase the coating production rate. In many preferable cases, the coating equipment can be fitted into production-line in online manner.

The coating deposition rates with 20W USPLD-apparatus are 2 mm³/min. While increasing the laser power to 80 W, the USPLD coating deposition rate is increased

to 8 mm³/min, accordingly. According to the invention, the increase in deposition rate can now be fully employed to high quality coating production.

In this patent application the term “coating” means forming material of any thickness on a substrate. Coating can thus also mean producing thin films with thickness of e.g. < 1 µm.

Various embodiments of the inventions are combinable in suitable part.

When read and understood the invention, the skilled men in the art may know many ways to modify the shown embodiments of the invention, however, without leaving the scope of the invention, which is not limited only to the shown embodiments which are shown as examples of the embodiments of the invention.

Figures

The described and other advantages of the invention will become apparent from the following detailed description and by referring to the drawings where:

Fig 1. illustrates an exemplary galvano -scanner set-up comprising two galvano-scanners employed in state of the art cold ablation coating/thin-film production and in machining and other work-related applications. The number of galvano-scanners directing the laser beam varies but is typically limited to one single galvano-scanner,

Fig 2. illustrates ITO-coating on polycarbonate sheet (~100 mm x 30 mm) produced by employing a prior art vibrating mirror (galvo-scanner), in different ITO thin-film thicknesses (30 nm, 60 nm and 90 nm).

Fig 3. illustrates the situation wherein prior art galvanometric scanner is employed in scanning laser beam resulting in heavy overlapping of pulses with repetition rate of 2 Mhz.

Fig 4. illustrates a copper oxide and ATO coated product according to invention.

Fig 5. illustrates one possible turbine scanner mirror employed in method according to the invention,

Fig 6. illustrates the movement of the ablating beam achieved by each mirror in the example of Fig 5,

Fig 7. illustrates beam guidance through one possible rotating scanner to be employed according to the invention,

Fig 8. illustrates beam guidance through one possible rotating scanner to be employed according to the invention,

Fig 9. illustrates beam guidance through one possible rotating scanner to be employed according to the invention,

Fig 10. illustrates one embodiment of coated product according to the invention,

Fig 11. illustrates one embodiment of coated product according to the invention,

Fig 12. illustrates some embodiments of coated product according to the invention,

Fig 13. illustrates one embodiment of coated product according to the invention,

Fig 14. illustrates one embodiment of coated product according to the invention,

Fig 15. illustrates one embodiment of coated product according to the invention,

Fig 16. illustrates one embodiment of coated product according to the invention,

Fig 17. illustrates one embodiment of coated product according to the invention,

Fig 18. illustrates one embodiment of coated product according to the invention,

Fig 19. illustrates one embodiment of coated product according to the invention,

Fig 20. illustrates one embodiment of coated product according to the invention,

Fig 21. illustrates one embodiment of coated product according to the invention,

Fig 22. illustrates one embodiment of coated product according to the invention,

Fig 23. illustrates one embodiment of coated product having two different coating layers according to the invention,

- Fig 24.** illustrates two embodiments of coated product according to the invention,
- Fig 25.** illustrates several embodiments of coated product according to the invention,
- Fig 26.** illustrates several embodiments of coated product according to the invention,
- Fig 27.** illustrates several embodiments of coated product according to the invention,
- Fig 28.** illustrates one embodiment of coated product according to the invention,
- Fig 29.** illustrates several embodiments of coated product according to the invention,
- Fig 30.** illustrates one embodiment of coated product according to the invention,
- Fig 31.** illustrates several embodiments of coated product according to the invention,
- Fig 32a.** illustrates an embodiment according to the invention, wherein target material ablated by scanning the laser beam with rotating scanner (turbine scanner).
- Fig 32b.** illustrates an exemplary part of target material of Figure 32a.
- Fig 32c.** illustrates an exemplary ablated area of target material of Figure 32b.
- Fig 33a.** illustrates an exemplary way according to the invention to scan and ablate target material with turbine scanner (rotating scanner).
- Fig 34a.** illustrates plasma-related problems of known techniques.
- Fig 34b.** illustrates plasma-related problems of known techniques.

Detailed Description of Embodiments of the Invention

According to the invention there is provided a method for coating a certain surface of a metal product by laser ablation in which method the uniform surface area to be

coated comprises at least 0.2 dm^2 and the coating is carried by employing ultra short pulsed laser deposition wherein pulsed laser beam is scanned with a rotating optical scanner comprising at least one mirror for reflecting said laser beam.

With metal products is hereby meant but not limited to metal products such as for construction as whole, interior and decorative use, for machinery, vehicles such as cars, trucks, motorcycles and tractors, airplanes, ships, boats, trains, rails, tools, medical products, electronic devices and their casings, lightning, profiles, frames, component parts, process equipment, pipes and tanks for various industries such as chemical industries, power and energy industries, space ships, plain metal sheets, military solutions, ventilation, mining, screws, baking equipment and bread cutting tools and knives, water pipes, drills and their parts etc. The metal product must not be necessarily of metal as such. According to the invention, all the products comprising metal surfaces regardless whether their metal content is 100 % or 1% can be coated with now presented method. Some of the possible embodiments of the invention are illustrated in figures 4 and 10-31.

Ultra Short Laser Pulsed Deposition is often shortened USPLD. Said deposition is also called cold ablation, in which one of the characteristic features is that opposite for example to competing nanosecond lasers practically no heat transfer takes place from the exposed target area to the surroundings of this area, the laser pulse energies being still enough to exceed ablation threshold of target material. The pulse lengths are typically under 50 ps, such as 5 – 30 ps. i.e. ultra short, the cold ablation being reached with pico-second, femto-second and atto-second pulsed lasers. The material evaporated from the target by laser ablation is deposited onto a substrate that is held near room temperature. Still, the plasma temperature reaches 1.000.000 K on exposed target area. The plasma speed is superior, gaining even 100.000 m/s and thus, better prospective for adequate adhesion of coating/thin-film produced.

In another preferred embodiment of the invention, said uniform surface area comprises at least 0.5 dm^2 . In a still preferred embodiment of the invention, said uniform surface area comprises at least 1.0 dm^2 . The invention accomplishes easily also the coating of products comprising uniform coated surface areas larger than 0.5 m^2 , such as 1 m^2 and over. As the process is especially beneficial for coating large surfaces with high quality plasma, it meets an underserved or unserved market of several different metal products.

In industrial applications, it is important to achieve high efficiency of laser treatment. In cold ablation, the intensity of laser pulses must exceed a

predetermined threshold value in order to facilitate the cold ablation phenomenon. This threshold value depends on the target material. In order to achieve high treatment efficiency and thus, industrial productivity, the repetition rate of the pulses should be high, such as 1 MHz, preferably over 2 MHz and more preferably over 5 MHz. As mentioned earlier, it is advantageous not to direct several pulses into same location of the target surface because this causes a cumulating effect in the target material, with particle deposition leading to bad quality plasma and thus, bad quality coatings and thin-films, undesirable eroding of the target material, possible target material heating etc. Therefore, to achieve a high efficiency of treatment, it is also necessary to have a high scanning speed of the laser beam. According to the invention, the velocity of the beam at the surface of the target should generally be more than 10 m/s to achieve efficient processing, and preferably more than 50 m/s and more preferably more than 100 m/s, even such speeds as 2000 m/s. However, in the optical scanners based on vibrating mirror the moment of inertia prevents achieving sufficiently high angular velocity of the mirror. The obtained laser beam at the target surface is therefore just a few m/s, figure 1 illustrating an example of such vibrating mirror, also called galvano-scanner.

As the present coating methods employing galvano-scanners can produce scanning widths at most 10 cm, preferably less, the present invention also accomplishes much more broader scanning widths such as 30 cm and even over 1 meter with simultaneously excellent coating properties and production rates.

According to one embodiment of the invention, rotating optical scanner is here meant scanners comprising at least one mirror for reflecting laser beam. Such a scanner and its applications are described in patent application FI20065867. According to another embodiment of the invention, rotating optical scanner comprises at least three mirrors for reflecting laser beam. In one embodiment of the invention, in the coating method employs a polygonal prism illustrated in figure 5. Here, a polygonal prism has faces 21, 22, 23, 24, 25, 26, 27 and 28. Arrow 20 indicates that the prism can be rotated around its axis 19, which is the symmetry axis of the prism. When the faces of the prism of the Fig. 5 are mirror faces, advantageously oblique in order to achieve scanning line, arranged such that each face in its turn will change, by means of reflection, the direction of radiation incident on the mirror surface as the prism is rotated around its axis, the prism is applicable in the method according to an embodiment of the invention, in its radiation transmission line, as part of a rotating scanner, i.e. turbine scanner. Fig. 5 shows 8 faces, but there may be considerably more faces than that, even dozens or

hundreds of them. Fig. 5 also shows that the mirrors are at the same oblique angle to the axis, but especially in an embodiment including several mirrors, the said angle may vary in steps so that, by means of stepping within a certain range, a certain stepped shift on the work spot is achieved on the target, illustrated in Fig. 6, among other things. The different embodiments of invention are not to be limited into various turbine scanner mirror arrangements regarding for example the size, shape and number of laser beam reflecting mirrors.

The structure of the turbine scanner, Fig. 5, includes at least 2 mirrors, preferably more than 6 mirrors, e.g. 8 mirrors (21 to 28) positioned symmetrically around the central axis 19. As the prism 21 in the turbine scanner rotates 20 around the central axis 19, the mirrors direct the radiation, a laser beam, for instance, reflected from spot 29, accurately onto the line-shaped area, always starting from one and the same direction (Fig. 6). The mirror structure of the turbine scanner may be non-tilted (Fig. 7) or tilted at a desired angle, e.g. Figs. 8 and 9. The size and proportions of the turbine scanner can be freely chosen. In one advantageous embodiment of the coating method it has a perimeter of 30 cm, diameter of 12 cm, and a height of 5 cm.

In an embodiment of the invention it is advantageous that the mirrors 21 to 28 of the turbine scanner are preferably positioned at oblique angles to the central axis 19, because then the laser beam is easily conducted into the scanner system.

In a turbine scanner according to be employed according to an embodiment of the invention (Fig. 5) the mirrors 21 to 28 can deviate from each other in such a manner that during one round of rotational movement there are scanned as many line-shaped areas (Fig. 6) 29 as there are mirrors 21 to 28.

According to the invention, the surface to be coated can comprise whole or a part of the metal product surface.

In one especially preferred embodiment of invention, thin metal sheets for various uses as in construction or interior finishing, the whole sheet is coated in order to gain the preferred effect or effects of coating. One such representative product according to invention comprising a copper thin sheet of 1200 mm x 1500 mm with thickness of 1 mm and coated first with CuO_2 and finished with a protective coating of transparent ATO (aluminumtitanoxide) is illustrated in figure 4. CuO_2 gives the

interior effect, ATO giving wear resistance as well as preventing the leakage of harmful copper compound into nature.

In one preferred embodiment of the invention laser ablation is carried out under vacuum of 10^{-1} to 10^{-12} atmospheres. High vacuum conditions require quite long pumping times, and thus prolonged production times of coatings. With certain high end-products this is not so big problem, but with for example commodity products especially comprising larger surfaces this definitely is. If taking into account to for example novel wear- and scratch-free coatings, chemically inert coatings, tribological coatings, thermally resistant and/or thermally conductive coatings, electrically conductive coatings and possibly simultaneously excellent transparencies, there simply aren't any coating methods available for said products, neither from technological point of view and/or from economical point of view.

Thus, in a specially preferred embodiment of invention, the laser ablation is carried out under vacuum of 10^{-1} to 10^{-4} atmospheres. According to the invention, excellent coating/thin-film properties can be achieved already in low atmospheres, leading to dramatically decreased processing times and enhanced industrial applicability.

According to the invention it is possible to conduct the coating in a manner wherein the distance between the target material and said uniform surface area to be coated is under 25 cm, preferably under 15 cm and most preferably under 10 cm. This accomplishes the development of coating chambers with drastically diminished volumes, making the overall price of coating production lines lower and decreasing further the time required for vacuum pumping.

In a preferred embodiment of the invention the ablated surface of said target material can be repeatedly ablated in order to produce defect-free coating. In case of most of the present coating technologies, the target material wears unevenly in a manner that the affected area cannot be reused for ablation and must thus be either discarded or sent for regeneration after certain use. The problem has been tackled by developing different techniques for feeding constantly new, non-ablated target surface for coating purposes by for example moving the target material in x/y-axis or by rotating a cylinder-formed target material. The present invention accomplishes simultaneously excellent coating properties and production rates as well as use of target material in a way wherein the good quality plasma retains its quality throughout the use of substantially whole piece of target material. Preferably, more than 50% of the single target material weight is consumed to production of good quality plasma according to the invention. With good quality plasma is here meant plasma for producing defect-free coatings and thin-films, the high quality of plasma

plume being maintained at high pulse frequencies and deposition rates. Some of such properties are described here below.

According to one embodiment of the invention, the average surface roughness of produced coating on said uniform surface area is less than 100 nm as scanned from an area of 1 μm^2 with Atomic Force Microscope (AFM). More preferably, the average surface roughness is less than 30 nm. With average surface roughness is here meant the average deviation from the centre line average curve fitted by a proper procedure, such as those available in AFM or profilometer. The surface roughness affects amongst the other the wear- and scratch-free properties, tribological properties as well as the transparency of coating on metal products coated according to the invention.

In a still preferable embodiment of the invention, the optical transmission of produced coating on said uniform surface area is no less than 88%, preferably no less than 90% and most preferably no less than 92%. It can even be higher than 98%. The optical transparency of a coating in metal products is especially important in uses wherein the original metallic look is preferred in addition to other advantages gained by the coating according to invention.

In another embodiment of the invention, produced coating on said uniform surface area contains less than one pinhole per 1 mm^2 , preferably less than one pinhole per 1 cm^2 and most preferably no pinholes at said uniform surface area. Pinhole is a hole going through or substantially through the coating. Pinholes provide a platform for erosion of the originally coated material for example by chemical or environmental factors. Single pinhole in for instance coating of chemical reactor or tubing, medical implant, space ship, different parts of different vehicles and their mechanical parts or further, in metallic construction or interior structure leads easily to dramatically lowered life-time of said product.

Thus, in another preferred embodiment said uniform surface area is coated in a manner wherein the first 50% of said coating on said uniform surface area does not contain any particles having a diameter exceeding 1000 nm, preferably 100 nm and most preferably 30 nm. If the early stages of the coating manufacturing process produce micrometer size particles, such particles can cause open corrosion pathways in the next layers of produced coating. Moreover, due to irregular shape of particles, it is extremely difficult to seal the surface underneath such particles. Additionally, such particles increase surface roughness substantially. The present

method allows even here increased lifetime and lowered maintenance cost of different metal products.

The metal product itself can comprise virtually whichever metal, metal compound such as metal alloys, oxides, carbides, nitrides or composite materials of these. According to the invention, said uniform surface area of metal product is coated with metal, metal oxide, metal nitride, metal carbide or mixtures of these. Non-limiting examples of metals include aluminum, molybdenum, titan, zirconium, copper, yttrium, magnesium, zinc, chromium, silver, gold, cobalt, tin, nickel, tantalum, gallium, manganese, vanadium, platinum and virtually whichever metal.

When producing coatings according to invention which comprise both excellent optical, wear, and scratch-free properties, especially advantageous metal oxides are for example aluminum oxide and its different composites such as aluminumtitanoxide (ATO), indiumtin oxide (ITO), yttrium stabilized zirconiumoxide.

If certain metal oxides such as titan oxide and zinc oxide are applied on surface thicknesses providing UV-activity of produced coating, the coating can possess self-cleaning properties. Such properties are highly desired in order to accomplish the use and decrease the maintenance cost of several metal products in both interior and exterior use.

The metal oxide coatings can be produced by either ablating metal or metals in active oxygen atmosphere or by ablating oxide-materials. Even in latter possibility, it is possible to enhance the coating quality and/or production rate by conducting the ablation in oxygen atmosphere. The same applies for nitrides as well.

According another embodiment of the invention, said uniform surface area of metal product is coated with carbon material comprising over 90 atomic-% of carbon, with more than 70% of sp^3 -bonding. Such materials include for example amorphous diamond, nano-crystalline diamond or even pseudo-monocrystalline diamond. Various diamond coatings give the metal product excellent tribological, wear- and scratch-free properties but increase also the heat-conductivity and –resistance.

In a still another embodiment of the invention, said uniform surface area of metal product is coated with material comprising carbon, nitrogen and/or boron in different ratios. Such materials include boron carbon nitride, carbon nitride (both C_2N_2 and C_3N_4), boron nitride, boron carbide or phases of different hybridizations of B-N, B-C and C-N phases. Said materials are diamond-like materials having low

densities, are extremely wear-resistant, and are generally chemically inert. For example carbon nitrides can be employed to protect metal products against corrosive conditions, as coatings for medical devices and implants, battery electrodes, humidity and gas sensors, semiconductor applications, protecting computer hard disks, in solar cells, tools, etc.

According to one embodiment of the invention certain uniform surface area of metal product is coated with organic polymer material. Such materials include but are not limited to chitosan and its derivatives, polysiloxanes, and different organic polymers.

By coating metal product with chitosan there are promising perspectives to produce a new class of metal products for marine and other water environments as well as new metal products for both interior and exterior use. Here, polysiloxanes are especially advantageous for manufacturing products with relatively high wear-resistance and scratch-free properties with simultaneously excellent optical transparencies.

According to still another embodiment of invention said uniform surface area is coated with inorganic material. Such materials include but are not limited to for instance stone and ceramic derived materials.

In an especially preferred embodiment of the invention, different metal sheets and 3D-metal structures were coated by ablating a target material comprising pink agate resulting in colored but opaque coating result.

According to one embodiment of invention, said uniform surface of the metal product is coated with only one single coating. According to another embodiment of the invention, said uniform surface of the metal product is coated with multilayered coating. Several coatings can be produced in for different reasons. One reason might be to enhance the adhesion of certain coatings to metal product surfaced by manufacturing a first set of coating having better adhesion to metal surface and possessing such properties that the following coating layer has better adhesion to said layer than to metal surface itself. Additionally, the multilayered coating can possess several functions not achievable without said structure. The present invention accomplishes the production of several coatings in one single coating chamber or in the adjacent chambers.

The present invention further accomplishes the production of composite coatings to metal product surface by ablating simultaneously one composite material target or two or more target materials comprising one or more substances.

According to invention the thickness of said coating on uniform surface of metal product is between 20 nm and 20 μm , preferably between 100 nm and 5 μm . The coating thicknesses must not be limited to those, because the present invention accomplishes the preparation of molecular scale coatings on the other hand, very thick coatings such as 100 μm and over, on the other hand.

The present invention further accomplishes the preparation of 3D-structures employing the metal component as a scaffold for growing said 3D-structure.

According to the invention there is also provided a metal product comprising a certain surface being coated by laser ablation wherein the coated uniform surface area comprises at least 0.2 dm^2 and that the coating has been carried by employing ultra short pulsed laser deposition wherein pulsed laser beam is scanned with a rotating optical scanner comprising at least one mirror for reflecting said laser beam. The benefits received with these products are described in more detail in the previous description of the method.

In one embodiment of the invention said uniform surface area comprises at least 0.5 dm^2 . In a more preferable embodiment of the invention said uniform surface area comprises at least 1.0 dm^2 . The invention accomplishes easily also the products comprising uniform coated surface areas larger than 0.5 m^2 , such as 1 m^2 and over.

According to one embodiment of the invention the average surface roughness of produced coating on said uniform surface area is less than 100 nm as scanned from an area of 1 μm^2 with Atomic Force Microscope (AFM). More preferably, the average surface roughness is less than 30 nm. With average surface roughness is here meant the average deviation from the centre line average curve fitted by a proper procedure, such as those available in AFM or profilometer. The surface roughness affects amongst the other the wear- and scratch-free properties, tribological properties as well as the transparency of coating on metal products coated according to the invention.

According to another embodiment of the invention the optical transmission of produced coating on said uniform surface area is no less than 88%, preferably no less than 90% and most preferably no less than 92%. In some cases the optical transmission can exceed 98%. The optical transparency of a coating in metal

products is especially important in uses wherein the original metallic look is preferred in addition to other gained advantages by the coating according to the invention.

According to still another embodiment of the invention said produced coating on said uniform surface area contains less than one pinhole per 1 mm^2 , preferably less than one pinhole per 1 cm^2 and most preferably no pinholes at said uniform surface area.

According to still another embodiment of the invention said uniform surface area is coated in a manner wherein the first 50% of said coating on said uniform surface area does not contain any particles having a diameter exceeding 1000 nm, preferably 100 nm and most preferably 30 nm.

The metal product according to the invention can comprise virtually whichever metal, metal compound such as metal alloys, oxides, carbides, nitrides or composite materials of these. As mentioned earlier, the definition of metal product in this connection must be understood in a manner, wherein the product comprises a certain metal surface, which has been coated according to now invented method. The metal content of the product scaffold (uncoated product) can thus vary everywhere between 0.1 to 100%.

According to one embodiment of the invention said uniform surface area of metal product is coated with metal, metal oxide, metal nitride, metal carbide or mixtures of these. The possible metals were described earlier in description of now invented coating method.

According to another embodiment of the invention said uniform surface area of metal product is coated with carbon material comprising over 90 atomic-% of carbon, with more than 70% of sp^3 -bonding. The possible carbon materials were described earlier in description of now invented coating method.

According to still another embodiment of the invention said uniform surface area of metal product is coated with material comprising carbon, nitrogen and/or boron in different ratios. Such materials were described earlier in description of now invented coating method.

According to still another embodiment of the invention said uniform surface area of metal product is coated with organic polymer material. Such materials were described earlier in more detail in description of now invented coating method.

According one embodiment of the invention said uniform surface area is coated with inorganic material. Such materials were described earlier in more detail in description of now invented coating method.

According to another preferred embodiment of the invention said uniform surface of metal product is coated with multilayered coating. According to another preferred embodiment of the invention said uniform surface of metal product is coated with single coating layer.

According to one preferred embodiment of the invention the thickness of said coating on uniform surface of metal product is between 20 nm and 20 μm , preferably between 100 nm and 5 μm . The invention accomplishes also coated metal products comprising one or several atomic layer coatings and thick coatings such as exceeding 100 μm , for example 1 mm. The present invention further accomplishes the 3D-structures prepared by employing the metal component as a scaffold for growing said 3D-structure.

Examples

Example to demonstrate known art problems – laser technology

Figure 2 represents the ITO-coating on polycarbonate sheet (~100 mm x 30 mm) produced by employing a prior art optical scanner, namely vibrating mirror (galvo-scanner), in different ITO thin-film thicknesses (30 nm, 60 nm and 90 nm). Although the ITO-coating is not deposited on metal substrate, the picture clearly demonstrates some of the problems associated with employing vibrating mirror as an optical scanner especially in ultra short pulsed laser deposition (USPLD) but also in laser assisted coatings in general. As a vibrating mirror changes its direction of angular movement at its end positions, and due to moment inertia, the angular velocity of the mirror is not constant near to its end positions. Due to vibrating movement, the mirror continuously brakes up and stops before speeding up again, causing thus irregular treatment of the target material at the edges of the scanned area. As it can be seen from figure 2, this in turn results in low quality plasma comprising particles especially in the edges of the scanned area and finally, in low quality and seemingly uneven coating result.

The coating parameters have been selected in order to demonstrate the uneven distribution of ablated material due to the nature of employed scanner. If selecting the parameters appropriately, the film quality can be enhanced, problems becoming invisible but not excluded.

Example to demonstrate known art problems –laser technology

Conventionally galvanometric scanners are used to scan a laser beam with a typical maximum speed of about 2-3 m/s, in practice about 1 m/s. This means that even 40-60 pulses are overlapping with a repetition rate of 2 MHz (Fig. 3).

Example to demonstrate known art problems – laser technology

Plasma related quality problems are demonstrated in Figure 34a and 34b, which indicate plasma generation according to known techniques. A laser pulse 1114 hits a target surface 1111. As the pulse is a long pulse, the depth h and the beam diameter d are of the same magnitude, as the heat of the pulse 1114 also heat the surface at the hit spot area, but also beneath the surface 1111 in deeper than the depth h . The structure experiences thermal shock and tensions are building, which while breaking, produce fragments illustrated F. As the plasma may be in the example quite poor in quality, there appears to be also molecules and clusters of them indicate by the small dots 1115, as in the relation to the reference by the numeral 1115 for the nuclei or clusters of similar structures, as formed from the gases 1116 demonstrated in the Figure 34b. The letter "o"s demonstrate particles that can form and grow from the gases and/or via agglomeration. The released fragments may also grow by condensation and/or agglomeration, which is indicated by the curved arrows from the dots to Fs and from the os to the Fs. Curved arrows indicate also phase transitions from plasma 1113 to gas 1116 and further to particles 1115 and increased particles 1117 in size. As the ablation plume in Figure 34b can comprise fragments F as well as particles built of the vapours and gases, because of the bad plasma production, the plasma is not continuous as plasma region, and thus variation of the quality may be met within a single pulse plume. Because of defects in composition and/or structure beneath the deepness h as well as the resulting variations of the deepness (Figure 34a), the target surface 1111 in Figure 34b is not any more available for a further ablations, and the target is wasted, although there were some material available.

Such problems are common with nanosecond-lasers in general, and present picosecond lasers, if they were employing the state of the art scanners.

Example of invention - 1

Figure 32a demonstrates a target material ablated with pico-second –range pulsed laser employing rotating scanner with speed accomplishing the ablation of target material with slight overlapping of adjacent pulses, avoiding the problems associated with prior art galvano-scanners. Figure 32b shows enlarged picture of one part of the ablated material, clearly demonstrating the smooth and controlled ablation of material on both x- and y-axis and thus, generation of high quality, particle-free plasma and further, high quality thin-films and coatings. Figure 32c demonstrates one example of possible x- and y-dimensions of one single ablation spot achieved by one or few pulses. Here, it can be clearly seen, that the invention accomplishes the ablation of material in a manner wherein the width of the ablated spot is always much bigger than the depth of the ablated spot area. Theoretically, the possible particles (if they would be generated) could now have a maximum size of the spot depth. The rotating scanner now accomplishes the production of good quality, particle free plasma with great production rate, with simultaneously large scanning width, especially beneficial for substrates comprising large surface areas to be coated. Furthermore, the figures 32a, 32b and 32c clearly demonstrate that opposite to present techniques, the already ablated target material area can be ablated for new generation of high class plasma – reducing thus radically the overall coating/thin-film producing cost.

Example of invention- 2

Figure 33a demonstrates an example wherein coating is carried out by employing a pico-second USPLD-laser and scanning the laser pulses with turbine scanner. Here, the scanning speed is 30 m/s, the laser spot-width being 30 μm . In this example, there is an 1/3 overlapping between the adjacent pulses.

) Examples of invention – coated products

The following samples were grown on various metal substrates by employing ultra short pulsed laser deposition (USPLD) with a picosecond-range laser (X-lase, 20-80 W) at 1064 nm. Substrate temperature varied from room temperature to 400 °C and target temperature in the range of room temperature to 700 °C. Both oxide, sintered graphite, sintered graphitic $\text{C}_3\text{N}_4\text{H}_x$ (Carbodeon Ltd Oy) and various metal targets were employed. When employing oxygen atmosphere, the oxygen pressure varied

in the range of 10^{-4} to 10^{-1} mbar. When employing nitrogen atmosphere, the nitrogen pressure varied in the range of 10^{-4} to 10^{-1} mbar. The employed scanner was a rotating mirror scanner accomplishing tunable velocity of the beam at the surface of the target between 1 m/s to 350 m/s. The employed repetition rates varied between 1 to 52 MHz, clearly demonstrating the importance of both the scanner and high repetition rates when producing high quality coatings in industrial manner. Deposited films were characterized by confocal microscope, FTIR and Raman spectroscopy, AFM, optical transmission measurements, ESEM and in some cases, electrical measurements (University of Kuopio, Finland; ORC, Tampere, Finland and Corelase Oy, Tampere Finland). The employed spot sizes varied between 20 to 80 μm . The wear tests were carried out by employing pin on disk-method (University of Kuopio, Finland), the tests being carried out at room temperature 22 C and 50 % (AD-coatings) or 25 % (others) relative humidity (without lubrication) with loads in the range 10-125 g using a hardened steel ball (AISI 420), 6 mm in diameter, as a pin. For AD-coatings the rotation speed was 300-600 rpm and for lenses 1 rpm. All the coatings possessed excellent wear properties as well as adhesions.

Example 1

A piece of mirror finish aluminium foil comprising 250 mm x 400 mm was coated by ablating sintered carbon with pulse repetition rate of 4 MHz, pulse energy 5 μJ , pulse length 20 ps and the distance between the target material and surface to be coated was 4 mm. The vacuum level was 10^{-5} atmospheres during the coating process. The process resulted in a uniform sky-blue coloured, transparent coating. The coating thickness was 200 nm and the average surface roughness was determined to be 8 nm as scanned from an area of 1 μm^2 with Atomic Force Microscope (AFM). No pinholes were found on any measured area.

Example 2

A thin sheet of copper comprising 300 mm x 400 mm was coated by ablating copper oxide with pulse repetition rate of 4 MHz, pulse energy 5 μJ , pulse length 17 ps and the distance between the target material and surface to be coated was 10 mm. The vacuum level was about 10^{-1} atmospheres during the coating process. The process resulted in a uniform pale-green coloured, non-transparent coating. The coating thickness was 5 μm and the average surface roughness was determined to be 50 nm as scanned from an area of 1 μm^2 with Atomic Force Microscope (AFM).

Example 3

The copper oxide coated sheet of copper of example 2 was coated by ablating aluminumtitan oxide (ATO) with pulse repetition rate of 15 MHz, pulse energy 5 μJ , pulse length 20 ps and the distance between the target material and surface to be coated was 6 cm. The vacuum level was 10^{-3} atmospheres during the coating process. The process resulted in a uniform pale-green coloured product, wherein ATO did not change the colour of original non-transparent copper oxide coating. The coating thickness was 420 nm and the average surface roughness was determined to be 40 nm as scanned from an area of $1\text{ }\mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes were found on any measured area of ATO-coating.

Example 4

A thin sheet of steel (thickness 1.5 mm) comprising 500 mm x 600 mm was coated by ablating titan oxide in oxygen atmosphere with pulse repetition rate of 20 MHz, pulse energy 4 μJ , pulse length 10 ps and the distance between the target material and surface to be coated was 1 mm. The vacuum level was 10^{-2} atmospheres during the coating process. The process resulted in transparent coating possessing coating thickness of 50 nm. The average surface roughness was determined to be 3 nm as scanned from an area of $1\text{ }\mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes were found on any measured area of titan oxide-coating. The optical transmission of TiO_2 –coating was determined to be better than 98%.

Example 5

A thin sheet of steel (thickness 1.5 mm) comprising 500 mm x 600 mm was coated by ablating titanium with pulse repetition rate of 20 MHz, pulse energy 4 μJ , pulse length 20 ps and the distance between the target material and surface to be coated was 10 mm. The vacuum level was 10^{-5} atmospheres during the coating process. The process resulted in metallic titanium coating possessing coating thickness of 280 nm. The average surface roughness was determined to be better than as scanned from an area of $1\text{ }\mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes were found on any measured area of titan oxide-coating.

Example 6

A thin sheet of steel (thickness 1.5 mm) comprising 500 mm x 600 mm was coated by ablating tantalum with pulse repetition rate of 20 MHz, pulse energy 5 μJ , pulse length 20 ps and the distance between the target material and surface to be coated was 10 mm. The vacuum level was 10^{-4} atmospheres during the coating process. The process resulted in metallic tantalum coating possessing coating thickness of

320 nm. The average surface roughness was determined to better than 3 nm as scanned from an area of $1\ \mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes were found on any measured area of tantalum coating.

Example 7

An unmarked aluminum can of $0.33\ \text{dm}^3$ volume, a 10 cm traditional metal screw and a piece of steel sheet (35 mm x 50 mm) were coated by ablating pink agate (crushed and sintered) with pulse repetition rate of 35 MHz and the distance between the target material to be coated was 2 cm. The vacuum level was 10^{-4} atmospheres during the coating process. The processes resulted in pink agate coloured, opaque coatings comprising thicknesses between 100 nm and 550 nm. The average surface roughness was determined to be better than 10 nm as scanned from an area of $1\ \mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes were found on any measured area of agate coating.

Example 8

A thin sheet of steel (thickness 1.5 mm) comprising 500 mm x 600 mm was coated by ablating cold-pressed chitosan with pulse repetition rate of 10 MHz, pulse energy $5\ \mu\text{J}$, pulse length 20 ps and the distance between the target material and surface to be coated was 20 mm. The vacuum level was 10^{-5} atmospheres during the coating process. The process resulted in partially opaque coating possessing coating thickness of 250 nm. The average surface roughness was determined to better than 10 nm as scanned from an area of $1\ \mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes were found on any measured area of polymer coating.

Example 9

A bone screw made of stainless steel was coated by ablating hot-pressed graphite with pulse repetition rate of 20 MHz, pulse energy $4\ \mu\text{J}$, pulse length 15 ps and the distance between the target material and surface to be coated was 1 mm. The vacuum level was 10^{-5} atmospheres during the coating process. The coating thickness was measured to $1\ \mu\text{m}$. The average surface roughness was determined to be 3 nm as scanned from an area of $1\ \mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes were found on any measured area of diamond coating. The carbon content was measured to be over 98% and the degree of sp^3 -bonding was approximately 86%.

Example 10

A bone screw made of stainless steel was coated by ablating hot-pressed $\text{C}_3\text{N}_4\text{H}_x$ with pulse repetition rate of 20 MHz, pulse energy $5\ \mu\text{J}$, pulse length 20 ps and the

distance between the target material and surface to be coated was 10 mm. The vacuum level was 10^{-5} atmospheres during the coating process. The coating thickness was measured to 1 μm . The average surface roughness was determined to be under 3 nm as scanned from an area of 1 μm^2 with Atomic Force Microscope (AFM). No pinholes were found on any measured area of carbon nitride coating.

Example 11

A thin sheet of copper comprising 300 mm x 400 mm was coated by ablating ITO in oxide form (90 wt.% In_2O_3 ; 10 wt.% SnO_2) with pulse repetition rate of 30 MHz, pulse energy 5 μJ , pulse length 20 ps and the distance between the target material and surface to be coated was 10.2 cm. Oxygen pressure varied in the range of 10^{-4} to 10^{-1} mbar. The process resulted in a uniform, transparent coating. The coating thickness was measured to 110 nm and the average surface roughness was determined to be under 2 nm as scanned from an area of 1 μm^2 with Atomic Force Microscope (AFM). No pinholes were found on any measured area of ITO coating.

Example 12

A thin sheet of copper comprising 300 mm x 400 mm was coated by ablating ITO from a metal target (90 wt.% In; 10 wt.% Sn) with pulse repetition rate of 27 MHz, pulse energy 5 μJ , pulse length 20 ps and the distance between the target material and surface to be coated was 10.2 cm. Oxygen pressure varied in the range of 10^{-4} to 10^{-1} mbar. The process resulted in a uniform, transparent coating. The coating thickness was 40 nm and the average surface roughness was determined to be under 2 nm as scanned from an area of 1 μm^2 with Atomic Force Microscope (AFM). No pinholes were found on any measured area of the ITO coating.

Example 13

A metal crasp according to figure 14 was coated with chromium metal by ablating chromium with pulse repetition rate of 4 MHz, pulse energy 5 μJ , pulse length 24 ps and the distance between the target material and surface to be coated was 15 cm. The vacuum level was 10^{-4} atmospheres during the coating process. The process resulted in a uniform, metallic coating. The coating thickness was measured to 320 nm and the average surface roughness was determined to be under 2 nm as scanned from an area of 1 μm^2 with Atomic Force Microscope (AFM). No pinholes were found on any measured area of chromium coating.

Example 14

A metal crasp according to example 13 was coated with carbon nitride by ablating sintered $C_3N_4H_x$ -material with pulse repetition rate of 6 MHz, pulse energy 5 μJ , pulse length 24 ps and the distance between the target material and surface to be coated was 5 cm. The vacuum level was 10^{-4} atmospheres during the coating process. The process resulted in a uniform, metallic coating. The carbon nitride coating thickness was measured to 390 nm and the average surface roughness was determined to be under 2 nm as scanned from an area of 1 μm^2 with Atomic Force Microscope (AFM). No pinholes were found on any measured area of carbon nitride (C_3N_4) coating.

Example 15

A metallic motor valve according to figure 17 was coated with carbon nitride by ablating sintered $C_3N_4H_x$ -material with pulse repetition rate of 4 MHz, pulse energy 5 μJ , pulse length 24 ps and the distance between the target material and surface to be coated was 3 cm. Nitrogen pressure varied in the range of 10^{-4} to 10^{-1} mbar. The process resulted in a uniform C_3N_4 -coating. The carbon nitride coating thickness was measured to 500 nm and the average surface roughness was determined to be under 2 nm as scanned from an area of 1 μm^2 with Atomic Force Microscope (AFM). No pinholes were found on any measured area of carbon nitride (C_3N_4) coating.

Example 16

A metallic cylinder of vehicle motor according to figure 15 was coated with aluminum oxide by ablating aluminium oxide in active oxygen atmosphere with pulse repetition rate of 26 MHz, pulse energy 5 μJ , pulse length 20 ps and the distance between the target material and surface to be coated was 2.5 cm. Oxygen pressure varied in the range of 10^{-4} to 10^{-1} mbar. The process resulted in a uniform, transparent coating. The aluminium oxide coating thickness was measured to 2.3 μm and the average surface roughness was determined to be under 2 nm as scanned from an area of 1 μm^2 with Atomic Force Microscope (AFM). No pinholes were found on any measured area of aluminum oxide coating.

Example 17

A metallic faucet according to figure 20 was coated with titan oxide by ablating titan metal in active oxygen atmosphere with pulse repetition rate of 9 MHz, pulse energy 5 μJ , pulse length 20 ps and the distance between the target material and

surface to be coated was 2.5 cm. Oxygen pressure varied in the range of 10^{-4} to 10^{-1} mbar. The process resulted in a uniform, transparent coating. The aluminium oxide coating thickness was measured to 25 nm and the average surface roughness was determined to be under 2 nm as scanned from an area of 1 μm^2 with Atomic Force Microscope (AFM). No pinholes were found on any measured area of aluminum oxide coating. The coated object was subjected to organic dirt after which it was subjected to light and certain humidity. The coating possessed self-cleaning properties.

Claims

1. A method for coating a certain surface of a metal product by laser ablation, **characterized** in that the uniform surface area to be coated comprises at least 0.2 dm² and the coating is carried by employing ultra short pulsed laser deposition wherein pulsed laser beam is scanned with a rotating optical scanner comprising at least one mirror for reflecting said laser beam.
2. A method according to claim 1, **characterized** in that said uniform surface area comprises at least 0.5 dm².
3. A method according to claim 1-2, **characterized** in that said uniform surface area comprises at least 1.0 dm².
4. A method according to claim 1-3, **characterized** in that the employed pulse frequency of said laser deposition is at least 1 MHz.
5. A method according to any of the preceding claims, **characterized** in that said laser ablation is carried out under vacuum of 10⁻¹ to 10⁻¹² atmospheres.
6. A method according to claim 5, **characterized** in that said laser ablation is carried out under vacuum on 10⁻¹ to 10⁻⁴ atmospheres.
7. A method according to any of the preceding claims, **characterized** in that the distance between the target material and said uniform surface area to be coated is under 25 cm, preferably under 15 cm and most preferably under 10 cm.
8. A method according to any of the preceding claims, **characterized** in that the ablated surface of said target material can be repeatedly ablated in order to produce defect-free coating.
9. A method according to claim 1, **characterized** in that the average surface roughness of produced coating on said uniform surface area is less than 100 nm as scanned from an area of 1 μm² with Atomic Force Microscope (AFM).
10. A method according to claim 1, **characterized** in that the optical transmission of produced coating on said uniform surface area is no less than 88%, preferably no less than 90% and most preferably no less than 92%.
11. A method according to claim 1, **characterized** in that the said produced coating on said uniform surface area contains less than one pinhole per 1 mm²,

preferably less than one pinhole per 1 cm^2 and most preferably no pinholes at said uniform surface area.

12. A method according to claim 1, **characterized** in that said uniform surface area is coated in a manner wherein the first 50% of said coating on said uniform surface area does not contain any particles having a diameter exceeding 1000 nm, preferably 100 nm and most preferably 30 nm.

13. A method according to claim 1, **characterized** in that said uniform surface area of metal product is coated with metal, metal oxide, metal nitride, metal carbide or mixtures of these.

14. A method according to claim 1, **characterized** in that said uniform surface area of metal product is coated with carbon material comprising over 90 atomic-% of carbon, with more than 70% of sp^3 -bonding.

15. A method according to claim 1, **characterized** in that said uniform surface area of metal product is coated with material comprising carbon, nitrogen and/or boron in different ratios.

16. A method according to claim 1, **characterized** in that said uniform surface area of metal product is coated with organic polymer material.

17. A method according to claim 1, **characterized** in that said uniform surface area is coated with inorganic material.

18. A method according to any of the preceding claims, **characterized** in that said uniform surface of metal product is coated with multilayered coating.

19. A method according to any of the preceding claims, **characterized** in that the thickness of said coating on uniform surface of metal product is between 20 nm and 20 μm , preferably between 100 nm and 5 μm .

20. A metal product comprising a certain surface being coated by laser ablation, **characterized** in that the coated uniform surface area comprises at least 0.2 dm^2 and that the coating has been carried by employing ultra short pulsed laser deposition wherein pulsed laser beam is scanned with a rotating optical scanner comprising at least one mirror for reflecting said laser beam.

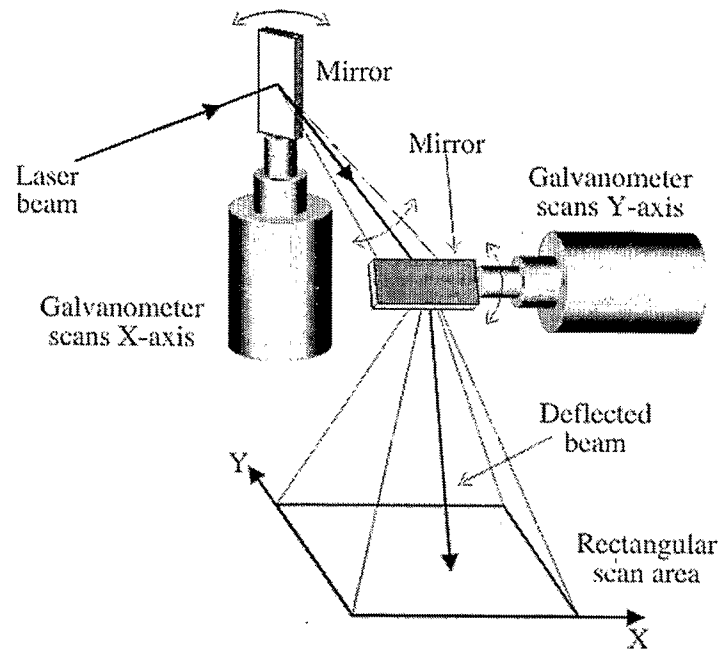
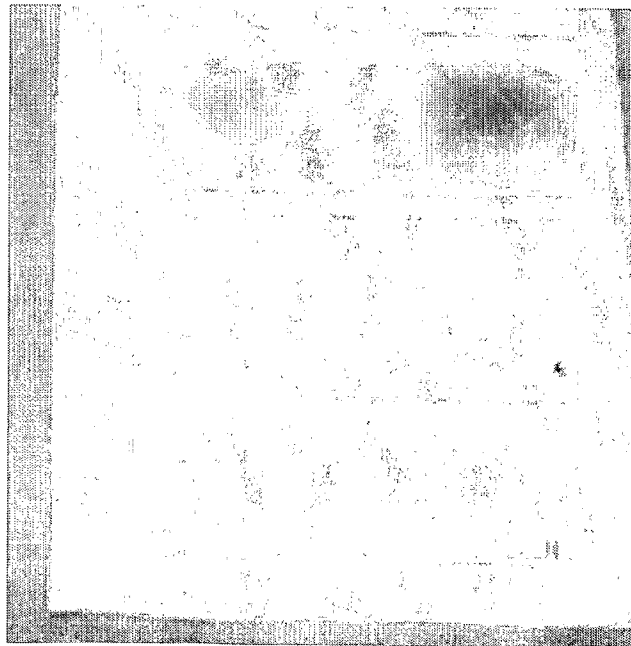
21. A metal product according to claim 20, **characterized** in that said uniform surface area comprises at least 0.5 dm^2 .

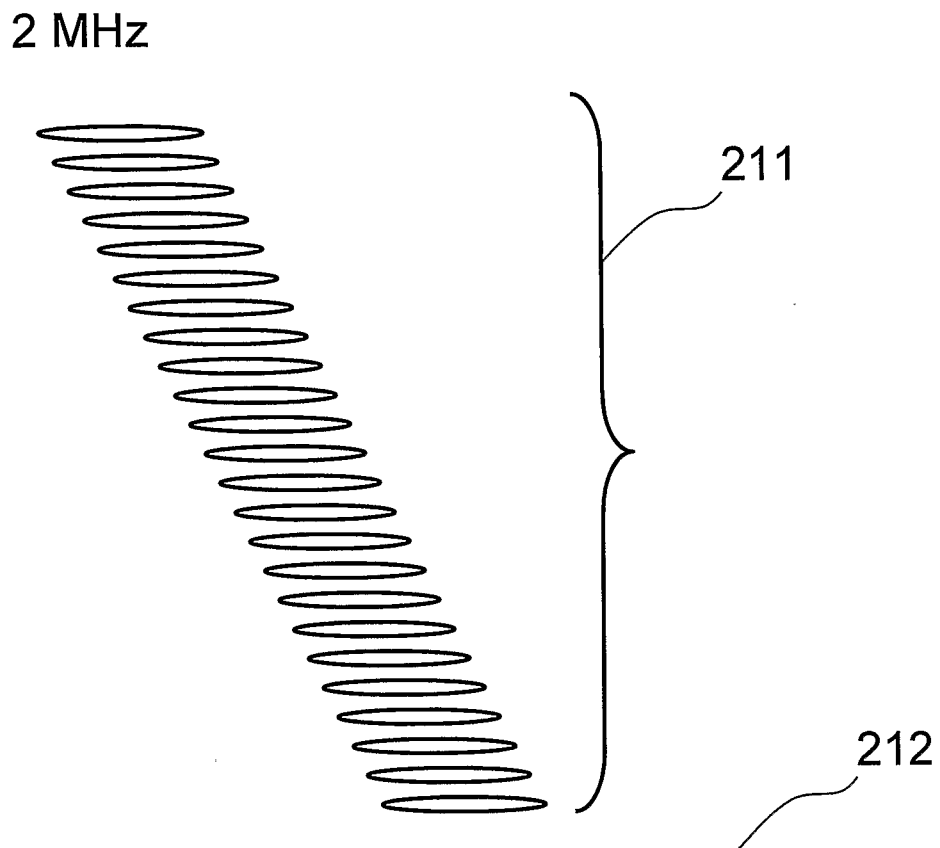
22. A metal product according to claim 20-21, **characterized** in that said uniform surface area comprises at least 1.0 dm^2 .
23. A metal product according to claim 20, **characterized** in that the average surface roughness of produced coating on said uniform surface area is less than 100 nm as scanned from an area of $1 \text{ }\mu\text{m}^2$ with Atomic Force Microscope (AFM).
24. A metal product according to claim 20, **characterized** in that the optical transmission of produced coating on said uniform surface area is no less than 88%, preferably no less than 90% and most preferably no less than 92%.
25. A metal product according to claim 20, **characterized** in that the said produced coating on said uniform surface area contains less than one pinhole per 1 mm^2 , preferably less than one pinhole per 1 cm^2 and most preferably no pinholes at said uniform surface area.
26. A metal product according to claim 20, **characterized** in that said uniform surface area is coated in a manner wherein the first 50% of said coating on said uniform surface area does not contain any particles having a diameter exceeding 1000 nm, preferably 100 nm and most preferably 30 nm.
27. A metal product according to claim 20, **characterized** in that said uniform surface area of metal product is coated with metal, metal oxide, metal nitride, metal carbide or mixtures of these.
28. A metal product according to claim 20, **characterized** in that said uniform surface area of metal product is coated with carbon material comprising over 90 atomic-% of carbon, with more than 70% of sp^3 -bonding.
29. A metal product according to claim 20, **characterized** in that said uniform surface area of metal product is coated with material comprising carbon, nitrogen and/or boron in different ratios.
30. A metal product according to claim 20, **characterized** in that said uniform surface area of metal product is coated with organic polymer material.
31. A metal product according to claim 20, **characterized** in that said uniform surface area is coated with inorganic material.

32. A metal product according to any of the preceding claims 20-31, **characterized** in that said uniform surface of metal product is coated with multilayered coating.

33. A metal product according to any of the preceding claims 20-32, **characterized** in that the thickness of said coating on uniform surface of metal product is between 20 nm and 20 μm , preferably between 100 nm and 5 μm .

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**Figure 1****Figure 2**



Laser spot scanning speed about 1 m/s

Figure 3

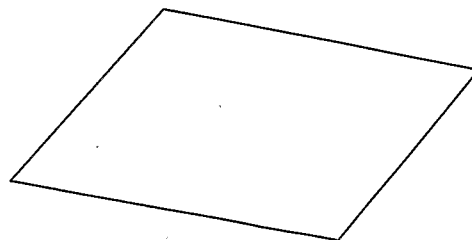


Figure 4

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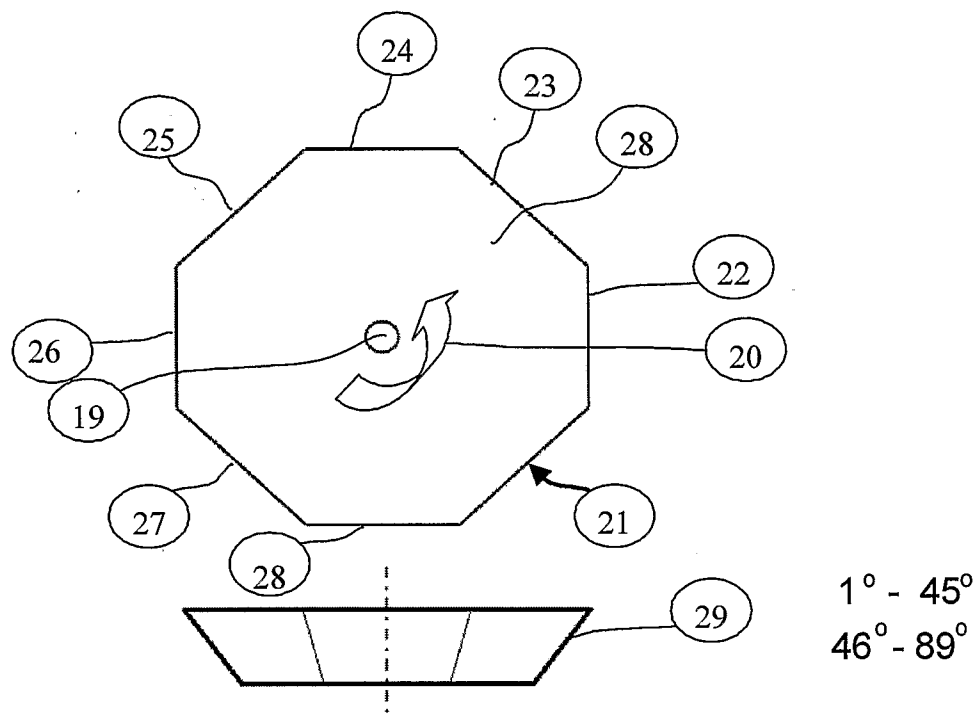


Figure 5

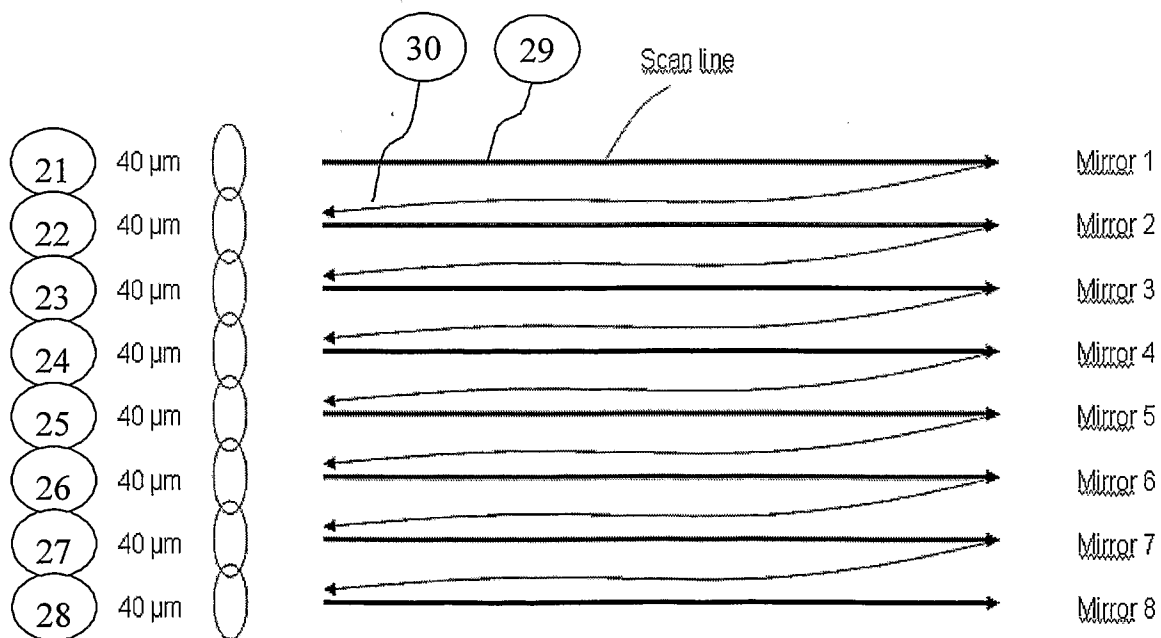


Figure 6

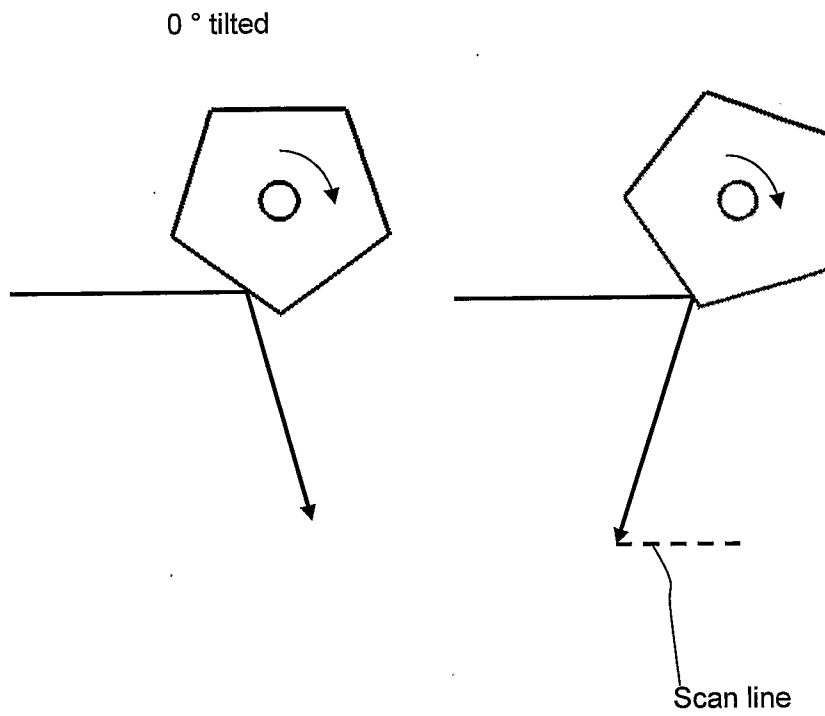


Figure 7

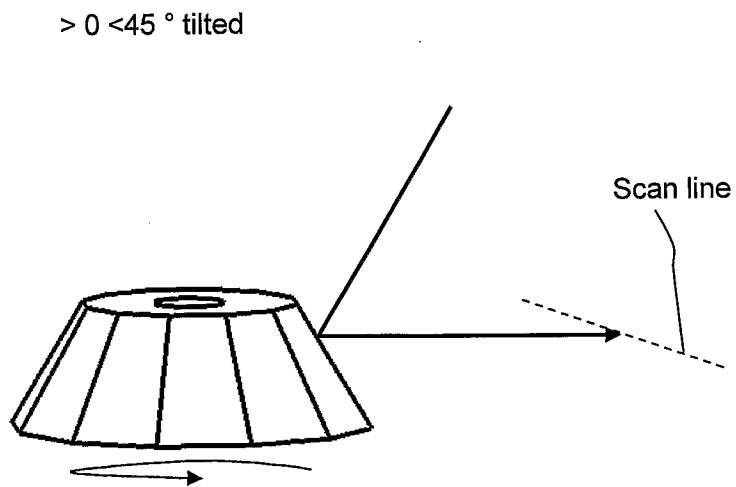


Figure 8

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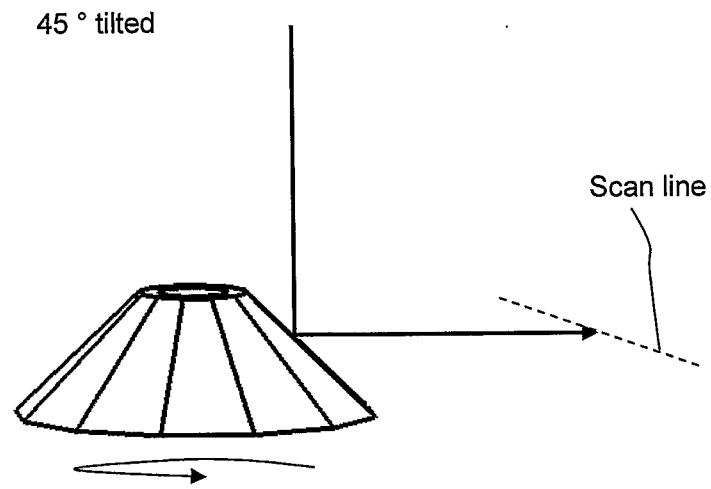


Figure 9

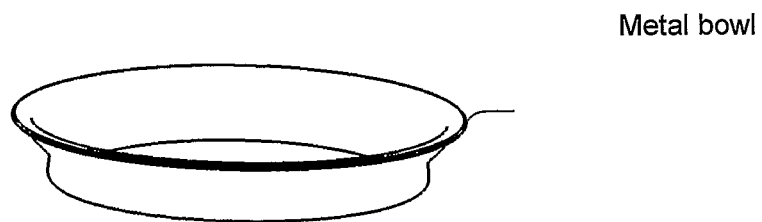


Figure 10

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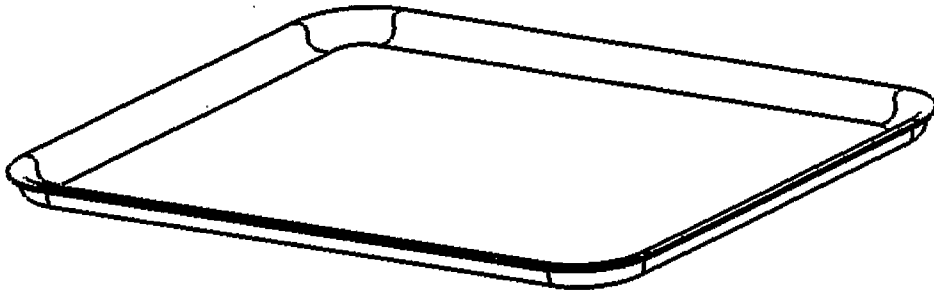


Figure 11

Drill



Figure 12

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Cutting tool

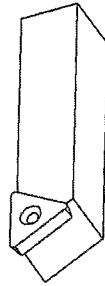


Figure 13

File or rasp

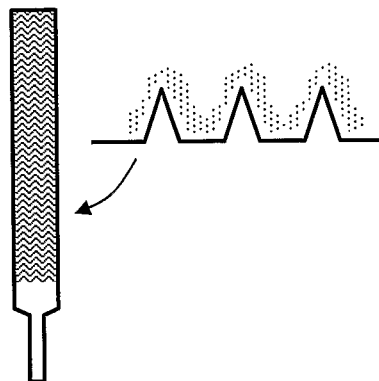


Figure 14

Cylinder in automobile

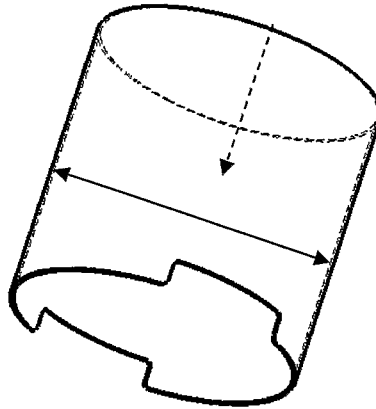


Figure 15

Turbine and blades

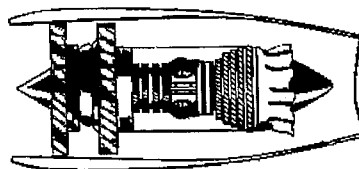


Figure 16

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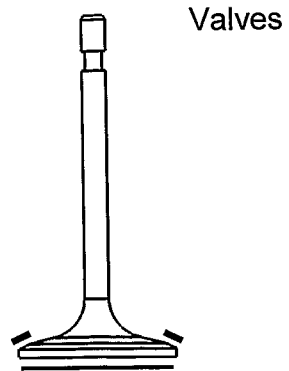


Figure 17

Weapons and their parts

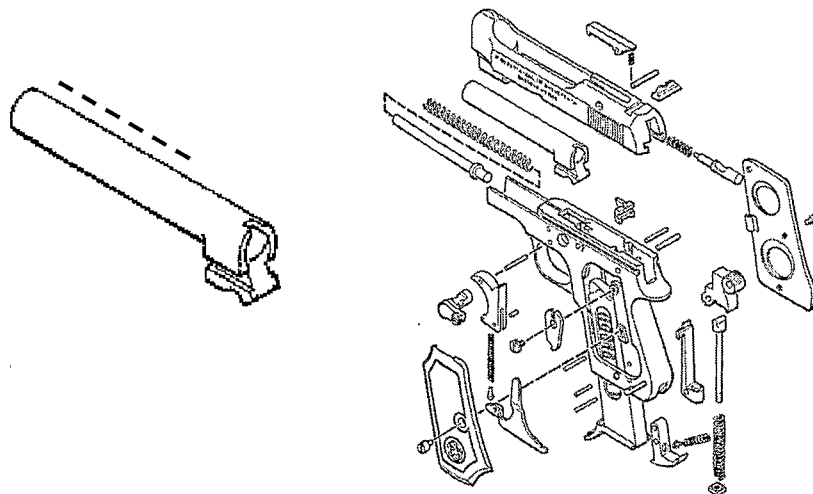


Figure 18

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Bearing

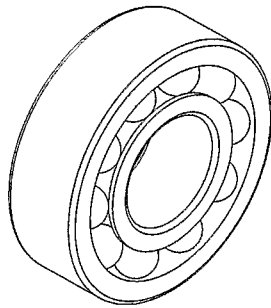


Figure 19

Faucets

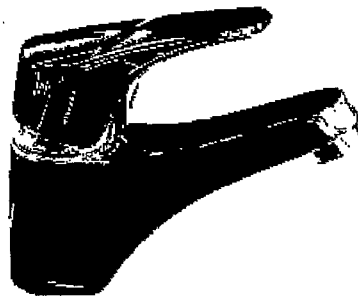


Figure 20

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Bottom sieve

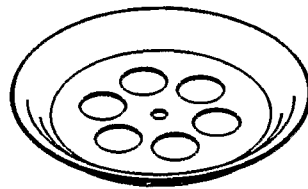


Figure 21

Washbasin of metal, kitchen sink

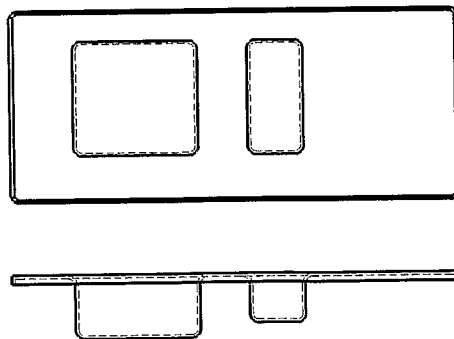


Figure 22

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Metal panel

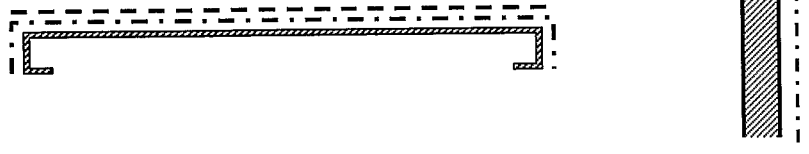
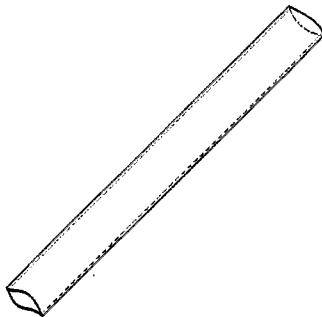


Figure 23

Metal pipes and railings



Handles, locks, lock cylinders



Figure 24

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Greenhouse lighting
equipment and mirrors

Other lighting equipment, e.g. outdoor light

Spa and swimming pool fixtures and fasteners

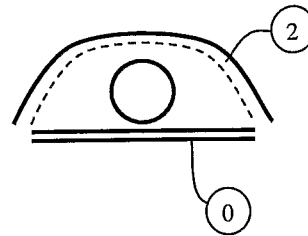
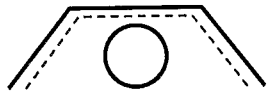


Figure 25



Contact surfaces for low- and high-voltage systems

Connectors, thin film conductors, RF shielding, etc.

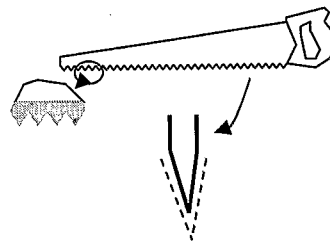
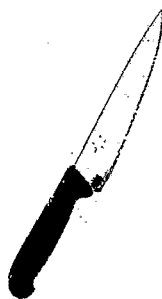
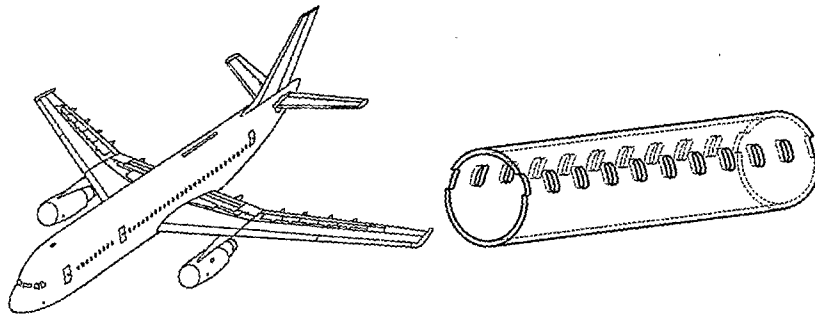


Figure 26

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Aircraft hull and its parts

Figure 27



Aircraft wheel

Figure 28

Medical instruments

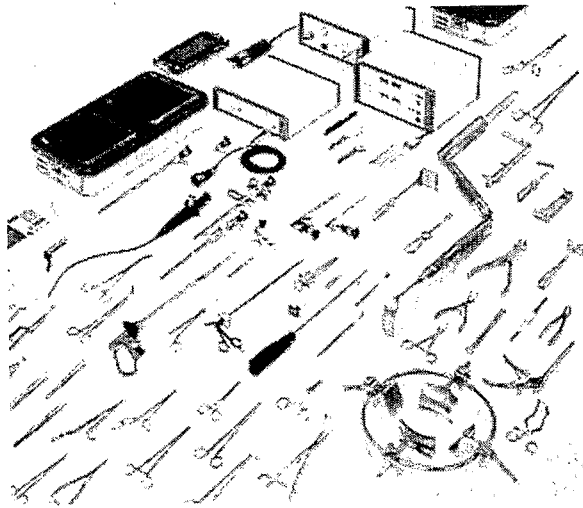


Figure 29

Implants (drilling, tapping and screws)



Figure 30

Implants (hip & knee)

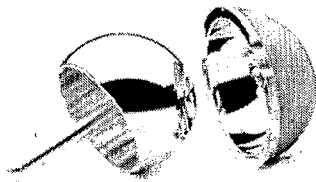
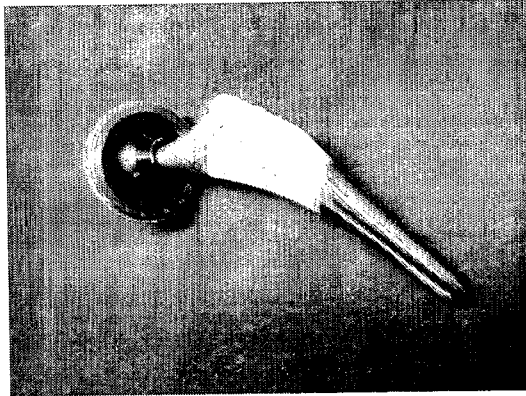


Figure 31

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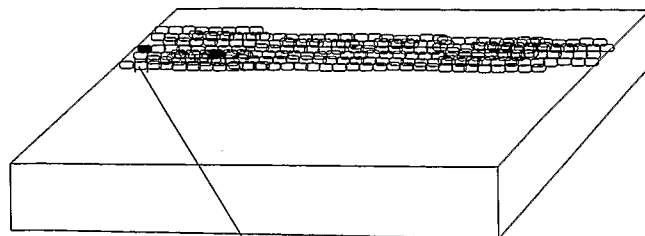


Figure 32a

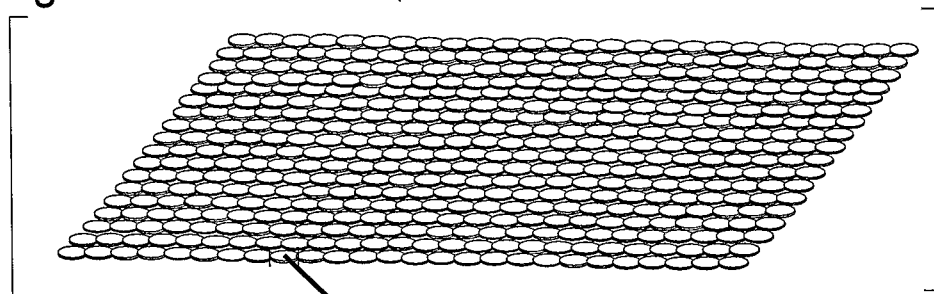


Figure 32b

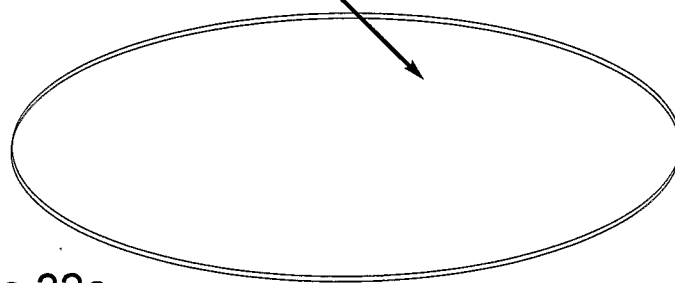


Figure 32c

$y = 50 - 200 \text{ nm}$,
for example 100 nm

$x = 1 \mu\text{m} - 1000 \mu\text{m}$,
for example $45 \mu\text{m}$

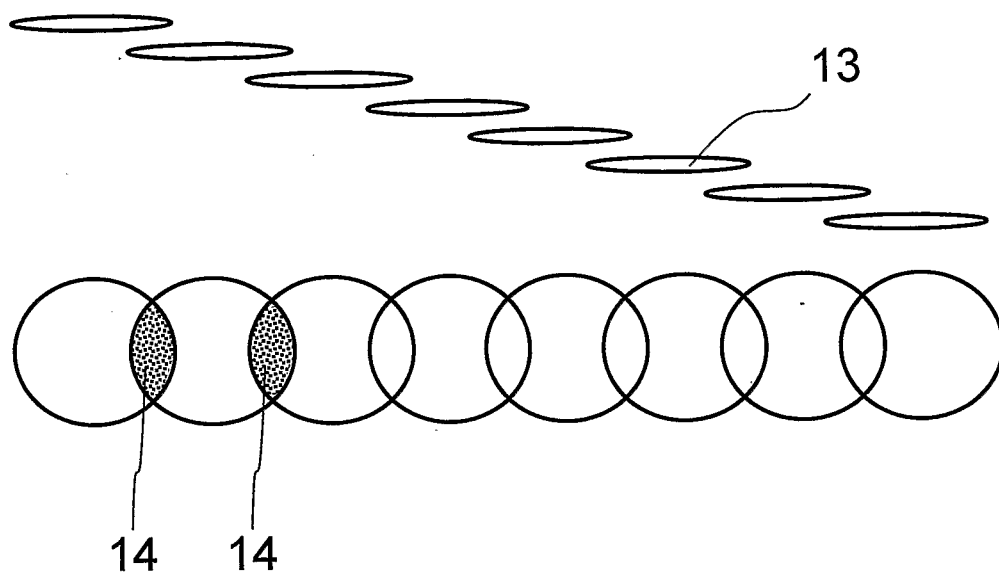


Figure 33a

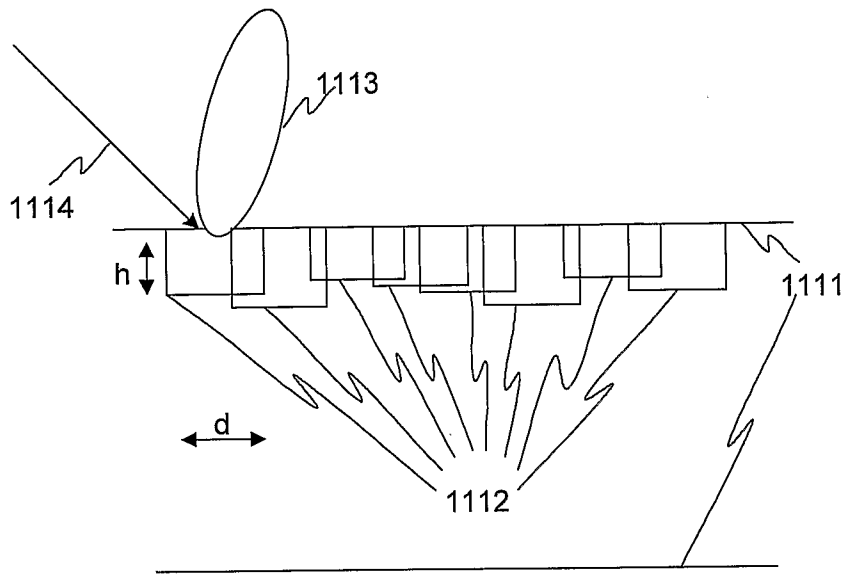


Figure 34a

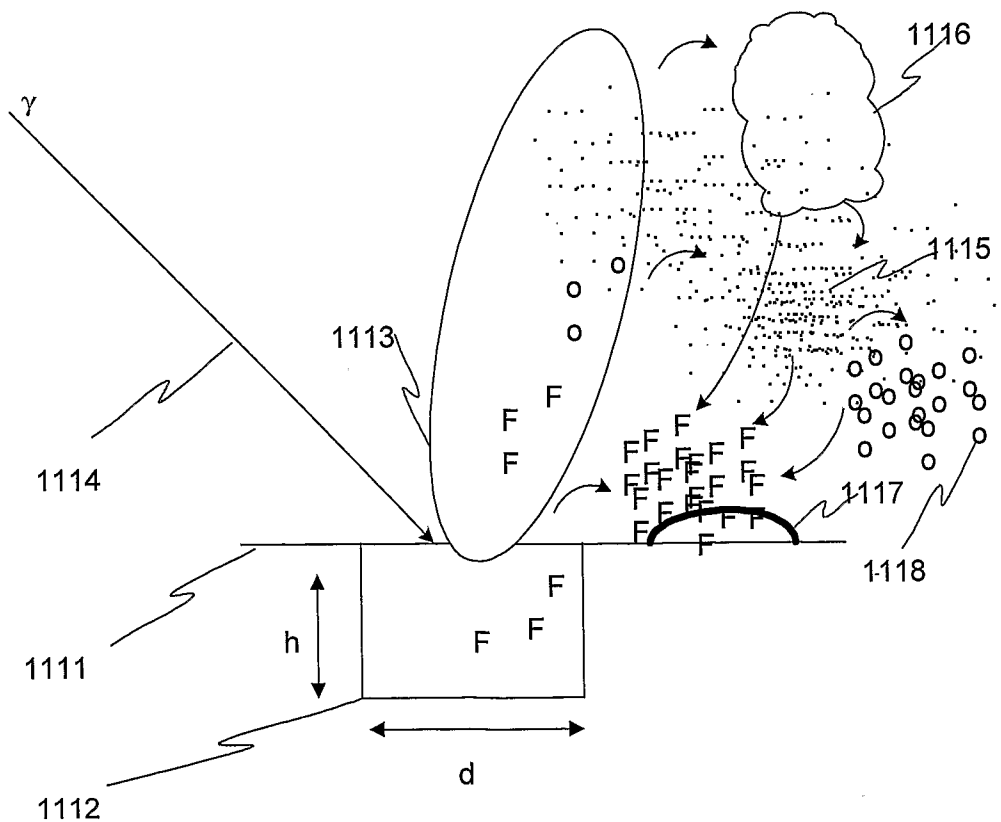


Figure 34b