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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
6 September 2013 (06.09.2013)

WIPO | PCT

(10) International Publication Number
WO 2013/128416 A2

(51) International Patent Classification:
B22F 3/105 (2006.01)

(21) International Application Number:
PCT/IB2013/051636

(22) International Filing Date:
1 March 2013 (01.03.2013)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
MI2012A000331 2 March 2012 (02.03.2012) IT

(71) Applicant: LEGOR GROUP S.P.A. [IT/IT]; Via del Lavoro 1, I-36050 Bressanvido (Vicenza) (IT).

(72) Inventors: BASSO, Andrea; c/o LEGOR GROUP S.p.A., Via del Lavoro 1, I-36050 Bressanvido (Vicenza) (IT). **POLIERO, Massimo**; c/o LEGOR GROUP S.p.A., Via del Lavoro 1, I-36050 Bressanvido (Vicenza) (IT).

(74) Agents: BIGGI, Cristina et al.; c/o BUGNION S.P.A., Viale Lancetti 17, I-20158 Milano (IT).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

(54) Title: SILVER-BASED ALLOY POWDER FOR MANUFACTURING OF 3-DIMENSIONAL METAL OBJECTS

(57) Abstract: The invention relates to a silver-based alloy powder comprising from 70% to 99.99 wt% of silver and from 0.01% to 5 wt% of at least one element chosen from germanium (Ge), aluminium (Al), silicon (Si) and boron (B), or a mixture thereof. The powder is used in a method of direct manufacturing or prototyping (for example, selective laser melting, selective laser sintering, or Electron Beam Melting) for the manufacturing of 3 -dimensional metal objects such as a piece of jewellery, a component for the watch, spectacle or pen industry; a component for the accessory industry; an object or part of an object of art; a component for the medical industry; or a component for the high-tech industries.

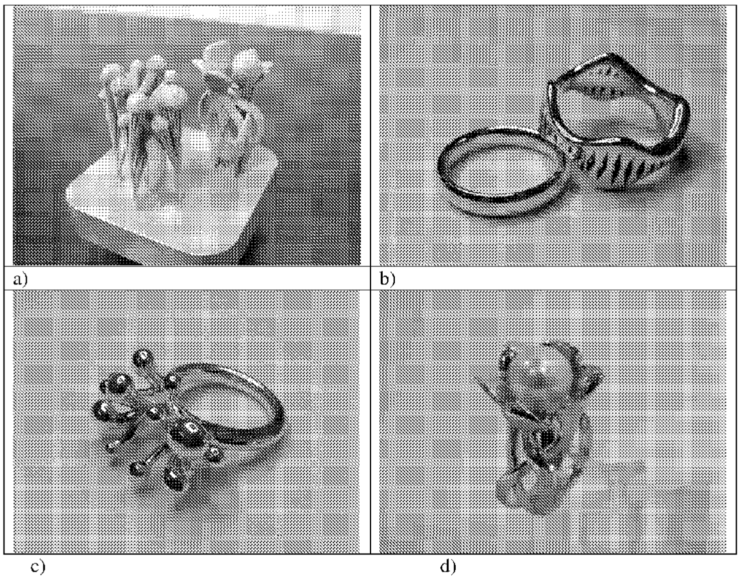


Fig. 5

WO 2013/128416 A2

DESCRIPTION

"SILVER-BASED ALLOY POWDER FOR MANUFACTURING OF 3-DIMENSIONAL METAL OBJECTS"

The present invention relates to a silver-based alloy powder and its use in the manufacturing of 3-dimensional metal objects, preferably pieces of jewellery. The powder is preferably used to manufacture 3-dimensional objects with an additive layer manufacturing method, preferably with a selective laser melting or electron beam melting process.

Background and state of the art

The direct manufacturing or prototyping of 3-dimensional metal objects by additive layer manufacturing (ALM, for example "Selective laser melting" SLM, "Selective laser sintering" SLS or "Electron Beam Melting" EBM) using metal or alloy powders has gained increasing importance in recent years. The technology nowadays is established for a diversity of different applications, which involve working with a variety of powders made of different steel alloys, titanium-based alloys, light metal alloys as well as nickel- and cobalt-chrome-based alloys. It is a technology that enables the rapid and inexpensive production or prototyping of metal parts directly from CAD data, with the potential to produce parts in complex designs which either cannot be manufactured by traditional manufacturing technologies at all or only with a time-, labour- and therefore cost-intensive consume.

The ALM process starts with uploading into a dedicated machine (for example a SLM, SLS or EBM-machine) the CAD data of a 3-dimensional object, which has formerly been digitally separated in 2-dimensional slices perpendicular to the later growing direction, with a typical slice thickness between 10 and 50 µm. After loading the metal alloy powder of choice, an amount of powder is moved from a reservoir and spread on a build platform by a roller or blade to form a layer of the desired thickness. Alternatively, the powder is not spread in a layer by a roller or blade, instead it is added, layer by layer, on a build platform via a nozzle only in the regions where it is actually needed, according to the CAD drawing. In both cases, where the powder is either spread by a roller/blade or added via a nozzle an excellent powder flowability is important in order to get a final object with good surface quality and bulk density.

After the addition of the powder on the build platform, the laser or electron beam, which works with a predefined power and speed, scans the 2-dimensional geometry of the first slice onto the powder bed, causing the metal powder particles to locally melt and fuse together. Then the build platform is lowered by an amount corresponding to the slice thickness, a next layer of metal powder is deposited on the platform and the energy beam scans the powder again as defined by the next slice of 2-dimensional CAD data. This is repeated until the full 3-dimensional part is finished. The solid finalised part is eventually removed from the platform and further processed by dedicated surface and heat treatments, if applicable.

In order for the process to run smoothly and in order to obtain a good surface quality and bulk density of the grown parts, the metal powder must provide a high flowability, otherwise even and homogeneous powder layers cannot be deposited with the necessary high consistency. Furthermore the metal powder must be able to absorb the laser or electron beam energy in such a way, that a defined local melt pool forms. Such a melt pool then fuses together to a dense volume with the neighboured areas and layers below, which have already been processed by the propagating beam in the preceding process steps.

Metal alloy powders of the formerly mentioned classes of conventional alloys, namely different steels, titanium alloys, aluminium or other light weight alloys, nickel- and cobalt-chrome alloys, have been successfully provided for the ALM technologies in recent years mainly by using existing alloy compositions which were already established for traditional production technologies. The necessary powder property spectrum is obtained by control of powder particle shape and size distribution during the powder manufacturing process, which consists in gas or water atomisation of a molten metal stream and subsequent sieving of the obtained powder to the desired size distribution. The fine-tuning of SLM, EBM or SLS process parameters like beam or laser power, wavelength and speed to the specific alloy powder properties have led to the already mentioned successful exploitation of the technology in a wide spread of different industries.

However, little success so far has been obtained with the exploitation of the technology in industries using silver-based alloys, like jewellery and watch industry but also medical industry or specialty applications in high-tech industries like aerospace. While dedicated small-scale laser melting machines, for cost-effective processing of smaller quantities of higher value metals like precious metals into, for example, jewellery products, have been most recently developed and introduced into the market, there is a lack of silver-based alloy powders which have been particularly developed for the laser or electron beam melting or sintering processes. Working with silver-based alloy powders in these processes is particularly difficult due to the known high reflectivities and high thermal conductivities of silver and most of its alloys. A high reflectivity drastically reduces the energy that can be adsorbed by the powder from the energy beam and leads to insufficient local melting and fusing. A high thermal conductivity leads to fast diffusion of the adsorbed energy into neighboured regions, which again leads to insufficiently high local beam energy adsorption and low density of grown metal parts. Furthermore, the exact reproduction of the surfaces of the parts becomes a problem, because the quick diffusion of heat leads to partial melting and fusing of metal powder particles far away from the predefined surface of the part, which results in increased surface roughness. This contradicts the particularly high specific requirements of the respective industries on exact reproduction of surface details, for example for a jewellery or medical item with a particular aesthetic or functional surface design as opposed for example to an automotive part where the focus mainly is on the bulk properties.

Similar processing difficulties in laser melting processes are also known for other alloys with high reflectivity and thermal conductivity, such as gold- and copper-based alloy powders, as for example obvious from the following papers: Mustaq Khan, Phil Dickens, Selective laser melting of pure gold, Gold Bulletin Vol. 43, No.2., p. 114, 2010; Becker, D., Meiners, W., Wissenbach, K., Additive manufacturing of components out of copper and copper alloys by Selective Laser Melting, Additive Manufacturing, International Conference, Loughborough University, 2011. They describe the need for a combination of particularly slow laser scanning speed and/or the use of extraordinary high laser power for processing such metals, which is either or both non-profitable and non-practicable.

The patent JP2009270130 reports that improvements in laser melting of silver and silver alloy powder can be obtained by sulphurizing the surface of the powder, such that its colour turns into a dark brown. This reportedly leads to an increase in energy adsorption by the laser beam and higher densification of as-grown parts. Obviously this solution is not generally applicable but restricted to easily sulphurizable silver-based alloys only (while advanced silver alloys with high resistance against sulphurization exist) and also introduces a high sulphur contamination in the final part.

In the "selective laser sintering" (SLS), the laser beam is not forming a complete pool of molten metal like during the SLM process, but only a partially molten state is achieved which leads to a sintering of the powder into a part with a certain residual porosity. The patent WO2005/025783 describes the fabrication of precious metal products via the SLS process using a mixture of at least two components 1) a basic precious metal powder with a composition near to the finally desired composition, and 2) a lower melting precious-metal containing powder. During the SLS process only the latter is molten and acts as a solder phase, which wets the higher melting metal powder and eventually sinters the mixture together. Further variations of the process are indicated for precious metal based powders in patent WO2005/025783, which range from adding a polymer-based binder phase to the powder mixture or using powders coated with a low-melting metal- or polymer-based phase. Such approaches are also described for other metals and their alloys for example in the patents US2005191200, US2004226405, CN1193849 and CN1333099. All these variations hence make use of powders with additives that act as sintering aids during the SLS process. Silver, as well as other alloy powders with a variety of different additions as sintering aids are also known from conventional press and sintering processes, metal injection moulding (MIM) or metal clay applications. Such powders, powder mixtures and additives are described for example in the patents JP2009167491 and JP2005325411 for press and sintering processes, the patents US5376328, US5328775, JP5132702, US 5000779 and EP0457350 for MIM processes, as well as the patents KR20040067174 and JP8269503 for metal clay applications. In particular, patent US 5000779 describes the use of a Pd-Cu-Ag alloy powder comprising between 5-60% of Pd, Ag and Cu and between 0.2 and 0.8 weight percent of one metalloid selected from boron, phosphorous, silicon and lithium. This alloy powder is used in a method called "supersolidus sintering". The elements boron, silicon, etc. are added to the metal alloy as "sintering aids" in order to lower the solidus temperature for supersolidus sintering and to help hardening of the final part. This process consists in die compaction, isostatic pressing or injection moulding of the powder, usually together with an additional binder component, followed by a heat treatment in a furnace.

The powder contains a maximum of 60% of Ag and the addition of boron, phosphorous, silicon and lithium is not performed in order to increase powder flowability, energy absorption from a laser or electron beam and densification of the final object, but only in order to lower the sintering temperature and help hardening.

None of the aforementioned known approaches provide viable solutions to the above-discussed issues connected to the use of silver alloy powders in direct manufacturing or prototyping of 3-dimensional metal objects by additive layer manufacturing (ALM, for example "Selective laser melting" SLM, "Selective laser sintering" SLS or "Electron Beam Melting" EBM). The preparation of special mixtures of powders, including low-melting 'solder'-type powders or binder components, or the preparation of coated powders involves extra time- and labor-intensive processing steps during powder manufacturing which significantly adds to processing costs. Processes that involve polymer binders furthermore require a separate sintering step after the layerwise manufacturing step, during which the final sintering takes place and the binder is removed from the parts; often a subsequent infiltration process with a low-melting alloy is required to obtain sufficiently dense parts.

In summary it is obvious that there is a strong need for silver-based alloy powders explicitly developed for ALM processes, in particular for selective laser melting, selective laser sintering and electron beam melting. Such powders should contain dedicated alloying additions which help to increase the beam energy adsorption during the manufacturing process. In addition such alloying additions should also increase the flowability of the powder to allow for ALM processing with high consistency and the potential for working with particularly fine powder and reduced layer thickness. In order to minimize processing costs, such additions should be able to be easily added to the alloy formulation during the pre-alloying step before atomization into the powder state.

One object of the present invention is thus to provide a silver-based alloy powder having the above describe properties and advantages with respect to the known powders.

Another object of the present invention regards the use of the silver-based alloy powder in a method of direct manufacturing or prototyping of 3-dimensional metal objects by additive layer manufacturing (ALM), for example Selective laser melting (SLM), Selective laser sintering (SLS) or Electron Beam Melting (EBM). Preferably, the method is Selective laser melting (SLM) or Electron Beam Melting (EBM).

In the context of the present invention it is intended that the term "additive layer manufacturing" can be replaced by one of the following equivalent expressions: 3D printing, Rapid Manufacturing (RM), Direct Manufacturing (DM), Digital Manufacturing, Rapid Prototyping (RP), Rapid Tooling (RT), Direct Tooling (DT), Additive Manufacturing (AM), Free Form Fabrication (FFF), Direct Light Fabrication (DLF). All these definitions refer to the same technique of making 3-dimensional objects layer by layer from a drawing, such as a CAD drawing.

In the context of the present invention, the definitions: Selective laser melting (SLM) and Selective laser sintering (SLS) have the same meaning, although metallurgically the processes are somewhat different as outlined before, and are intended equivalent to each of the following terms: Direct Metal Laser Melting (DMLM), Direct Metal Laser Sintering (DMLS), Laser Cusing, Laser Engineered Net Shaping (LENS), Laser Powder Forming (LPF), Metal Powder Laser Forming (MPLF), Laser Metal Forming (LMF), Direct Laser Forming (DLF), Powder Laser Melting (PLM), Laser Direct Deposition and Laser Powder Cladding, even though particular differences between these related technologies exist especially with respect to the specific powder supply mechanism.

Another aim of the invention is a metal object obtained or obtainable from the silver-based alloy powder of the invention with one of the above method of direct manufacturing or prototyping. Preferably such metal object is a piece of jewellery.

The invention will be hereinafter described in details with the help of the Figures, in which:

- Figure 1 shows a scanning electron microscopy picture of the powder of the invention after sieving and air-classification;
- Figure 2 shows the powder flowability of two silver-based alloy powder; deposited layer thickness 15µm: a) binary 92.5 wt% silver - 7.5 wt% copper alloy powder without further additions, b) 92.5 wt% silver alloy with additions of B, Ge and Si (see example I 9 in table 1);
- Figure 3 shows the metallographic porosity analysis for 92.5 wt% silver alloys (balance: copper), layer thickness 15µm, 95 W laser power: a) binary 92.5 wt% silver - 7.5 wt% copper alloy powder without further additions; b) 92.5 wt% silver alloy with ~ 1.5 wt% of additions (see example II 8 in table 2); c) 92.5 wt% silver alloy with ~ 2.5 wt% additions (see example II 10 in table 2); d) 92.5 wt% silver alloy with ~ 4 wt% additions (see example II 15 in table 2);
- Figure 4 shows: a) four simple ring shapes during the growing process; b) the same four rings as-grown on the platform after removal from the machine;
- Figure 5 shows: 2 jewellery designs in the as-grown state and still connected to the platform via the required support structures (a); 4 finished items with excellent surface quality obtained with the powder of the invention (b),(c), (d).

The present invention regards a silver-based alloy powder for use in a method of direct manufacturing or prototyping of 3-dimensional metal objects, comprising from 70% to 99.99 wt% of silver and from 0.01% to 5 wt%

of at least one element chosen from germanium (Ge), aluminium (Al), silicon (Si) and boron (B), or a mixture thereof.

Preferably, the amount of silver is from 80% to 96 wt%. Preferably, the at least one element is present in an amount from 0.1% to 4 wt%. More preferably the quantity of the at least one element is from 0.5% and 4 wt%. Even more preferably, the amount of the at least one element is from 2% to 4 wt%.

In one embodiment the at least one element is one of Ge or B or Al. In other embodiments a mixture of B with Si or Ge or Al is used. In further embodiments a mixture of all four elements can be used. When only one element or more than one element is used, the amount employed of the single element or of the sum of more than one element is included in the above ranges.

The amount of the at least one element in the silver-based alloy powder varies according to the level of flowability of the powder needed. For example, when good levels of flowability of the powder are needed the amount of the at least one element is preferably from 0.01% to 1 wt%, depending also from the size distribution of the powder.

Preferably, the silver-based alloy powder of the present invention have powder particle sizes included in the range 1- 45 µm.

When improvement of the beam energy absorption in order to increase density of the final object and reduced surface roughness is needed, the amount of the at least one element is, preferably, in the range of 0.5 wt% and 5 wt %, depending in a general way on the required level of process speed, consistency, surface and bulk quality as well as on the size distribution of the powder.

In fact, the Applicant has found that small additions of silicon, germanium, aluminium and/or boron to silver-based alloy powders are very effective in significantly increasing the flowability of the respective alloy powders.

Without being bound to any particular theory, it is assumed that the beneficial effect of these additions is related to a mechanism of oxide layer formation on the surface of the silver alloy powder particles, namely the preferential formation of silicon oxide, germanium oxide, boron oxide, aluminium oxide or combinations and variations thereof. All these elements have higher affinity to oxygen than the common alloying elements and therefore a higher tendency to form thin surface oxide layers on top of the silver alloy powder particles during the powder manufacturing process or during subsequent storage or handling. The formation of surface oxide layers on the powder particles can explain a lower tendency to agglomeration of the alloy powder particles, because the surface activity, namely the ability or tendency to form metal-to-metal atom bonds between powder particles that are in contact to each other, is drastically reduced by the presence of such surface oxide layers.

The applicant has also found that with the additions of silicon, germanium, aluminium and/or boron to silver-based alloy powders a significant improvement in beam energy adsorption during ALM processes like SLM, SLS and

EBM can be obtained. This improvement can manifest itself amongst others by:

- an increase in densification during processing with constant laser power and speed;
- the possibility to increase the beam speed at constant laser power while maintaining the same high level of densification;
- a reduced surface roughness on the as-grown parts.

While a reduced surface roughness is obvious from inspection of as-built parts, a high level of densification manifests itself by a reduced level of residual porosity as revealed by metallographic cross sectional analysis or surface finishing of as-built parts.

The beneficial effect of the additions is attributed to a combination of a decrease in reflectivity of the metal surfaces and a decrease of the thermal conductivity of the alloy. According to Edelmetall-Taschenbuch, ed. Günter Beck, Degussa AG, Frankfurt; Verlag Hüthig GmbH, Heidelberg, 1995; p. 153-156, additions like germanium and aluminium have a particularly strong increasing influence on electrical resistivity of silver, which in general is inversely related to the thermal conductivity of metals and their alloys. Furthermore it is assumed that the aforementioned surface oxide layer formation on powder particles, which supposedly is obtained by the same alloying additions, also contributes to lower reflectivity and higher energy absorption during the beam treatment. The surface oxide layer formation can contribute also to lowering of the heat diffusion between neighboured powder particles. The latter especially explains also the reduction of surface roughness on as-grown parts, because lower heat conduction between adjacent powder particles reduces the unwanted effect of partial melting and sintering of powder particles next to the surface boundary as defined by the CAD geometry.

In a preferred embodiment of the invention the silver-based alloy powder further contains at least one of the following metals: Cu, Au, Pd, Pt, Mn, Co, Ni, Fe, Zn, Sn, In, Ga, Ru, Ir, Rh, or a mixture thereof.

The above metals are common alloying elements normally used to vary the basic properties of silver, such as colour, hardness, workability, corrosion resistance, wear resistance, optical and acoustic properties and so on. The at least one alloying element can be included in the powder in the following amounts:

$0 \leq Cu \leq 29.99$ wt%; $0 \leq Au \leq 20$ wt%; $0 \leq Pd \leq 20$ wt%; $0 \leq Pt \leq 20$ wt%; $0 \leq Mn \leq 20$ wt%; $0 \leq Co \leq 15$ wt%; $0 \leq Ni \leq 10$ wt%; $0 \leq Fe \leq 10$ wt%; $0 \leq Zn \leq 10$ wt%; $0 \leq Sn \leq 10$ wt%; $0 \leq In \leq 10$ wt%; $0 \leq Ga \leq 10$ wt%; $0 \leq Ru \leq 5$ wt%; $0 \leq Ir \leq 5$ wt%; $0 \leq Rh \leq 5$ wt%. Mixtures of the listed alloy elements can be present in the silver-based alloy powder.

The preferred alloying element is copper.

In further preferred embodiments the silver-based alloy powder comprises the silver-based alloys commonly used in jewellery and for other decorative metalware applications, namely: 800 Ag (which is an alloy of Ag and mainly Cu comprising 80 wt% of Ag); 835 Ag (which is an alloy of Ag and mainly Cu comprising 83.5 wt% of Ag); 900 Ag (which is an alloy of Ag and mainly Cu comprising

90 wt% of Ag); 925 Ag (which is an alloy of Ag and mainly Cu comprising 92.5 wt% Ag; so-called sterling silver); 959 Ag (which is an alloy of Ag and mainly Cu comprising 96 wt% Ag; so-called Brittania silver); 999 Ag (which is an alloy of Ag and mainly Cu comprising 99.9 wt% Ag).

Another object of the invention is a process for the preparation of the silver-based alloy powder of the invention.

The process of silver-based alloy powder manufacturing starts with weighing and mixing either the pure metals and/or suitable master alloys in the right weight proportion corresponding to the desired final powder alloy composition. Alternatively, a completely pre-alloyed material of the desired composition can be used if available from a corresponding pre-processing step. With "completely pre-alloyed material" is intended an alloy of the desired final composition, that has been obtained via a separate preceding manufacturing step which then involved usage of pure elements or master alloys. With "master alloy" is intended a pre-material which contains difficult-to-process elements like for example silicon, boron in exactly defined concentrations usually much higher than required in the final alloy. By using the master alloy in the right proportion and mixing it with the other elements or master alloys, the addition(s) then are "diluted" to the level desired for the final composition. A master alloy, once prepared, can be used conveniently for the preparation of different final alloy compositions.

The starting materials can be in any possible form, such as powder, granules, chopped wire, sectioned sheet or rod.

The material is placed in a crucible, preferably made of graphite, clay graphite or ceramic, and then heated to a temperature sufficiently high for allowing complete melting and homogenization of the alloy, preferably at a temperature between 500°C and 1600°C. The heating is preferably realized via induction heating, resistance heating or torch heating. The heating can be carried out in an open equipment on air, but preferably a protective gas cover is used to avoid excessive oxidation and uptake of gas by the melt. Alternatively a closed equipment, with a melting chamber that can be closed with a lid, can be used which may allow for a continuous flow of protective cover gas, or even an evacuation of the chamber followed by a backfill with protective gas.

After complete melting and homogenization is achieved, the metal temperature is preferably adjusted to a temperature typically around 100 - 200°C above the liquidus temperature of the alloy.

After that, the atomization process is initiated by letting the metal flow through a tiny nozzle. This is preferably done by either of the two following methods: lifting of a stopper rod, which formerly closed a pour hole in the bottom of a crucible, or tilt pouring the metal into a pre-heated tundish with the nozzle embedded in the bottom of the tundish.

When the liquid metal leaves the nozzle, it is finally sprayed into tiny melt droplets with the aid of high pressure gas or high pressure water. Preferably "gas atomization" is applied for obtaining predominantly spherical powder particles. The droplets then are quenched by a cooling media, such as water, a mix of water and alcohol, or a protective gas and eventually solidify to powder particles. The resulting powder particle size and shape distribution amongst others depends on the alloy composition, melt temperature and velocity, the nozzle geometry, the pressure and temperature of the atomization gas or water, as well as the cooling media.

The powder is collected at the bottom of a tank that is completely or partially filled with the cooling media, usually in a so-called receiver, which can be dismantled from the tank later on. Part of the powder can also be collected in an additional receiver connected to a cyclone, which may be required to remove especially fine powder particles travelling with the processing gases. After cooling and drying the powder, the desired powder particle size fraction is obtained by sieving and/or air-classification.

The silver-based alloy powder of the present invention is used to make metal objects, preferably jewellery articles, for examples rings, earrings, bracelets, broches, chains, necklaces or pendants, components for the watch, spectacle or pen industry, components for the accessory industry (for examples closures, clasps or buttons for clothes or bags), objects or part of objects of art, for decoration or tableware, components for the medical industry or components for the high-tech industries, such as automotive and aerospace industry.

The metal objects obtainable with the silver-based alloy powder of the invention are preferably manufactured with an additive layer manufacturing process (ALM), preferably with a selective laser melting process (SLM), a selective laser sintering process (SLS) or an electron beam melting process (EBM).

The additive layer manufacturing process comprises the steps of:

- preparing a digital drawing of a 3-dimensional object digitally separated in 2-dimensional slices perpendicular to the later growing direction of the object;
- loading the said digital drawing into an additive layer manufacturing process machine, preferably a selective laser melting machine, a selective laser sintering machine or an electron beam melting machine, comprising a build platform on which the object is built layer by layer;
- spreading the silver-based alloy powder on a build platform by a roller or blade to form a layer of powder or adding the powder by a nozzle only in the regions where it is actually needed, according to the digital drawing;
- scanning, with a laser or electron beam, the 2-dimensional geometry of the first slice of the digital drawing onto the powder layer, causing the silver-based alloy powder particles to locally melt and fuse together or to sinter;
- lowering the build platform by an amount corresponding to the 2-dimentional slice thickness;
- depositing a next layer of silver-based alloy powder on the build platform;

- scanning, with a laser or an electron beam, the powder again as defined by the next 2-dimensional slice;
- repeating the depositing and scanning steps until the full 3-dimensional part is finished.

The solid finalised part is eventually removed from the build platform and further preferably processed by dedicated surface and heat treatments.

The 2-dimentional slice thickness is preferably between 10 and 50 µm.

The digital drawing is preferably a CAD drawing.

EXAMPLES

Example for silver alloy powder manufacturing

4 kg of pre-alloyed material with a composition corresponding to example II-13 of Table 2 (see below) was heated to a melt temperature of approximately 1150-1200°C in an open melting equipment using a graphite crucible with a nitrogen cover gas. Atomization was initiated by the stopper rod-mechanism and a metal flow through a graphite nozzle with an approximate internal diameter of 1.5 mm. The liquid metal stream was gas atomized using nitrogen gas of ambient temperature with a pressure of approximately 25 bars. The powder was collected in a tank filled with water and allowed to settle for a few hours. After decanting the excessive water from the receiver, the powder was dried on hot air (~ 50°C) over night. A desired size fraction of 10-30µm was obtained by sieving and air-classification. The resulting fraction of over- and undersized powder was remelted again, atomized and processed in a similar way, resulting in a total of ~3kg of usable powder in the desired size range, which corresponds to a 75% yield of

usable powder. A scanning electron microscopy picture of the powder after sieving and air-classification is shown in Figure 1.

Improvement of powder flowability

The silver-based alloy powder compositions reported in table 1 below have been produced using the above process.

Table 1

Example Nr.	wt% B	wt% Si	wt% Ge	wt% Al
I 1	0.02			
I 2	0.01	0.05		
I 3	0.01	0.15		
I 4	0.015		0.5	
I 5	0.015			0.5
I 6		0.2	0.5	
I 7		0.2		0.5
I 8			0.5	0.5
I 9	0.01	0.1	0.4	
I 10	0.01	0.1		0.4
I 11			0.9	
I 12				0.9
I 13	0.01	0.15	0.75	
I 14	0.01	0.15	0.5	0.3

In order to measure the effect of the additions of B, Si, Ge and/or Al on the flowability properties of the powder, the ability to evenly deposit thin (10-20μm) layers of powder in a common SLM machine was tested.

A reliable quantification of flowability is a difficult task, and usually common methodologies for quantifying flowability fail to qualify powders which are flowable enough for ALM processes. Therefore, the above test was considered to be suitable for testing the flowability of the powder in the context of the invention.

Figure 2 compares the flowability of a binary silver-based alloy powder containing 7.5 wt% Cu (reference) with a powder containing additions of germanium, silicon and boron (example Nr. I 9, table 1) at the expense of copper. Both powders were characterized by spherical particles and an identical size distribution with 95% of the powder particles being in the size range between 10 and 30 µm. The figure clearly demonstrates the different ability of generating an even powder layer of a layer thickness of 15µm in the SLM machine, which is attributed to the beneficial influence of the additions on the flowability of the powder.

Table 1 lists also some further examples of silver-based alloy compositions with 92.5 wt% silver (balance Cu) and a maximum of nearly 1 wt% addition, for which a significant beneficial effect on powder flowability was observed.

Improvement of densification during laser or electron beam melting

The silver-based alloy powder compositions described in table 2 have been produced using the above described process.

Table 2

Example Nr.	wt% B	wt% Si	wt% Ge	wt% Al
II 1	0.015		0.5	

II 2	0.015			0.5
II 3			0.5	0.5
II 4			0.9	
II 5				0.9
II 6	0.01	0.15	0.75	
II 7	0.01	0.15	0.5	0.3
II 8		0.2	1.3	
II 9	0.01	0.15		1.3
II 10	0.01	0.2	1.15	1.15
II 11	0.01		2.5	
II 12	0.01			2.5
II 13			3.5	
II 14				3.5
II 15		0.35	3.65	
II 16		0.35		3.65
II 17	0.01	0.2	2.3	2.3
II18	0.01	0.1	4.5	
II19	0.01	0.1		4.5

Additions of silicon, germanium, aluminum and/or boron to the silver-based alloy powders of the invention determine, not only an improvement of flowability, but also a significant improvement in beam energy adsorption during ALM. The higher absorption of beam energy can determine:

- an increase in densification during processing with constant laser power and speed;
- the possibility to increase the beam speed at constant laser power while maintaining the same high level of densification; and/or

- a reduced surface roughness on the as-grown parts.

While a reduced surface roughness is obvious from inspection of as-built parts, a high level of densification manifests itself by a reduced level of residual porosity as revealed by metallographic cross sectional analysis or surface finishing of as-built parts.

Figure 3 shows for example the metallographic cross sectional porosity analysis of a series of SLM trials carried out with a layer thickness of 15 µm on a silver alloy powder with 92.5 wt% silver, containing increasing levels of additions of boron, silicon, germanium and aluminium at the expense of copper. The powders were characterized by comparable size and shape distributions (10-30µm, spherical). An addition of in sum ~ 1.5 wt% (example II 8, table 2) provides a significantly lower level of porosity if compared to an otherwise binary 925 silver-copper alloy powder. A very high level of densification with the same SLM process parameters is obtained if the level of additions in sum is increased to significantly higher contents in the range of 2-4 wt% (examples II 10 and II 15).

Obviously, the additions lead to a significantly improved beam energy absorption during the beam melting process, which allows for more complete local powder melting and fusing of consecutive layers to dense parts with considerably lower residual level of porosity.

Table 2 lists some examples of silver-based alloy compositions with 92.5 wt% silver (balance Cu) for which a significant beneficial effect on densification during SLM processing was observed.

Example of parts produced from silver-based alloy powder of the invention by additive layer manufacturing

This example describes the use of the silver alloy powder (alloy composition II-13), manufactured according to the above method, for the production of 925 silver jewellery items by selective laser melting. A laser melting equipment with a nominal maximum laser energy of 100 W and a nominal fiber laser spot size between ~ 20-30 µm was used. Approximately 2.5 kg of powder were loaded in the powder reservoir. Parts were grown on a 50mm x 50 mm platform with a powder layer thickness of 15µm, a laser power of 95 W and a laser speed of 200 mm/s.

Figure 4 shows four simple ring shapes during the growing process and the same 4 rings as-grown on the platform after removal from the machine. Figure 5 shows 2 intricate jewellery designs in the as-grown state and still connected to the platform via the required support structures, as well as examples for finished items with excellent surface quality eventually obtained from these manufacturing jobs.

CLAIMS

1. Use of a silver-based alloy powder comprising from 70% to 99.99 wt% of silver and from 0.01% to 5 wt% of at least one element chosen from germanium (Ge), aluminium (Al), silicon (Si) and boron (B), or a mixture thereof, for the manufacture of a 3-dimensional metal object with a direct manufacturing or prototyping process, preferably with an additive layer manufacturing (ALM) process.
2. Use of the powder according to claim 1, in which the powder comprises from 70% to 99.99 wt% of silver and from 0.01% to 5 wt% of at least one element chosen from germanium (Ge) or boron (B).
3. Use of the powder according to claim 1 or 2, comprising from 70% to 99.99 wt% of silver and from 0.01% to 5 wt% of at least boron (B) and germanium (Ge), or boron (B) and silicon (Si), or boron (B) and aluminium (Al).
4. Use of the powder according to any claim 1 to 3, comprising from 70% to 99.99 wt% of silver and from 0.01% to 5 wt% of boron (B), germanium (Ge), silicon (Si) and aluminium (Al)
5. Use of the powder according to any claim 1 to 4, in which the amount of silver is from 80% to 96 wt%.
6. Use of the powder according to claim 1, in which said at least one element is present in an amount from 0.1% to 4 wt%, preferably from 0.5% and 4 wt%, more preferably from 2% to 4 wt%.
7. Use of the powder according to any claim 1 to 6, comprising powder particles having sizes included in the range 1 - 45 µm.

8. Use of the powder according to any claim 1 to 7, further comprising at least one of the following alloying element: Cu, Au, Pd, Pt, Mn, Co, Ni, Fe, Zn, Sn, In, Ga, Ru, Ir, Rh, or a mixture thereof.

9. Use of the powder according to claim 8, in which the at least one alloying element can be included in the powder in the following amounts: $0 \leq Cu \leq 29.99$ wt%; $0 \leq Au \leq 20$ wt%; $0 \leq Pd \leq 20$ wt%; $0 \leq Pt \leq 20$ wt%; $0 \leq Mn \leq 20$ wt%; $0 \leq Co \leq 15$ wt%; $0 \leq Ni \leq 10$ wt%; $0 \leq Fe \leq 10$ wt%; $0 \leq Zn \leq 10$ wt%; $0 \leq Sn \leq 10$ wt%; $0 \leq In \leq 10$ wt%; $0 \leq Ga \leq 10$ wt%; $0 \leq Ru \leq 5$ wt%; $0 \leq Ir \leq 5$ wt%; $0 \leq Rh \leq 5$ wt%.

10. Use of the powder according to claim 8 or 9, in which the alloying element is copper.

11. Use of the powder according to any claim 1 to 10, in which said additive layer manufacturing (ALM) process is chosen among: selective laser melting (SLM), selective laser sintering (SLS) and electron beam melting (EBM).

12. Use of the powder according to claim 1 or 11, in which said 3-dimensional metal object is a piece of jewellery, preferably a ring, earrings, a bracelet, a broche, a chain, a necklace or a pendant; a component for the watch, spectacle or pen industry; a component for the accessory industry, preferably a closure, clasp or button for clothes or bags; an object or part of an object of art, for decoration or tableware; a component for the medical industry; or a component for the high-tech industries, preferably for the automotive and aerospace industry.

13. A process for the manufacturing of a 3-dimensional metal object, comprising the steps of:

- preparing a digital drawing of a 3-dimensional object digitally separated in 2-dimensional slices perpendicular to the later growing direction of the object;
- loading the said digital drawing into an additive layer manufacturing process machine, preferably a selective laser melting machine, a selective laser sintering machine or an electron beam melting machine, comprising a build platform on which the object is built layer by layer;
- spreading a silver-based alloy powder comprising from 70% to 99.99 wt% of silver and from 0.01% to 5 wt% of at least one element chosen from germanium (Ge), aluminium (Al), silicon (Si) and boron (B), or a mixture thereof, on a build platform by a roller or blade to form a layer of powder, or adding the powder by a nozzle only in the regions where it is actually needed, according to the digital drawing;
- scanning, with a laser or electron beam, the 2-dimensional geometry of the first slice of the digital drawing onto the powder layer, causing the silver-based alloy powder particles to locally melt and fuse together or to sinter;
- lowering the build platform by an amount corresponding to the 2-dimentional slice thickness;
- depositing a next layer of silver-based alloy powder on the build platform;
- scanning, with a laser or an electron beam, the powder again as defined by the next 2-dimensional slice;

- repeating the depositing and scanning steps until the full 3-dimensional part is finished.

14. A 3-dimensional metal object obtainable with the process of claim 13.
15. The 3-dimensional metal object according to claim 14, in which the object is a piece of jewellery, preferably a ring, earrings, a bracelet, a broche, a chain, a necklace or a pendant; a component for the watch, spectacle or pen industry; a component for the accessory industry, preferably a closure, clasp or button for clothes or bags; an object or part of an object of art, for decoration or tableware; a component for the medical industry; or a component for the high-tech industries, preferably for the automotive and aerospace industry.
16. A silver-based alloy powder comprising from 70% to 99.99 wt% of silver and from 0.01% to 5 wt% of at least one element chosen from germanium (Ge) or boron (B).
17. The silver-based alloy powder according to claim 16, comprising from 70% to 99.99 wt% of silver and from 0.01% to 5 wt% of at least boron (B) and germanium (Ge), or boron (B) and silicon (Si), or boron (B) and aluminium (Al).
18. The silver-based alloy powder according to claim 16 or 17, comprising from 70% to 99.99 wt% of silver and from 0.01% to 5 wt% of boron (B), germanium (Ge), silicon (Si) and aluminium (Al)
19. The powder according to any claim 16 to 18, in which the amount of silver is from 80% to 96 wt%.
20. The powder according to claim 16, in which said at

least one element is present in an amount from 0.1% to 4 wt%, preferably from 0.5% and 4 wt%, more preferably from 2% to 4 wt%.

21. The powder according to any claim 16 to 20, comprising powder particles having sizes included in the range 1 - 45 µm.

22. The powder according to any claim 16 to 21, further comprising at least one of the following alloying element: Cu, Au, Pd, Pt, Mn, Co, Ni, Fe, Zn, Sn, In, Ga, Ru, Ir, Rh, or a mixture thereof.

23. The powder according to claim 22, in which the at least one alloying element can be included in the powder in the following amounts: $0 \leq Cu \leq 29.99$ wt%; $0 \leq Au \leq 20$ wt%; $0 \leq Pd \leq 20$ wt%; $0 \leq Pt \leq 20$ wt%; $0 \leq Mn \leq 20$ wt%; $0 \leq Co \leq 15$ wt%; $0 \leq Ni \leq 10$ wt%; $0 \leq Fe \leq 10$ wt%; $0 \leq Zn \leq 10$ wt%; $0 \leq Sn \leq 10$ wt%; $0 \leq In \leq 10$ wt%; $0 \leq Ga \leq 10$ wt%; $0 \leq Ru \leq 5$ wt%; $0 \leq Ir \leq 5$ wt%; $0 \leq Rh \leq 5$ wt%.

24. The powder according to claim 22 or 23, in which the alloying element is copper.

25. A process for the preparation of the silver-based alloy powder according to any claim 16 to 24 comprising the steps of:

- providing a mixture of pure or pre-alloyed metals;
- heating the mixture at a temperature between 500°C and 1600°C to give a molten mixture;
- atomizing the molten mixture by flowing the mixture through a nozzle and spraying it into droplets by applying high pressure gas or high pressure water
- optionally drying the collected powder and subsequently sieving and/or classifying it to obtain a

defined size distribution.

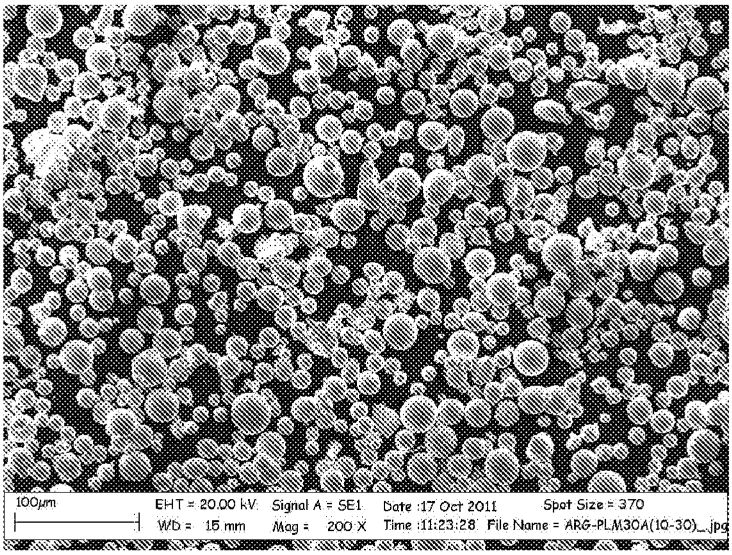
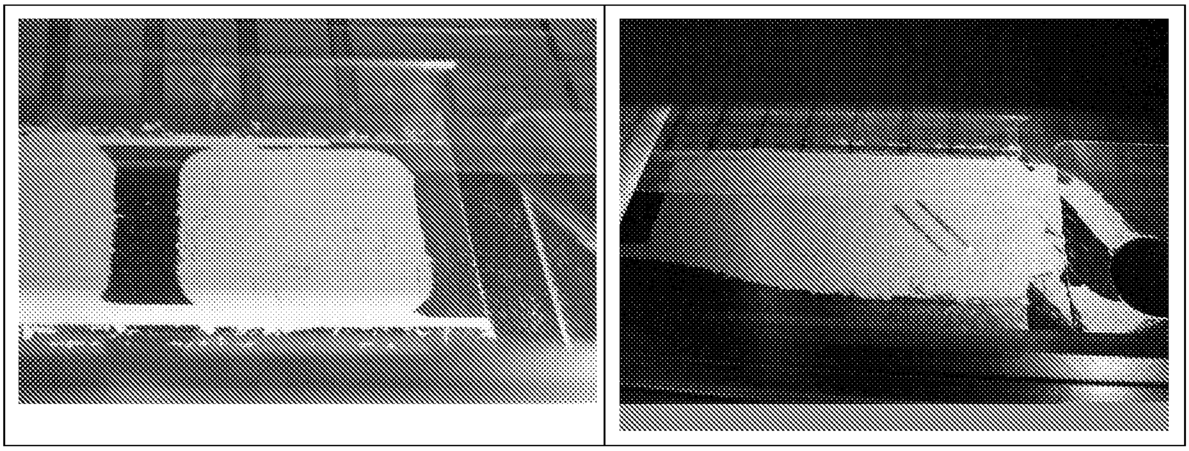

100µm
EHT = 20.00 kV
Signal A = SE1
Date :17 Oct 2011
Spot Size = 370
WD = 15 mm
Mag = 200 X
Time :11:23:28
File Name = ARG-PLM30A(10-30)_.jpg

Fig. 1



a) b)

Fig. 2

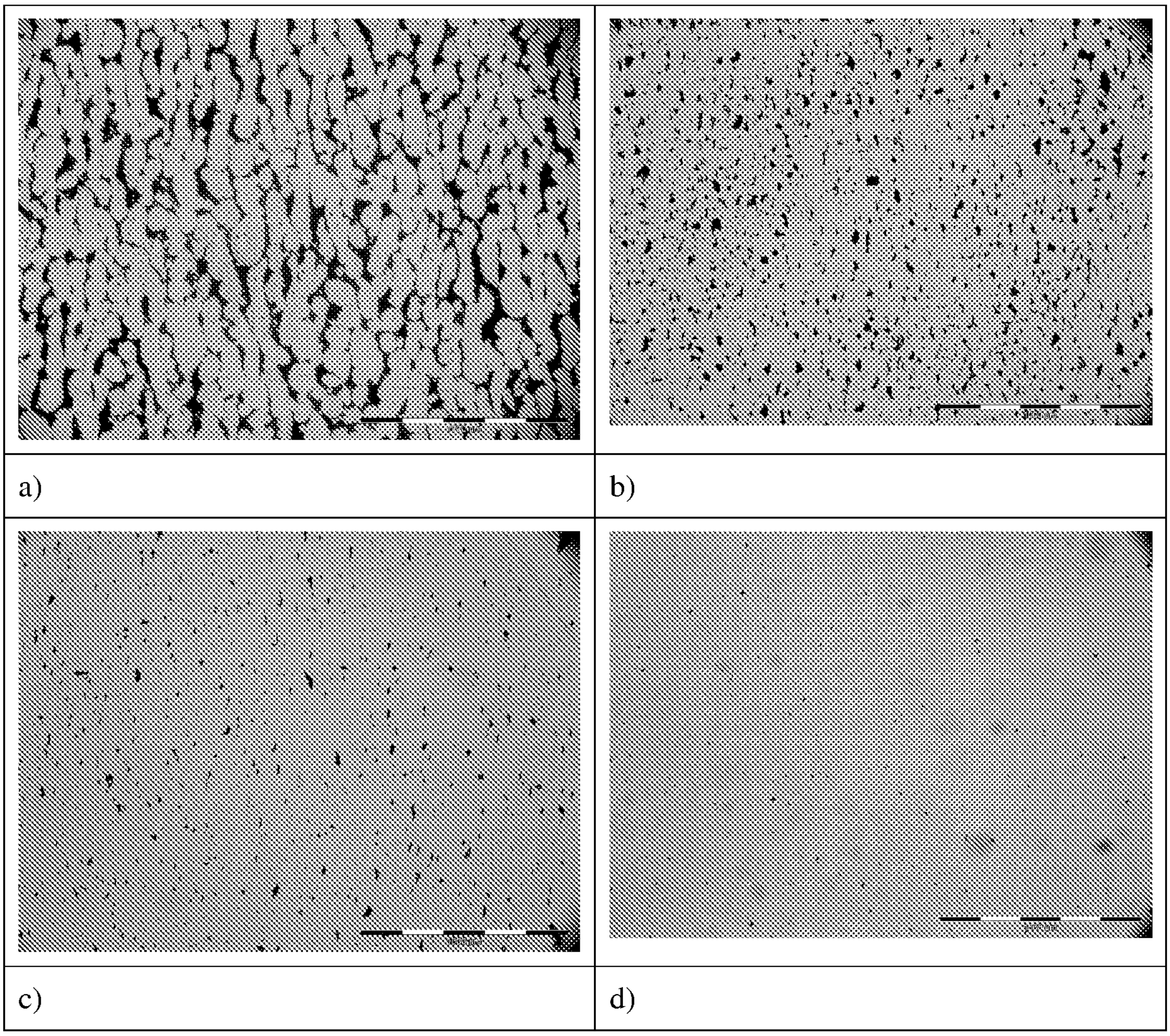


Fig. 3

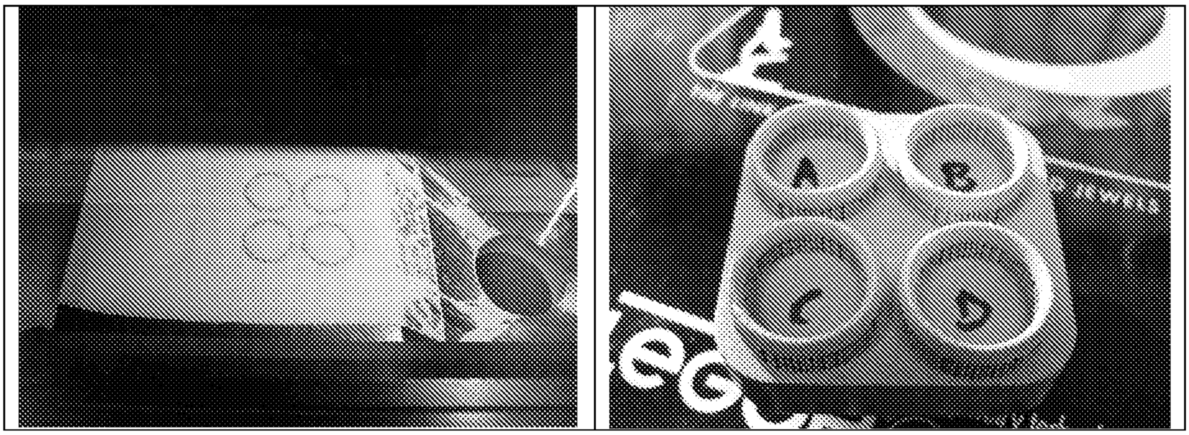
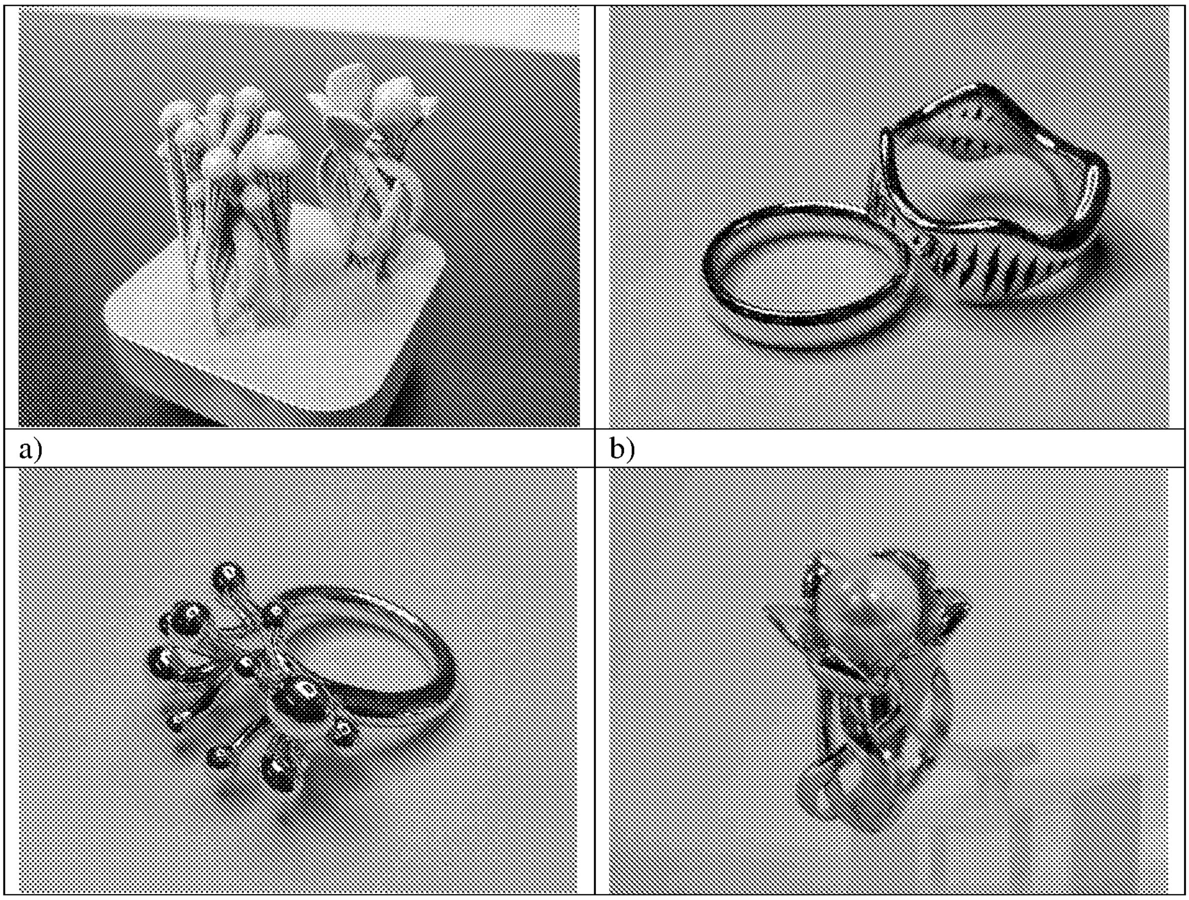


Fig. 4



a) b)

c) d)

Fig. 5