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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
27 April 2023 (27.04.2023)

WIPO | PCT

(10) International Publication Number
WO 2023/067191 A1

(51) International Patent Classification:
B22F 1/054 (2022.01) *B22F 1/107* (2022.01)
B22F 9/24 (2006.01) *B22F 9/30* (2006.01)
B22F 1/0545 (2022.01) *B22F 7/06* (2006.01)

(21) International Application Number:
PCT/EP2022/079478

(22) International Filing Date:
21 October 2022 (21.10.2022)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
21204082.8 21 October 2021 (21.10.2021) EP
22163294.6 21 March 2022 (21.03.2022) EP

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(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, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, 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, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *as to the identity of the inventor (Rule 4.17(i))*
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

Published:
— *with international search report (Art. 21(3))*
— *in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE*

(54) **Title:** COMPOSITION FOR SINTERING COMPRISING AN ORGANIC SILVER PRECURSOR AND PARTICLES OF AGGLOMERATED SILVER NANOPARTICLES

(57) **Abstract:** The present invention relates to a composition that is suitable for joining two components by sintering. The composition comprises an organic silver precursor as defined herein and particles that have an average size of ≤ 20 µm and that comprise agglomerated silver nanoparticles. The ratio of the weight of the silver precursor to the weight of the particles is ≤ 0.25.

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Composition for sintering comprising an organic silver precursor and particles of agglomerated silver nanoparticles

Field of the Invention

The present invention relates to a composition that is suitable for joining two components by sintering. The composition comprises an organic silver precursor and particles that comprise agglomerated silver nanoparticles. The ratio of the weight of the silver precursor to the weight of the particles is ≤ 0.25.

Background of the Invention

Recent developments in electronics and microtechnology have been dominated by increasing miniaturization and greater complexity of components. This progressive miniaturization, in particular in power electronics, has resulted in a higher power density and an associated increase in the operating temperature of the components. Higher power as well as space- and weight-saving designs are making heat management in electronic housings difficult, resulting in more intense heating of the solder joints. This may lead to localized overheating that may result in destruction of the solder joint. The reliability of alloys currently in use is approaching its limits.

Soft solders are generally used in areas where temperature-sensitive materials are to be joined. This involves microelectronics and electrical engineering in particular. In the past, solders containing lead were frequently used for this purpose, but due to their health and environmental hazards they are no longer allowed in many countries and have had to be replaced by other solder materials.

The most common replacement of lead in joining materials is silver. Due to its very high melting temperature (961.8 °C) and very high conductivity, which is even higher than the conductivity of copper, silver provides numerous advantages in joining components. However, the high melting point prohibits the use of elemental silver as solder material. Therefore, silver-organic complexes that provide silver particles in the nanometer range are commonly used to alleviate these issues.

Due to a phenomenon known as size-dependent melting point depression, silver particles in the lower nanometer range have significantly lower melting temperatures than the respective bulk material. Such a melting temperature reduction is exploited during sintering. It is thus possible to obtain silver layers with silver nanoparticles at low temperatures of 200 °C to 300 C.

Silver (nano)particles that are formed by heating silver-organic complexes can be used as sintering material. The silver-organic complexes are applied to a joint between two components as paste or as compacted powder (pellet). Subsequent heat treatment to join the components may be performed at ambient or elevated pressure.

The existing prior art discloses applications of silver-organic complexes.

EP 2 838 690 B1 discloses a sintering material containing silver(I)-2-[2-(2-methoxyethoxy)ethoxy]acetate as silver precursor which forms silver nanoparticles at a temperature below 200°C. The sintering material also contains uncoated and agglomerated silver particles, wherein the weight ratio between the silver precursor and the silver particles is between 1:0.25 to 1:1.5. The sintering material may additionally contain a copper organic precursor which also forms nanoparticles upon heating. The sintering material could be prepared as a paste when the components are suspended in alcohol or as a powder.

EP 2159270 A1 discloses a process for the production of electrically conductive structures, wherein a solution of a metal carboxylate in a coordinating liquid is applied on the surface by means of in jet printing. The solution is then heated, leading to at least partial decomposition of the carboxylate and formation of the respective metal such as Ag.

DE 10 2009 040 076 A1 discloses a metal paste, wherein metal particles are enclosed in a coating containing at least one organic compound. The paste also contains a metal precursor and a solvent to suspend the components. Lastly, the paste contains sintering agents in form of either organic peroxides, inorganic peroxides or inorganic acids. DE 10 2009 040 078 A1 discloses a similar approach, wherein the sintering agents are selected from salts of organic acids, esters of organic acids or carbonyl complexes.

DE 10 2007 046 901 A1 discloses a joining method in which elemental silver is formed from a silver precursor between the contact surfaces. The silver sintering paste used contains silver oxide, silver lactate, or silver carbonate as the silver precursor, each of which forms metallic silver at temperatures below 300°C, in particular below 250°C. The silver sintering paste also contains a gel composed of carboxylic acid components and amine components, and a polar solvent such as alcohol. The silver precursor and silver or copper particles are dispersed in the gel.

Despite significant progress in joining material technologies, a number of issues remain. For example, known sintering pastes contain a relatively high proportion of additives which makes it difficult to obtain contamination-free silver sintering layers. During the sintering process,

additives may decay and some decomposition products may gas out, which results in the formation of voids and sintering layers having a high porosity. Furthermore, various additives and silver organic complexes significantly decrease the content of elemental silver in the material, thus increasing amounts of sintering material might be required for efficient joining. In contrast to known sintering pastes, the composition according to the invention forms contamination-free sintering layers of low porosity with minimal use of material.

Based on the above-mentioned state of the art, the objective of the present invention is to provide means and methods to improve Ag-based sintering, particularly pressure-less and low-pressure-assisted Ag-based sintering processes. This objective is attained by the subject-matter of the independent claims of the present specification, with further advantageous embodiments described in the dependent claims, examples, figures and general description of this specification.

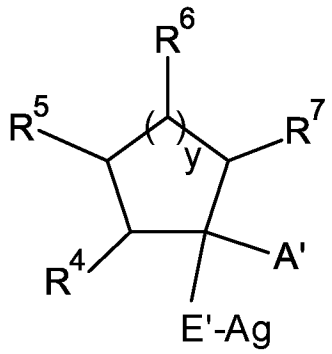
Summary of the Invention

A first aspect of the invention relates to a composition for sintering. The composition comprises:

a. a silver precursor of formula (I):

$$A\text{-}(R^1\text{-}X)_m\text{-}(R^2)\text{-}E\text{-}Ag \qquad (I), \text{ or}$$

a silver precursor of formula (II):



(II), or

a mixture of the silver precursors of formula (I) and/or (II) or a complex formed thereof, wherein

- A and A' is selected from Z-Y- and Ag-Y-, wherein
  - Y is selected from -O-, -S-, -N(R^3)-, -N=, =N-, -O-C(=O)-, particularly -O-, -N(R^3)-, -N=, =N-, -O-C(=O)-, more particularly -O-, -O-C(=O)-,

with R^3 being selected from H, a C_1-C_6-alkyl, and an aryl, wherein the aryl is optionally substituted by one or more substituents independently selected from a C_{1-4}-alkyl, and

- Z is selected from H, a C_1-C_6-alkyl and an aryl, wherein the aryl is optionally substituted by one or more substituents independently selected from a C_{1-4}-alkyl,

- each R^1 independently of any other R^1 is selected from a C_1-C_{18}-alkyl, particularly a C_1-C_{12}-alkyl, more particularly a C_1-C_6-alkyl,
- R^2 is a C_1-C_{18}-alkyl, particularly a C_1-C_{12}-alkyl, more particularly a C_1-C_6-alkyl,
- X is selected from O, S, -N(R^3)-, particularly from O and S, more particularly O,
  - wherein R^3 is defined as above,
- E and E' is selected from -O-, -S-, -N=, =N-, -C(=O)-O- or -N(R^3)-,
  - wherein R^3 is defined as above,
- m is between 1 and 27, particularly between 1 and 18, more particularly between 1 and 10, even more particularly between 1 and 7, wherein the sum of C atoms of all R^1 does not exceed 54, particularly 36, more particularly 18,
- R^4, R^5, R^6, R^7 are each independently selected from H and C_{1-4}-alkyl, particularly H and C_{1-2}-alkyl, more particularly H,
- y is between 1 and 3, particularly y is 1 or 2, more particularly y is 1,

b. a particle comprising, particularly consisting of, agglomerated silver nanoparticles, wherein said particle has an average size of ≤ 20 µm, wherein the ratio of the weight of the silver precursor to the weight of the particle is ≤ 0.25, particularly between 1:4 and 1:15.

Terms and definitions

For purposes of interpreting this specification, the following definitions will apply and whenever appropriate, terms used in the singular will also include the plural and vice versa. In the event that any definition set forth below conflicts with any document incorporated herein by reference, the definition set forth shall control.

The terms “comprising,” “having,” “containing,” and “including,” and other similar forms, and grammatical equivalents thereof, as used herein, are intended to be equivalent in meaning and to be open ended in that an item or items following any one of these words is not meant to be an exhaustive listing of such item or items, or meant to be limited to only the listed item or items. For example, an article “comprising” components A, B, and C can consist of (i.e., contain only) components A, B, and C, or can contain not only components A, B, and C but also one or more other components. As such, it is intended and understood that “comprises” and similar forms thereof, and grammatical equivalents thereof, include disclosure of embodiments of “consisting essentially of” or “consisting of.”

Where a range of values is provided, it is understood that each intervening value, to the tenth of the unit of the lower limit, unless the context clearly dictate otherwise, between the upper and lower limit of that range and any other stated or intervening value in that stated range, is encompassed within the disclosure, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included in the disclosure.

Reference to “about” a value or parameter herein includes (and describes) variations that are directed to that value or parameter per se. For example, description referring to “about X” includes description of “X.”

As used herein, including in the appended claims, the singular forms “a,” “or,” and “the” include plural referents unless the context clearly dictates otherwise.

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art.

In the context of the present invention, the term “particle” relates to a particle that comprises or (essentially) consists of agglomerated nanoparticles. Several nanoparticles agglomerated to form said particle. A particle that is suitable for the composition claimed has an average size of ≤ 20 µm, particularly of less than 20 µm. A particle may be obtained from silver nitrate by reduction with sodium borohydride in aqueous solution. As the agglomeration is a random process, the shape of particles may vary. Typically, a particle has a dendritic (irregularly branched/hyperbranched) structure that is formed during the agglomeration of several nanoparticles. The overall shape of a particle may be irregularly shaped, spherical or in form of a flake.

In the context of the present invention, the term “nanoparticle” relates to a metallic particle, particularly a silver or copper particle, more particularly a silver particle, having a size in the nanometer range, particularly having a size from 100 nm to 250 nm.

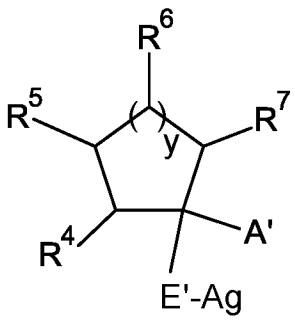
Detailed Description of the Invention

A first aspect of the invention relates to a composition for sintering. The composition comprises:

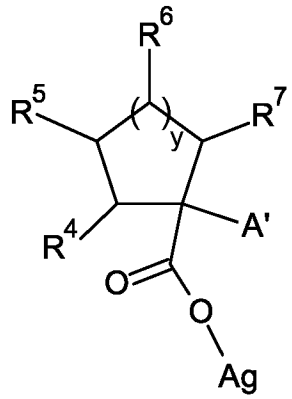
a. a silver precursor of formula (I):

$A\text{-}(R^1\text{-}X)_m\text{-}(R^2)\text{-}E\text{-}Ag$ (I), or

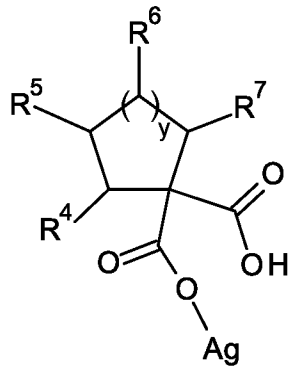
a silver precursor of formula (II), particularly of formula (IIa), more particularly of formula (IIb):



(II),



(IIa),



(IIb), or

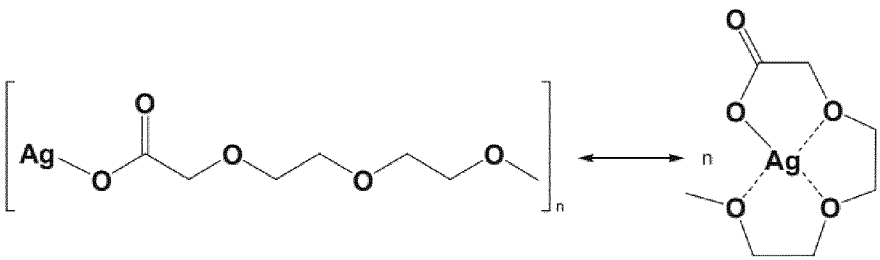
a mixture of the silver precursors of formula (I) and/or (II), or a complex formed thereof, wherein

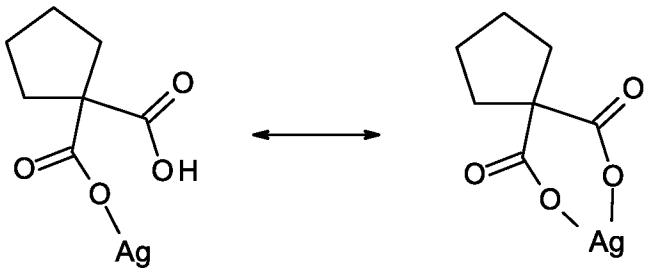
- A and A’ is selected from Z-Y- and Ag-Y-, wherein
  - Y is selected from -O-, -S-, -N(R^3)-, -N=, =N-, -O-C(=O)-, particularly -O-, -N(R^3)-, -N=, =N-, -O-C(=O)-, more particularly -O-, -O-C(=O)-, with R^3 being selected from H, a C_1-C_6-alkyl, and an aryl, wherein the aryl is optionally substituted by one or more substituents independently selected from a C_{1-4}-alkyl, and
  - Z is selected from H, a C_1-C_6-alkyl and an aryl, particularly a C_1-C_6-alkyl and an aryl, wherein the aryl is optionally substituted by one or more substituents independently selected from a C_{1-4}-alkyl,

- each R^1 independently of any other R^1 is selected from a C_1-C_{18}-alkyl, particularly a C_1-C_{12}-alkyl, more particularly a C_1-C_6-alkyl,
- R^2 is a C_1-C_{18}-alkyl, particularly a C_1-C_{12}-alkyl, more particularly a C_1-C_6-alkyl,
- X is selected from O, S, -N(R^3)-, particularly from O and S, more particularly O,
  - wherein R^3 is defined as above,
- E and E' is selected from -O-, -S-, -N=, =N-, -C(=O)-O- or -N(R^3)-,
  - wherein R^3 is defined as above,
- m is between 1 and 27, particularly between 1 and 18, more particularly between 1 and 10, even more particularly between 1 and 7, wherein the sum of C atoms of all R^1 does not exceed 54, particularly 36, more particularly 18,
- R^4, R^5, R^6, R^7 are each independently selected from H and C_{1-4}-alkyl, particularly H and C_{1-2}-alkyl, more particularly H,
- y is between 1 and 3, particularly y is 1 or 2, more particularly y is 1,

b. a particle comprising, particularly consisting of, agglomerated silver nanoparticles, wherein said particle has an average size of ≤ 20 µm, wherein the ratio of the weight of the silver precursor to the weight of the particle is ≤ 0.25, particularly between 1:4 and 1:15.

The composition according to the present invention comprises a silver precursor in form of an organic silver salt or a complex formed thereof (see Scheme 1), and a particle that comprises agglomerated silver nanoparticles.





Scheme 1: Possible conformations of a precursor in the composition according to the first aspect of the invention.

In certain embodiments, the silver precursor is selected from a precursor according to formula (I) or (II), particularly ((I) or (IIa), more particularly (I) or (IIb).

In certain embodiments, the silver precursor is a precursor according to formula (I).

The average diameter of a silver nanoparticle in the particle (agglomerate) is in the nanometer range, particularly from 100 nm to 250 nm. The agglomerated silver nanoparticles sinter at relatively low temperatures and pressures. While silver as a bulk material has a melting temperature of 961.8 °C, the nanoparticles sinter at ca. 200 °C. The silver nanoparticles may be obtained from silver nitrate by reduction with sodium borohydride in aqueous solution. The silver nanoparticles are agglomerated to form a particle, particularly a particle having a dendritic structure. The overall shape of the particle may be irregularly shaped, spherical or in form of a flake. The agglomerated silver nanoparticles essentially consist of Ag. Neither the particle nor a silver nanoparticle of the agglomerate is pre-coated.

In certain embodiments, the particle has a dendritic structure. In certain embodiments, the particle has a branched or hyperbranched structure.

In certain embodiments, the particle is in form of a flake.

In certain embodiments, the particle is not coated. In certain embodiments, the agglomerated silver nanoparticles are not coated.

The composition may be used for joining metallic or metallized substrates, in particular copper, silver, gold, nickel, steel (Fe) substrates. Standard methods for example as described in EP 2 838 690 B1 (particularly paragraphs [0015] to [0017], [0026], examples 1 and 2) may be applied.

In contrast to standard Ag-based sintering materials, the composition of the present invention is characterized by a high silver content. The ratio of the weight of the silver precursor to the

weight of the particle is 1:4 (0.25) or lower. This allows the preparation of a composition with a total Ag content of 90 % to 95 %.

The ratio of silver precursor to agglomerated silver particles is selected to facilitate the formation of a contamination-free silver layer at the joint between two components. Furthermore, the formation of volatile composition products that result from the decay of the precursor during the sintering process is reduced, which results in a reduced risk of void formation, reduced risk of delamination of the metal layers, and a higher density of the sintering layer obtained. The formation of the silver layer is achieved under mild heat and pressure conditions, wherein the sintering process is particularly performed under air, Ar, N_2, N_2/O_2, H_2 or formic acid atmosphere. The melting temperature and molten phase of the precursor can me modulated by altering the length of the precursor. The melting temperature increases with increasing m.

During the sintering process, the precursor melts to form a molten phase. Subsequently, the organic moiety of the silver precursor decomposes with increasing temperature to release Ag. In case of formula (I), particularly linear moieties facilitate the decomposition. Contamination-free sintering layers are particularly achieved when the decomposition products of the silver precursor are volatile. During decomposition, volatile decomposition products such as CO, CO_2, and formaldehyde form a reducing atmosphere. Such gases reduce oxides that may be present on the surfaces to be joint. This reduction on the surfaces to be joint leads to better adhesion by diffusion of Ag into the metal surface.

In certain embodiments, the alkyl moiety of R^1 is a linear alkyl.

In certain embodiments, the alkyl moiety of R^1 is a linear C_1-C_6-alkyl.

In certain embodiments, the alkyl moiety of R^1 is methyl or ethyl.

In certain embodiments,

- R^1 is ethyl for all m, or
- R^1 bound to A is methyl and all other R^1 are ethyl (in case of $m \geq 2$).

In certain embodiments, Z is H or a linear C_1-C_6-alkyl.

In certain embodiments, Z is H or a linear C_1-C_3-alkyl.

In certain embodiments, Z is H or -CH_3.

In certain embodiments, Z is a linear C_1-C_6-alkyl in case of A being Z-Y-.

In certain embodiments, Z is a linear C_1-C_3-alkyl in case of A being Z-Y-.

In certain embodiments, Z is -CH_3 in case of A being Z-Y-.

In certain embodiments, Z is H in case of A' being Z-Y-.

In certain embodiments, Y is selected from -N(R^3)-, -O-C(=O)-, -O-, -S-.

In certain embodiments,

- Y is selected from -N(R^3)-, -O-C(=O)- in case of A and A' being Ag-Y-, and/or
- Y is selected from -O-, -S-, -N(R^3)- in case of A and A' being Z-Y-.

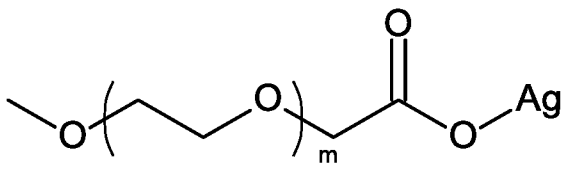
In certain embodiments,

- Y is selected from -N(R^3)-, -O-C(=O)- in case of A being Ag-Y-, and/or
- Y is selected from -O-, -S-, -N(R^3)- in case of A being Z-Y-.

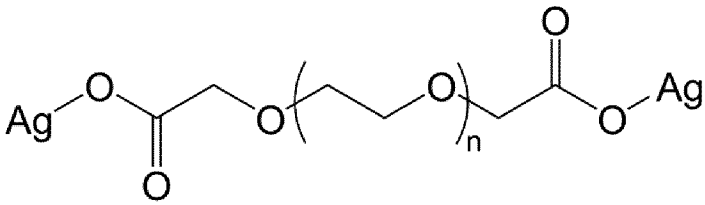
In certain embodiments, E and E' is -C(=O)-O-.

In certain embodiments, m is between 1 and 3.

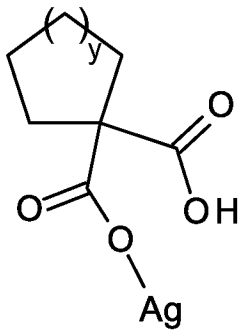
In certain embodiments, the silver precursor is a compound of a formula (IV), (V), or (VIa), (VIb), (VIc), or a mixture thereof,



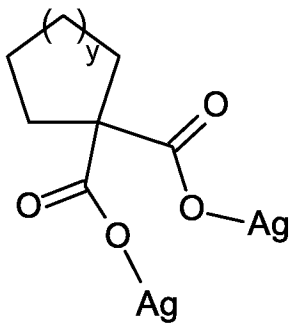
(IV),



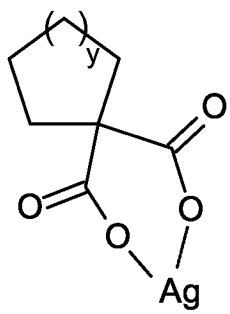
(V),



(VIa),



(VIb),



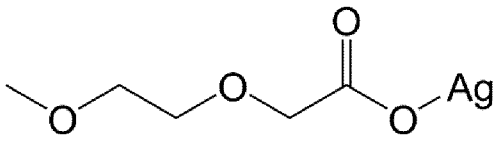
(VIc),

wherein m is defined as above, particularly m is between 1 and 3,
n is m-1, particularly n is between 1 and 3,
y is 1 or 2.

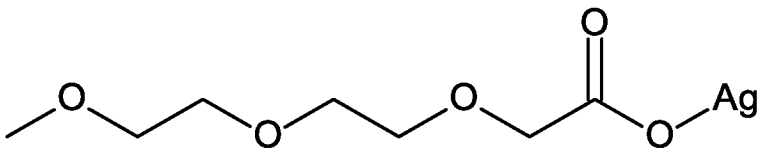
In certain embodiments, the silver precursor is a compound of a formula (IV), (V), or (VIa), (VIb), (VIc), particularly (IV) or (VI).

In certain embodiments, the silver precursor is a compound of a formula (IV), (V), or (VIa), (VIb).

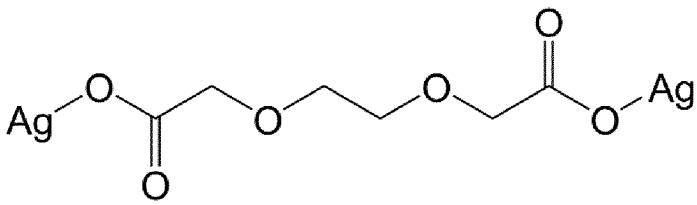
In certain embodiments, the silver precursor is a compound of a formula (VIIa), (VIIb), (VIII) or (IXa), (IXb), (IXc), or a mixture thereof,



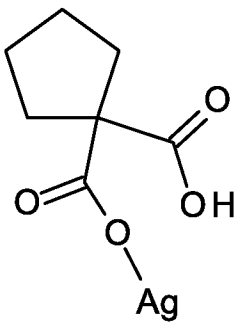
(VIIa),



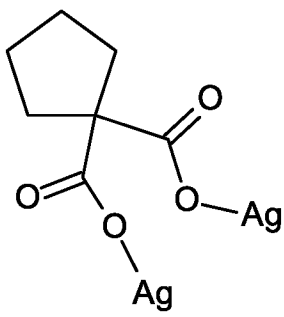
(VIIb),



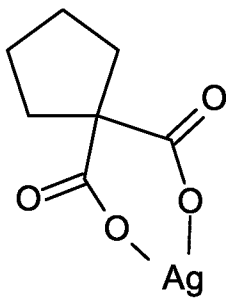
(VIII),



(IXa),



(IXb),



(IXc).

In certain embodiments, the silver precursor is a compound of a formula (VIIa), (VIIb), (VIII), (IXa), (IXb, or (IXc), particularly (VIIa), (VIIb), (IXa), (IXb), or (IXc).

In certain embodiments, the silver precursor is a compound of a formula (VIIa), (VIIb), (VIII), (IXa), or (IXb), particularly (VIIa), (VIIb), (IXa), or (IXb).

In certain embodiments, the melting temperature or the decomposition temperature of the silver precursor is below 200°C and/or the silver precursor exhibits a molten phase over a temperature range between 20°C and 40°C.

In certain embodiments, the melting temperature or the decomposition temperature of the silver precursor is below 200°C.

In certain embodiments, the silver precursor exhibits a molten phase over a temperature range between 20°C and 40°C.

As described above, the ratio of silver precursor to agglomerated silver particles is selected to facilitate the formation of a contamination-free silver sintering layer, to avoid the formation of voids, to reduce the risk of delamination and to obtain a sintering layer having a high density, i.e. having no or only small pores. Particularly the formation of voids and the number of pores as well as the pore size depends on the amount of decomposition products that result from the decay of the precursor. In this regard, the amount of precursor should be minimal. On the other hand, sufficient precursor is required to allow for an efficient sintering process. A good balance between reducing unwanted side effects as described above and achieving efficient sintering may be obtained by an optimized ratio of the weight of the silver precursor to the weight of the particle such as a ratio between 1:5 and 1:9.

In certain embodiments, the ratio of the weight of the silver precursor to the weight of the particle is between 1:5 and 1:9, particularly between 1:5 and 1:7.

When selecting a suitable ratio of the weight of the silver precursor to the weight of the particle, the size/weight of the organic moiety of the silver precursor may be taken into account. The higher the weight of the organic moiety, the less Ag per amount precursor is provided during the sintering process. Thus, a composition that comprises a relatively large amount of particles may be used in case of silver precursors having a large organic moiety (e.g. weight of the silver precursor to the weight of the particle is 1:9), while a composition that comprises a relatively small amount of particles may be used in case of silver precursors having a small organic moiety (e.g. weight of the silver precursor to the weight of the particle is 1:5).

In certain embodiments, the average size of the particle is in the range of 0.5 µm to 20 µm, particularly 1 µm to 10 µm.

In certain embodiments, the average size of one silver nanoparticle of the agglomerated silver nanoparticles is 100 nm to 250 nm.

Sintering materials may be applied to a joint between two components as paste or as compacted powder (pellet) before subsequent heat treatment to join the components. A paste may be obtained by standard methods, for instance as described in EP 2 838 690 B1 (particularly paragraphs [0015] to [0017], [0021], [0023], [0024], [0026], examples 1 and 2).

In certain embodiments, the composition is in form of a dried powder or a paste.

For better handling of the composition before the sintering process, e.g. during application of the composition on surfaces to be joined, the composition may comprise a solvent. Typically, only as much solvent is added as is necessary to obtain a highly viscous, spreadable paste. Suitable solvents for adjusting the viscosity are ethers such as glycol ethers or alcohols such as ethanol.

In certain embodiments, the composition comprises a solvent selected from

- an alcohol, particularly C_{1-4}-OH, more particularly ethanol,
- an ether, particularly a glycol ether, more particularly a glycol ether comprising 4 to 200 C atoms, particularly 4 to 10 C atoms, even more particularly a glycol ether selected from 2-(2-ethoxyethoxy)ethan-1-ol (CH_3CH_2-O-CH_2CH_2-O-CH_2CH_2-OH), 1-methoxypropan-2-ol (CH_3-O-CH_2-CH(CH_3)-OH), and 2-isopropoxyethanol (CH_3-CH(CH_3)-O-CH_2CH_2-OH).

In certain embodiments, the composition comprises a solvent selected from an ether, particularly a glycol ether, more particularly a glycol ether comprising 4 to 200 C atoms, particularly 4 to 10 C atoms, even more particularly a glycol ether selected from 2-(2-ethoxyethoxy)ethan-1-ol (CH_3CH_2-O-CH_2CH_2-O-CH_2CH_2-OH), 1-methoxypropan-2-ol (CH_3-O-CH_2-CH(CH_3)-OH), and 2-isopropoxyethanol (CH_3-CH(CH_3)-O-CH_2CH_2-OH).

In certain embodiments, the composition in form of a paste is free of metal alcoholates.

In certain embodiments, the composition comprises as much solvent so that a spreadable paste is obtained.

In certain embodiments, the paste has a viscosity between 15 and 30 Pa*s.

In certain embodiments, the composition comprises up to 25 % (w/w), particularly 2 % (w/w) solvent in relation to the total mass of the composition.

When a solvent is added, the precursor may form a complex as depicted in Scheme 1.

Particularly gold and silver surfaces are difficult to join by sintering techniques as gold or silver surfaces are often contaminated by NiO, SiOR or organic compounds. Also, Cu surfaces may be difficult to join since Cu surfaces are often oxidized and thus contaminated by CuO. Such

contaminants complicate an equal wetting of a gold or silver surface by sintering materials which are typically free of fluxing agents. In contrast to this, soldering materials often contain fluxing agents to overcome this obstacle. However, when soldering is applied for joining relatively large surfaces, there is an increased risk of void formation due to the liquid phase that is formed during soldering.

The composition described herein may be used for joining components with gold or silver surfaces by sintering. Particularly the component in form of a paste mixed with Ag_2O is suitable for joining components having a gold or silver surface. The addition of Ag_2O to the paste facilitates wetting of the surfaces to be joined. Ag_2O is a further source for the formation of Ag nanoparticles.

To join copper substrates, an ENIG (Electroless Nickel Immersion Gold) surface finish may be applied, wherein the copper substrate is separated from an outer gold layer by a Ni-barrier. The Ni-barrier comprises NiO, which may penetrate the gold layer through pores in the gold layer when heat is applied. As described above, NiO impedes sintering. When a sintering paste is used that comprises additionally silver oxide, the pores in the gold layer are sealed and thus sintering of ENIG-treated surfaces enabled.

In certain embodiments, the composition in form of a paste comprises additionally silver oxide, particularly silver (I) oxide.

The amount of Ag_2O is adjusted in such a way that an evenly wetting can be achieved, while the release of gas equivalents is preferably minimized.

In certain embodiments, the composition in form of a paste contains 5-30 % (w/w), particularly 8-20 % (w/w), more particularly 8-10 % Ag_2O in relation to the total mass of the paste.

In certain embodiments, the ratio of the weight of the silver oxide to the weight of the silver precursor is between 1:10 and 1:12.

Best results were achieved for pastes that were prepared from a composition that comprises a weight ratio of silver precursor to particle is larger or equal to 1:7, particularly between 1:6 and 1:7. Otherwise the proportion of the silver precursor is too small and the paste becomes too dry.

In certain embodiments, the weight of the silver precursor to the weight of the particle in the composition in form of a paste is larger or equal to 1:7, particularly between 1:6 and 1:7, more particularly 1:6, in case Ag_2O is additionally added.

The composition as described herein is suitable for sintering substrates such as copper, silver, gold, nickel, steel (Fe) surfaces at mild temperature, particularly between 180 °C and 300 °C, more particularly between 220 ° and 270 °C, and pressure-assisted conditions. If a sintering process under low to mid pressure-assisted conditions shall be performed, additional silver and/or copper particles may be added to the composition in form of a paste. Sintering is ideally performed from 2-20 MPa. For pressure-assisted sintering, the sintering paste has to be pre-dried, i.e. the viscosity has to be increased. This can only be achieved by adding additional silver and/or copper particles to increase the proportion of solid components and thus to decrease the proportion of molten components. The molten components of the paste remain liquid. The addition of additional silver and/or copper particles further decreases the proportion of the silver precursor and thus reduces the proportion of organic moieties which is beneficial for sintering at high pressures. Furthermore, the electric and thermal conductivity in the unsintered paste increases. In the sintered Ag layer, thermal conductivity is increased compared to layers obtained by known methods.

The addition of silver and/or copper particles is not only beneficial for sintering processes under high pressure but also beneficial for sintering relatively large surfaces under mild pressure conditions (≤ 15 MPa). The addition of additional silver particles increases the packing density. The close-packing of silver nanoparticles contributes to achieve an Ag sintering layer of high quality, particularly when large surfaces are joined. The packing density of the silver nanoparticles in the paste may be increased with increasing pressure. However, no further increase in the packing density was observed at pressures > 15 MPa. Thus, optimum package of the silver nanoparticles in the paste obtained from the composition described herein is already obtained under mild pressure conditions. In contrast to this, standard sintering techniques do not allow joining large surfaces at low pressure but usually require high pressure conditions of at least 25 MPa. However, high pressure conditions during sintering large surfaces increase the risk of fractures or cracks in components to be sintered such as ceramics or semiconductors. A paste obtained from the composition described herein that contains additional silver and/or copper particles is particularly suitable for sintering fragile components such as GaN-, SiC-semiconductors or ceramic substrates such as DBCs (direct bonded copper). Such a paste may also particularly be suitable for joining Cu- or Ni- or stainless-steel components, wherein the joint surface has a size of up to 3000 mm².

For the same reasons as described above, standard sintering techniques are not applicable to all-in-one-sintering, wherein several sintering layers are simultaneously obtained.

As Ag is quite expensive, a mixture of additional silver and copper particles or only additional copper particles may be used instead of additional silver particles.

In certain embodiments, the composition in form of a paste comprises additionally metallic silver or copper.

In certain embodiments, the composition in form of a paste comprises additionally metallic silver.

In certain embodiments, the metallic silver is in form of a particle that comprises, particularly consists of, agglomerated silver nanoparticles, wherein said particle has an average size of ≤ 20 µm, particularly 1-20 µm, more particularly 5-10 µm.

In certain embodiments, the metallic copper is in form of a particle that comprises, particularly consists of, agglomerated copper nanoparticles, wherein said particle has an average size of ≤ 20 µm, particularly 1-20 µm, more particularly 5-10 µm.

In certain embodiments, the particle has a dendritic structure. In certain embodiments, the particle has a branched or hyperbranched structure.

The same silver particles as described above (particles that comprise agglomerated silver nanoparticles) may be used for adding additional metallic silver particles.

In certain embodiments, the outer shape of the particle may be irregularly shaped, spherical or in form of a flake.

In certain embodiments, the particle is in form of a flake.

In certain embodiments, the composition in form of a paste contains up to 40 % (w/w), copper in relation to the total mass of the paste.

In certain embodiments, the composition in form of a paste contains up to 20 % (w/w), particularly 10 % (w/w) metallic silver and/or copper in relation to the total mass of the paste. If the paste is not spreadable after the addition of additional metallic silver particles, a solvent as described above may be added to adjust the viscosity of the paste.

In certain embodiments, the ratio of the weight of the metallic silver and/or copper to the weight of the silver precursor is between 6:1 and 7:1

Best results were achieved for pastes that were prepared from a composition that comprises a weight ratio of silver precursor to particle is larger or equal to 1:7, particularly between 1:6 and 1:7. Otherwise the proportion of the silver precursor is too small and the paste becomes too dry.

In certain embodiments, the weight of the silver precursor to the weight of the particle in the composition in form of a paste is larger or equal to 1:7, particularly between 1:6 and 1:7, more particularly 1:6, in case metallic silver and/or copper is additionally added.

In certain embodiments,

- the ratio of the weight of the silver oxide to the weight of the silver precursor in the composition in form of a paste is between 1:10 and 1:12, and/or
- the ratio of the weight of the metallic silver and/or copper to the weight of the silver precursor in the composition in form of a paste is between 6:1 and 7:1.

Another aspect of the invention relates to a sintering method, wherein the composition according to the first aspect is used.

Method steps as described in EP 2 838 690 B1 (particularly paragraphs [0015] to [0017], [0021] to [0024], [0026], examples 1 and 2) may be performed.

In certain embodiments, sintering is performed at a temperature between 180 °C and 300 °C, particularly between 220 °C and 270 °C.

Description of the Figures

Fig. 1 shows a sintering layer obtained by using a sintering paste without addition of Ag-particles.

Fig. 2 shows a sintering layer obtained by using a paste with addition of additional Ag-particles.

Fig. 3 shows values of typical viscosity of a paste without dilution. 1.Run: 15 Pa*s; 2. Run: 16 Pa*s; 3. Run: 19 Pa*s.

Fig. 4 shows typical values of viscosity of the pastes with a dilutant, wherein the dilutant is diethyleneglycolmonoethylether. 1% 1.Run: 1% diethyleneglycolmonoethylether, 12 Pa*s; 1% 2. Run: 1% diethyleneglycolmonoethylether, 12 Pa*s; 2 % 1. Run: 2% diethyleneglycolmonoethylether, 9 Pa*s; 2% 2. Run: 2% diethyleneglycolmonoethylether, 8 Pa*s

Fig. 5 shows thermal conductivity of different sintering layers. For each paste a paste with precursor and particles were used in a ratio of 1:9 and to 10g of the mixture 1g of diethyleneglycolmonoethylether was added and the given additional silver

powder: P7_1_1: Additional silver flake 3µm 5mass%; P7_1_2: Additional silver flake 3µm 10mass%; P7_1_3: Additional silver flake 3µm 15mass%; P7_2_1: Additional silver flake 20µm 5mass%; P7_2_2: Additional silver flake 20µm 10mass%; P7_2_3: Additional silver flake 20µm 15mass%; P7_3_1: Additional silver flake 10µm 5mass%.

Fig. 6 shows pressureless sintering of two 10 mm x 10 mm IGBT Die on Cu-DBC in nitrogen atmosphere after performing a mandrel bend test.

Fig. 7 shows pressureless sintering of a 4 mm x 4 mm diode on Cu-DBC in nitrogen atmosphere. Cohesive failure after die shear test.

Fig. 8 shows Au-finished ceramic substrate (left) and die (right) after shear test, which resulted in a cohesive failure. Left: Dots after sintering and shearing; right: LED wetting after shearing.

Fig. 9 shows shear values of sintered shear bodies on copper plates at different sintering pressures. Low pressure: 3-5 MPa, medium pressure: 10 MPa.

Fig. 10 shows cross-section of die shear body (Cu) on substrate (Cu).

Fig. 11 shows a paste prepared according to example 2 and 3. Preparation of Ag-based paste with addition of Cu-particles of size 3-7 µm. The resulting paste has a Cu-metal content of 55 %wt.

Examples

Example 1: Preparation of a precursor and Ag particles

Ag(I)-2-[2-(2-methoxyethoxy)ethoxy]acetate (silver precursor) was prepared as described in Example 1 in EP 2 838 690 B1, particularly paragraph [0029].

Silver particles were prepared as described in Example 1 in EP 2 838 690 B1, particularly paragraph [0032].

Characterization of sintering pastes

A paste was prepared using the precursor and Ag particles as described above. The preparation was performed according to EP 2 838 690 B1. The weight ratio of precursor to particle was 1:5. Typical values of viscosity of the pastes: 15-30 Pa*s. (Fig. 3).

In another experiment, a paste with different rates of dilution was tested. The paste was prepared as described above. Additionally, 1 %wt or 2 %wt diethyleneglycolmonoethylether was added (Fig. 4).

The used equipment was a BYK Gardner CAP 2000+ Viscosimeter with spindle 6. The measurements were performed at 25 °C with a runtime depending on the RPM and a holdtime of 30s. For 50-100 RPM, the runtime is 12 seconds, for 20-50 RPM the runtime is 20 seconds and for 5-20 RPM the runtime is 30 seconds.

Characterization of sintering layers

Thermal conductivity:

Sintering layers obtained by pressureless sintering using a paste without additional Ag_2O or additional metal particles: 250 – 280 W/m*K (Fig. 5).

Sintering layers obtained by pressure-assisted sintering using a paste with additional Ag particles: 270 – 300 W/m*K (Fig. 5).

The measurement of the thermal conductivity was performed on sintered silver stripes with a length of 50 mm, a wide of 5 mm and a thickness of 65 µm, which were sintered on polished steel plates pressureless at 250 °C and removed from these plates before measuring.

Sheartest:

Sheartest after pressureless sintering

Pressureless sintering using a paste consisting of precursor and particles in a ratio of 1:9 without additional Ag_2O or additional metal particles: 20-80 N/mm² on Cu-substrates, resulted in a cohesive failure.

As a further proof of bond strength, a mandrel bend test (in accordance to ASTM D522, ISO 6860, BS 3900-E11) was performed after pressureless sintering of two 10 mm x 10 mm IGBT Dies on Cu-DBC in nitrogen atmosphere (Fig. 6). Briefly, the sintered samples were bended over a cone with a diameter of 20 mm during the mandrel bend test.

Cohesive failure after a die shear test was observed after pressureless sintering of a 4 mm x 4 mm diode on Cu-DBC in nitrogen atmosphere (Fig. 7).

Pressureless sintering using a paste with additional Ag_2O: 30-80 N/mm² on a substrate with Au-finish, resulting in a cohesive failure (Fig. 8).

Several substrate materials had been used, such as DBC-substrates with Au or Ag finish or bare copper plates. As “die” the inventors used either standard IGBT-Si-Dies (10 mm x 10 mm; IGBT: insulated-gate bipolar transistor) or dummy-dies (2,3 mmx2,3 mm) with Ag or Cu finish (Fig. 6-8).

The sintering profile applied is the following:

- 5 K/ min to 90°C, holding this temperature for 10 min,
- heating up with 5 K/ min to 250 °C;
- holding this temperature for 30-60 min.
- Moderate cool down in the oven to prevent cracking of the silver interconnect. In the case of Cu-substrates, sintering in a box oven with N_2-atmosphere was conducted to prevent the formation of surface oxides.

For die-shear the inventors used either a “Sigma Lite” by xyztec BV or a “Nordson Dage” by Nordson Corporation.

Pressureless sintering was performed using a paste without additional Ag_2O or additional metal particles: 20-60 N/mm². The paste which was used has a ratio of precursor to silver particles of 1 to 7 without an addition of Ag_2O. Pressureless sintering was performed on two 10 mm x 10 mm IGBT Dies on Cu-DBC in nitrogen atmosphere.

Pressureless sintering was performed using a paste with additional Ag_2O: 30-80 N/mm². The paste which was used has a ratio of precursor to silver particles of 1 to 7. To 10g of this paste 1.5g Ag_2O was added with an amount of 200 mg of diethyleneglycolmonoethylether. Also here, pressureless sintering was performed on two 10 mm x 10 mm IGBT Dies on Cu-DBC in nitrogen atmosphere.

Sheartest after pressure-assisted sintering

Pressure-assisted sintering using a paste with additional Ag-particles gives sintered shear bodies on a copper substrate with a resulting shear strength of 40-80 MPa.

Fig. 9 shows shear values of sintered shear bodies on copper plates at different sintering pressures.

For shear force testing, silver shear bodies (2,3mm*2,3mm) were sintered with the silver paste after adding additional silver powder (usage of particles synthesized mentioned above and silver particles in a size of 1-3 µm; each 10 %wt) on copper plates under different sintering pressures under nitrogen (Fig. 9 and 10).

Table 1: Shear values observed after shear test.

Variant	Maximum force [MW,N]	Shear strength [N/mm^2]
2MPa-15min-Cu	301.9	57.3

Pressure-assisted sintering was performed using a paste consisting of precursor and particles in a ratio of 1 to 8. To 10g of this mixture 1g of diethyleneglycolmonoethylether was added and 2g of additional Ag-particles. The resulting shear strength was between 40-80 N/mm². The sintering of shear test bodies was performed on copper plates or DBC-substrates with copper finish with 80 µm stencil printed paste which was pre-dried 5 min at 105 °C before setting the shear bodies. The sintering temperature was 250 °C and the used pressure was between 2-25 MPa.

Optical analysis

Addition of Ag-particles for pressure-assisted sintering: sintering of glass-plates for optical analysis of sintered Ag-Joints (Fig. 1 and 2).

Figure 1 shows a sintering layer obtained by using a sintering paste without addition of Ag-particles.

Figure 2 shows a sintering layer obtained by using a paste with addition of additional Ag-Particles.

With addition of Ag-Particles the degassing channels can be decreased while pressure-assisted sintering Ag-Joints with higher density can be achieved.

Example 2:

Paste with addition of Ag_2O gives strong interconnection on all common gold surfaces independent of the layers of the gold finish (Ni/NiO or no Ni/NiO): pressureless sintering gives shear values of > 40N/mm2; while sintered joint on Ni/NiO based gold finish without additional Ag_2O shows low shear force of <20N/mm^2. Pressureless sintering using a paste with additional Ag_2O: 30-80 N/mm² on a substrate with Au-finish, resulted in a cohesive failure. The paste which was used has a ratio of precursor to silver particles of 1 to 9. To 10g of this paste 1.5g Ag_2O was added with an amount of 200 mg of diethyleneglycolmonoethylether.

Several substrate materials had been used, such as DBC-substrates with Au or Ag finish or bare copper plates. As “die”, the inventors used either standard IGBT-Si-dies (10 mm x 10 mm) or dummy-dies (2,3 mmx2,3 mm) with Ag or Cu finish (Fig. 8).

Example 3:

Paste with addition of copper powder (20-60 %wt) gives strong interconnection on copper based surfaces (Fig. 11). A paste was prepared according to the method given above. After preparation of the Ag-based paste Cu-particles of the size 3-7 µm were added. The resulting paste has a Cu-metal content of 55 %wt.

With this material die shear test experiments were conducted as given above. Sintering was performed on a Cu-substrate and shear buddies (2.3 mm x 2.3 mm). Sintering was done pressure assisted (5 MPa, 250 °C, 5 min) in a nitrogen atmosphere. Shear values are given in Table 2.

Table 2: Shear values

Probe 3	
Measured value (N)	area-normed value (N/mm^2)
255.17	48.24
260.42	49.23
307.28	58.09
112.43	21.25
220.73	41.73

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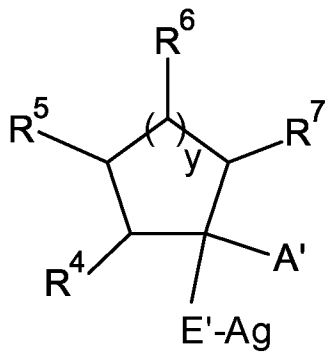
Claims

1. A composition for sintering comprising:

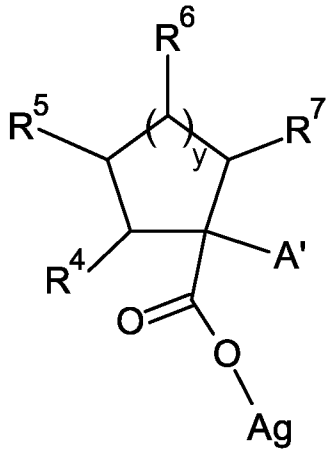
   a. a silver precursor of formula (I):

   $A\text{-}(R^1\text{-}X)_m\text{-}(R^2)\text{-}E\text{-}Ag$ (I), or

   a silver precursor of formula (II), particularly of formula (IIa):



(II),



(IIa), or

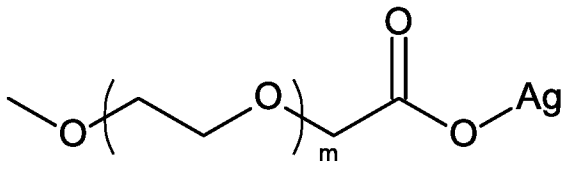
   a mixture of the silver precursors of formula (I) and/or (II), or a complex formed thereof, wherein

   - A and A' is selected from Z-Y- and Ag-Y-, wherein
     - Y is selected from -O-, -S-, -N(R^3)-, -N=, =N-, -O-C(=O)-, particularly -O-, -N(R^3)-, -N=, =N-, -O-C(=O)-, more particularly -O-, -O-C(=O)-, with R^3 being selected from H, a C_1-C_6-alkyl, and an aryl, wherein the aryl is optionally substituted by one or more substituents independently selected from a C_{1-4}-alkyl, and
     - Z is selected from H, a C_1-C_6-alkyl and an aryl, wherein the aryl is optionally substituted by one or more substituents independently selected from a C_{1-4}-alkyl,
   - each R^1 independently of any other R^1 is selected from a C_1-C_{18}-alkyl, particularly a C_1-C_{12}-alkyl, more particularly a C_1-C_6-alkyl,
   - R^2 is a C_1-C_{18}-alkyl, particularly a C_1-C_{12}-alkyl, more particularly a C_1-C_6-alkyl,

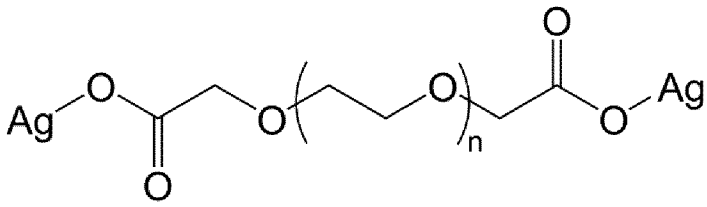
- X is selected from O, S, -N(R^3)-, particularly from O and S, more particularly O,
  - wherein R^3 is defined as above,
- E and E' is selected from -O-, -S-, -N=, =N-, -C(=O)-O- or -N(R^3)-,
  - wherein R^3 is defined as above,
- m is between 1 and 27, particularly between 1 and 18, more particularly between 1 and 10, even more particularly between 1 and 7, wherein the sum of C atoms of all R^1 does not exceed 54, particularly 36, more particularly 18,
- R^4, R^5, R^6, R^7 are each independently selected from H and C_{1-4}-alkyl, particularly H and C_{1-2}-alkyl, more particularly H,
- y is between 1 and 3, particularly y is 1 or 2, more particularly y is 1,

b. a particle comprising, particularly consisting of, agglomerated silver nanoparticles, wherein said particle has an average size of ≤ 20 µm, wherein the ratio of the weight of the silver precursor to the weight of the particle is ≤ 0.25, particularly between 1:4 and 1:15.

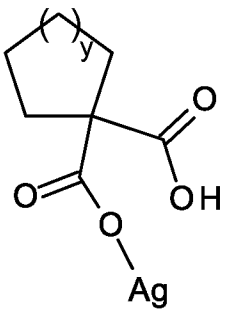
2. The composition according to claim 1, wherein the alkyl moiety of R^1 is a linear alkyl, particularly a linear C_1-C_6-alkyl, more particularly methyl or ethyl.
3. The composition according to claim 1, wherein Z is a linear C_1-C_6-alkyl, particularly a linear C_1-C_3-alkyl, more particularly -CH_3.
4. The composition according to any of the previous claims, wherein
   - Y is selected from -N(R^3)-, -O-C(=O)- in case of A being Ag-Y-, and/or
   - Y is selected from -O-, -S-, -N(R^3)- in case of A being Z-Y-.
5. The composition according to any of the previous claims, wherein E is -C(=O)-O-.
6. The composition according to any of the previous claims, wherein m is between 1 and 3.
7. The composition according to any of the previous claims, wherein the silver precursor is a compound of a formula (IV), (V), (VIa), (VIb) or (VIc), or a mixture thereof,



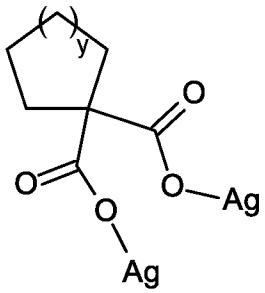
(IV),



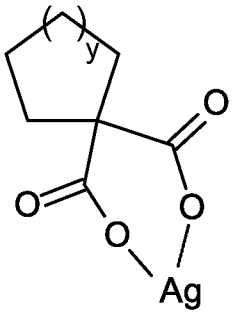
(V),



(VIa),



(VIb),



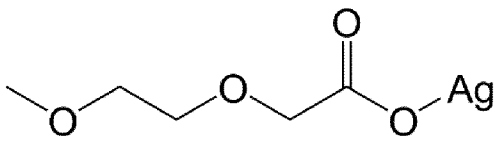
(VIc),

wherein m is as defined above,

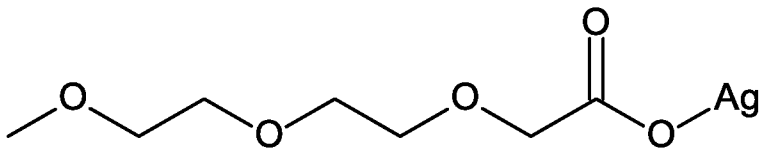
n is m-1,

y is 1 or 2;

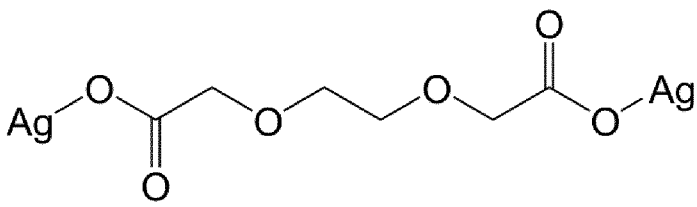
particularly the silver precursor is a compound of a formula (VIIa), (VIIb), (VIII), (IXa), (IXb) or (IXc), or a mixture thereof,



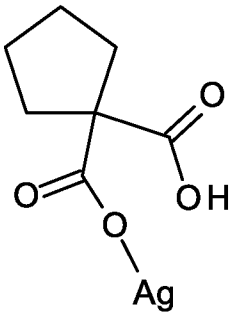
(VIIa),



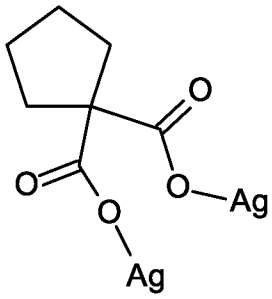
(VIIb),



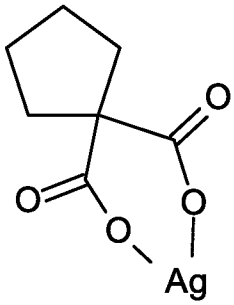
(VIII),



(IXa),



(IXb),



(IXc).

8. The composition according to any of the previous claims, wherein the melting temperature or the decomposition temperature of the silver precursor is below 200°C and/or the silver precursor exhibits a molten phase over a temperature range between 20°C and 40°C.

9. The composition according to any of the previous claims, wherein the ratio of the weight of the silver precursor to the weight of the particle is between 1:5 and 1:9, particularly between 1:5 and 1:7.

10. The composition according to any of the previous claims, wherein the average size of the particle is in the range of 0.5 µm to 20 µm, particularly 1 µm to 10 µm.

11. The composition according to any of the previous claims, wherein the composition is in form of a dried powder or a paste.

12. The composition according to any of the previous claims, wherein the composition comprises a solvent selected from

    - an alcohol, particularly C_{1-4}-OH, more particularly ethanol,
    - an ether, particularly a glycol ether, more particularly a glycol ether comprising 4 to 200 C atoms, particularly 4 to 10 C atoms, even more particularly a glycol ether selected from 2-(2-ethoxyethoxy)ethan-1-ol (CH_3CH_2-O-CH_2CH_2-O-CH_2CH_2-OH), 1-methoxypropan-2-ol (CH_3-O-CH_2-$CH(CH_3)$-OH), and 2-isopropoxyethanol (CH_3-$CH(CH_3)$-O-CH_2CH_2-OH).

13. The composition in form of a paste according to claim 12, wherein the paste comprises additionally silver oxide.

14. The composition in form of a paste according to claim 12, wherein the paste comprises additionally metallic silver and/or copper.

15. The composition in form of a paste according to any of claims 13 to 14, wherein

- the ratio of the weight of the silver oxide to the weight of the silver precursor is between 1:10 and 1:12, and/or
- the ratio of the weight of the metallic silver and/or copper to the weight of the silver precursor is between 6:1 and 7:1.

Fig. 1

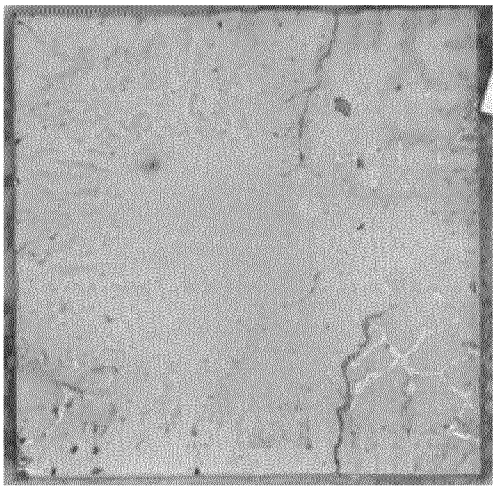


Fig. 2

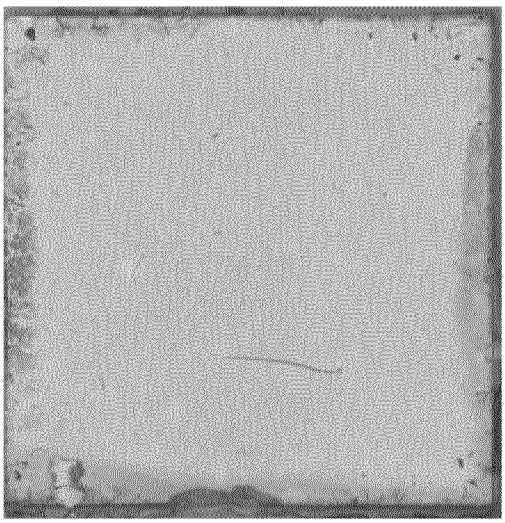


Fig. 3

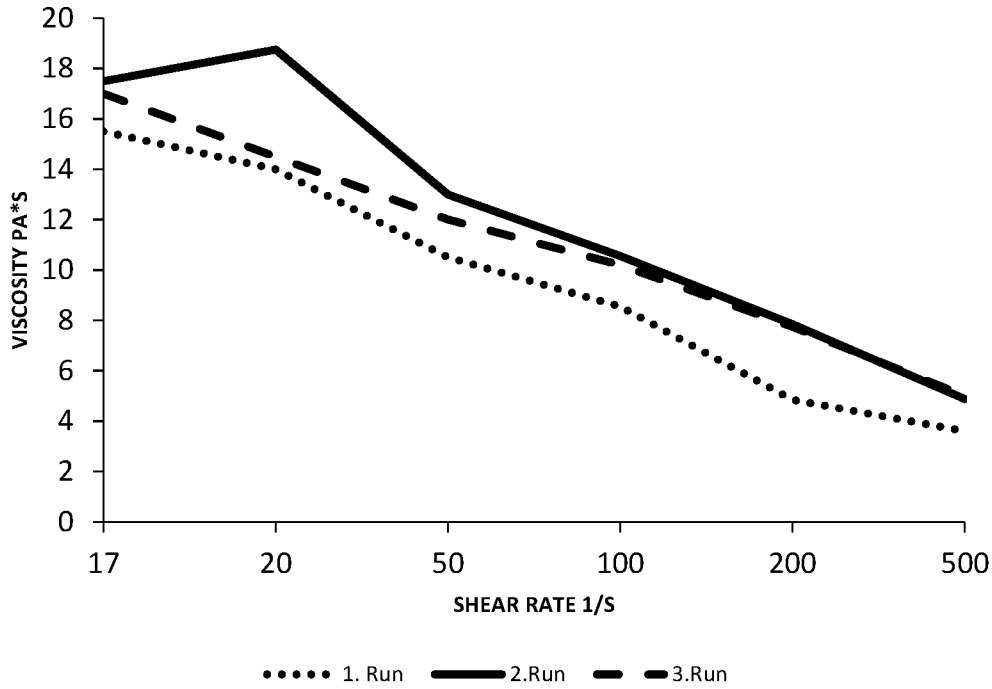

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14
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8
6
4
2
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17
20
50
100
200
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SHEAR RATE 1/S
1. Run
2.Run
3.Run

Fig. 4

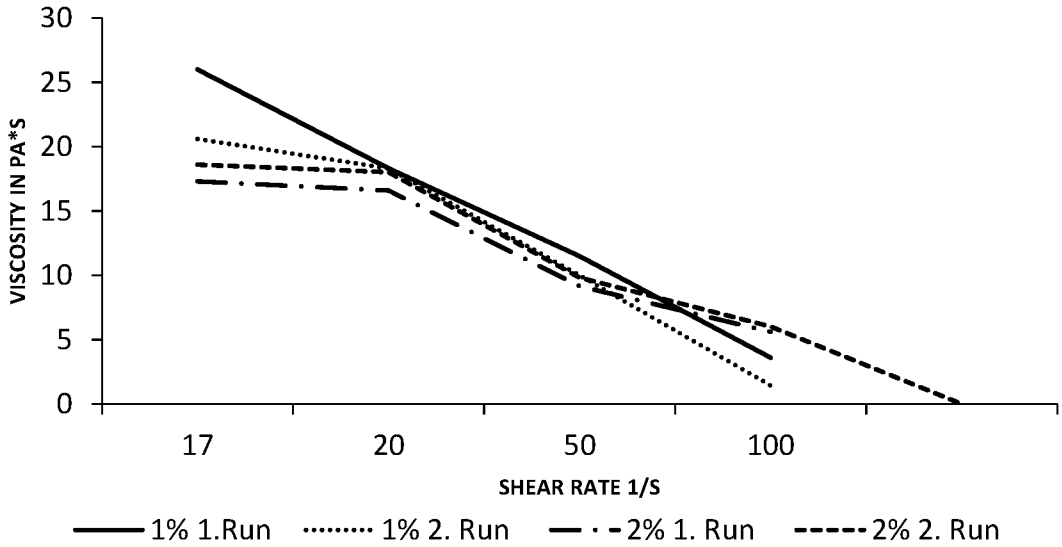

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VISCOSITY IN PA*S
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100
SHEAR RATE 1/S
1% 1.Run
1% 2. Run
2% 1. Run
2% 2. Run

Fig. 5

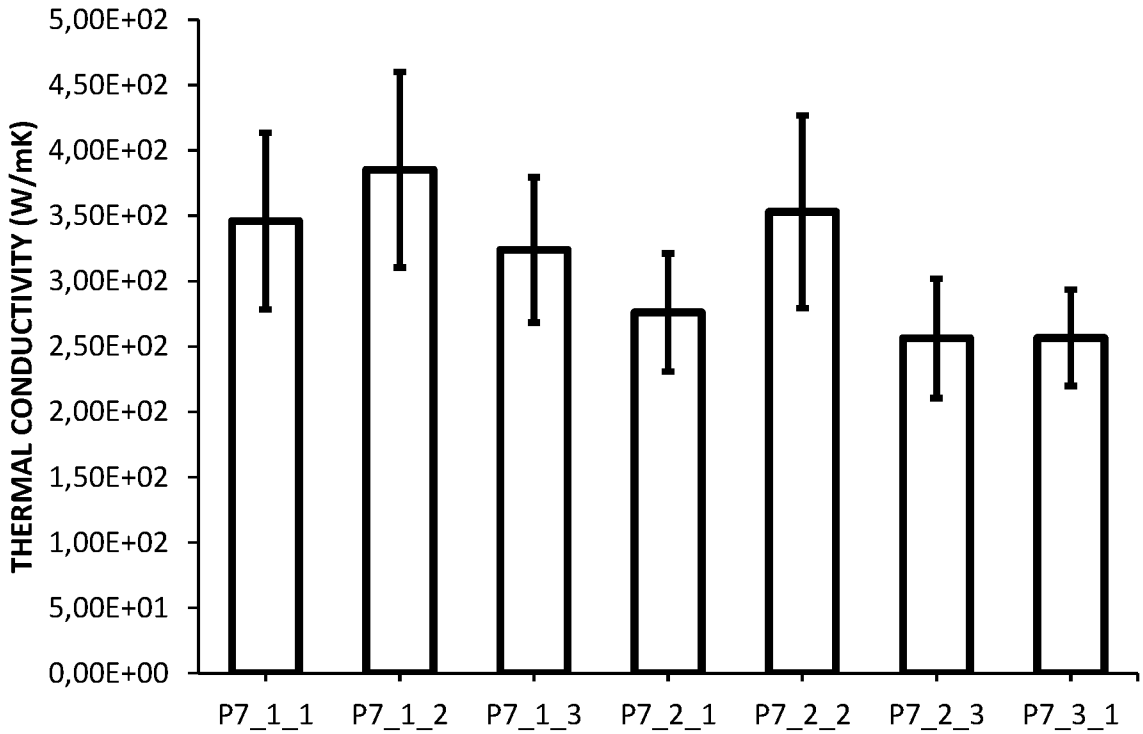

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P7_3_1

Fig. 6

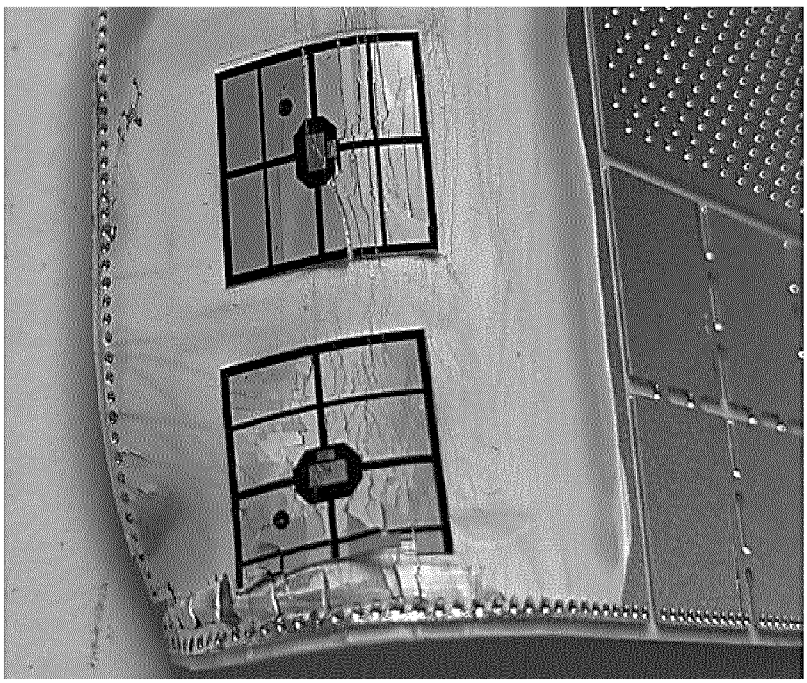


Fig. 7

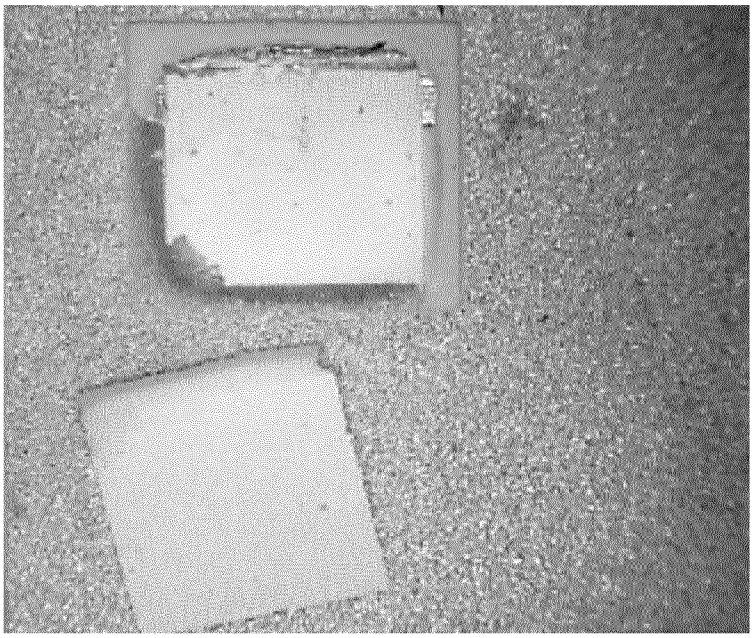
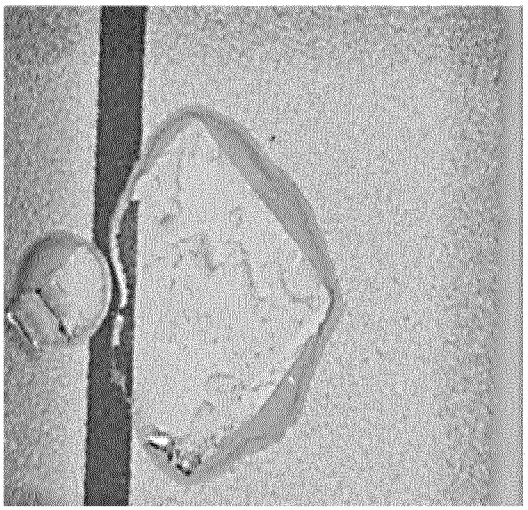


Fig. 8



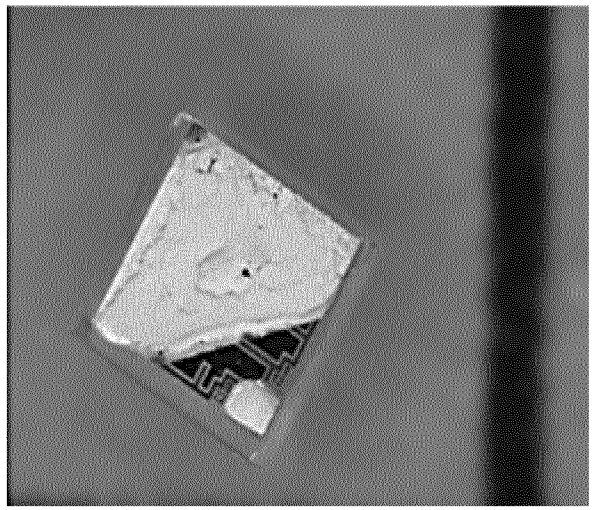


Fig. 9

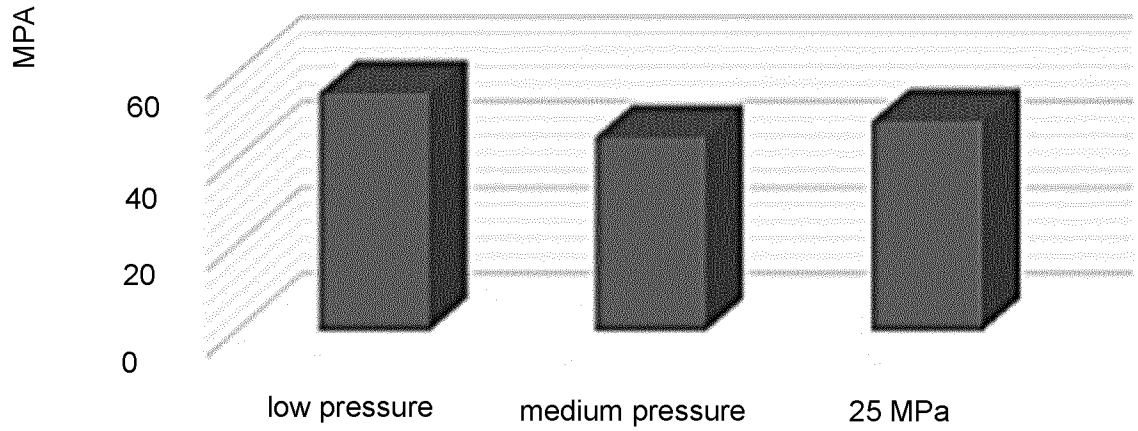


Fig. 10

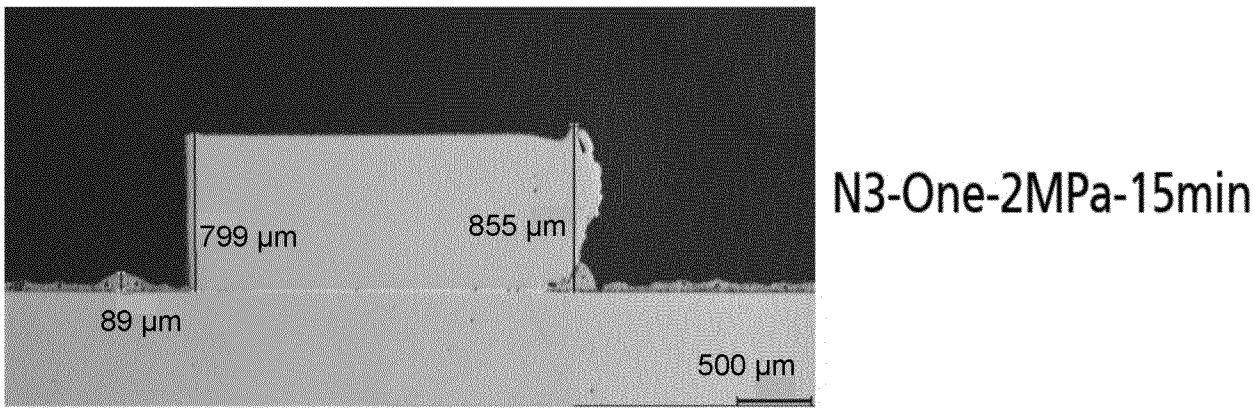
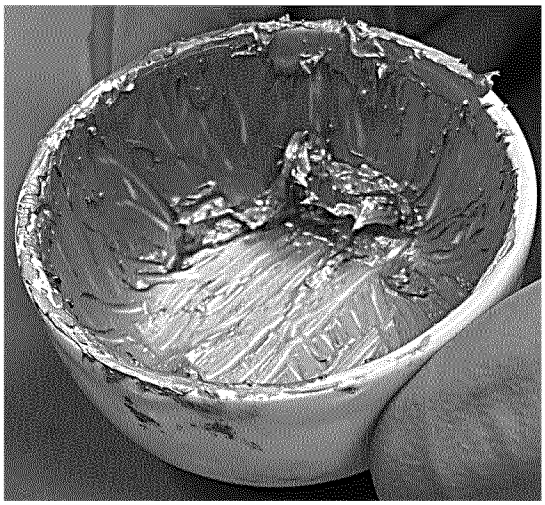


Fig. 11



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2022/079478

A. CLASSIFICATION OF SUBJECT MATTER
INV. B22F1/054 B22F9/24 B22F1/0545 B22F1/107 B22F9/30
ADD. B22F7/06

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 838 690 B1 (NANO JOIN GMBH [DE]) 17 July 2019 (2019-07-17) cited in the application paragraphs [0014] - [0016]	1-15
A	US 2010/021704 A1 (YOON SUNG-HO [KR] ET AL) 28 January 2010 (2010-01-28) the whole document	1-14
A	US 2010/055828 A1 (SCHMITT WOLFGANG [DE] ET AL) 4 March 2010 (2010-03-04) the whole document	1-14
A	US 2006/043346 A1 (KODAS TOIVO T [US] ET AL) 2 March 2006 (2006-03-02) the whole document	1-14

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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

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

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

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 December 2022	19/12/2022

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Forestier, Gilles

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2022/079478

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