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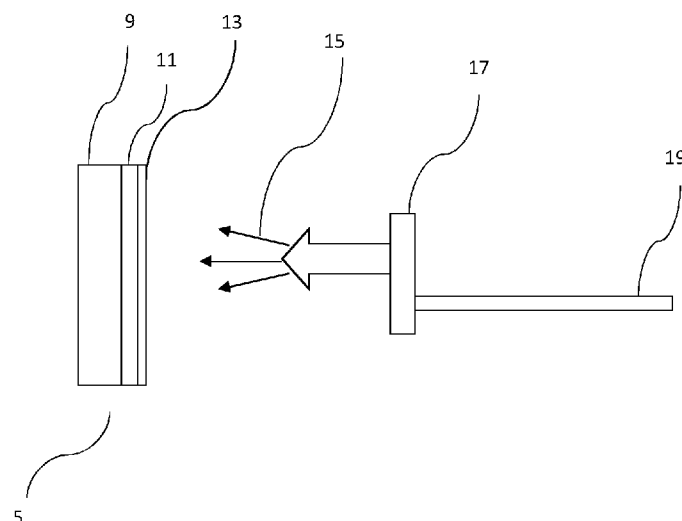
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Figure 1



(57) Abstract: The present invention relates to a system comprising: a first work piece having at least one platinum group metal (PGM) containing surface; and a complementary work piece having at least one metal-containing surface; wherein said at least one PGM-containing surface of the first work piece can be brought into contact with said at least one metal-containing surface of the complementary work piece when in use; wherein a ceramic coating material composition is adhered to at least one of said surfaces. The invention also relates to the use of such a system in a glass manufacturing process.

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Coating composition, method of coating, coated product, system and useField of the Invention

The present invention relates to a system comprising two complementary work pieces, which can be brought into contact when the system is in use. The present
5 invention particularly relates to systems which are suitable for high temperature applications, such as molten glass processing.

Background

The glass manufacturing industry, amongst other industries, uses platinum group metals (PGMs) to form necessary work pieces, or substrates, through which
10 molten glass is processed and formed into useful products. Typical substrates would include, for example, refractories, bushings, dies, stoppers and stirrers. PGM substrates are used in the harsh glass manufacturing and processing environment due to their chemically inert nature and ability to withstand high temperatures without loss of shape or other types of disintegration.

15 Substrates for the glass processing industry may not be formed solely or entirely of PGMs. It is often the case that the PGMs is used to encase a cheaper ceramic body to form a useful substrate for use, or alternatively, for example the PGMs may be provided as a layer on an alternative metal material, for example molybdenum. In addition, different PGMs containing alloys may be employed with
20 properties attuned to the particular manufacturing process in which they are used.

In fiberglass manufacture it is known to extrude molten glass through a plate having a series of apertures. The plate is typically made of Pt or a Pt-alloy. It is known to provide the plate with an oxide layer to reduce PGM losses as a result of oxidation of the substrate over time.

25 For instance, WO2008/027480 in an example describes a Pt-20Rh surface coated with a 0.008 or 0.012 inch (203 or 305 micron) thick coating of plasma sprayed zirconia (PSZ).

CN102676972 in an example describes a plate made of a Pt-Ir or Pt-Rh alloy coated with one of alumina / 3wt% titanium oxide; zirconia / 8 wt% yttrium oxide; or alumina powder.

DE102014008386 and DE202014011082 describe an example of a Pt-Rh sheet
5 with a coating of 93% zirconium oxide and 7% yttrium oxide.

CN101967313 describes examples of Pt or a Pt-Rh alloy having a coating made from a mixture of: silica, alumina, sodium silicate and sodium tetraborate.

JPH06298543 describes examples of a Pt or Pt-Rh alloy which are repeatedly dip coated in a powder of Pt and partially stabilized zirconia (PSZ). The proportion of
10 Pt in the powder is sequentially reduced so that the layers in the dip coated product form a gradient with the highest Pt content in the layer adjacent the Pt or Pt-Rh alloy, and the lowest Pt content in the last applied layer. The layer structure is then sintered to form a layer with a gradual Pt gradient.

EP0381179 describes examples of Pt or Pt-Rh alloy with a coating of Al₂O₃ or
15 85% Al₂O₃ – 15% ZrO₂.

US4532184 describes plates made of Pt, Ir, Rh or a combination thereof, having a flame sprayed coating of glass and metal oxides.

In some manufacturing processes two or more PGM substrates will be arranged in a manner which results in one or more surfaces of the two or more PGMs
20 substrates being in contact with each other. This is often the case for thin ring bushings, or dies, utilised in the manufacture of some glass products. When two opposing PGM substrate surfaces are in contact in this way, it is possible, and even inevitable in some processes, that the two metal surfaces in contact will become bonded to each other during use. This is problematic for a number of
25 reasons including; the substrate, or work pieces, cannot then be reused, and are typically melted down and recycled into replacement parts; time is lost in laborious removal and replacement of the bonded parts which has an associated high level of plant shut down time.

Currently zirconia paper may be used to try to alleviate the bonding, referred to above, between contacting surfaces of PGM substrate metal surfaces. However, these papers are not always effective at preventing the bonding from occurring, and necessarily include an additional process set-up step, as the paper must be manually positioned between the metal surfaces of interest. Furthermore, the paper does not always stay in place and moves from the surface of interest prior to the process starting up, thus providing no protection for the two or more metal surfaces which come into contact with one another, and hence the surfaces are still likely to become bonded to each other.

Preferred embodiments of the present invention seek to overcome one or more of the above disadvantages of the prior art. In particular, preferred embodiments of the present invention seek to provide a means of preventing two or more PGM containing surfaces from bonding to each other when in use in an industrial process.

Summary of Invention

According to a first aspect of the invention, there is provided a system comprising:

a first work piece having at least one platinum group metal (PGM) containing surface; and

a complementary work piece having at least one metal-containing surface; wherein said at least one PGM-containing surface of the first work piece can be brought into contact with said at least one metal-containing surface of the complementary work piece when in use;

characterized in that a ceramic coating material composition is adhered to at least one of said surfaces.

In a preferred embodiment the metal-containing surface of the complementary work piece is a PGM-containing surface.

According to a further aspect of the invention, there is provided a metal debonding coating composition.

According to a further aspect of the invention, there is provided a method of applying a metal debonding coating composition to a substrate.

- 5 According to a further aspect of the invention, there is provided a substrate which has had a metal debonding coating composition adhered to at least one metal surface, in this embodiment the metal debonding coating composition is referred to as a ceramic coating material composition. The difference in nomenclature is used as the metal debonding coating composition properties may have changed
- 10 between being applied to the substrate and being adhered to the substrate in a way that renders it suitable for use in a process. However, as will be made clearer below, the metal debonding coating composition and the ceramic coating material composition are inextricably linked and belong to the same invention.

- According to a further aspect of the invention, there is provided use of the
- 15 substrate which has had the ceramic coating material composition adhered to at least one metal surface, or the system according to the invention, in a glass manufacturing process.

- According to a further aspect of the invention, there is provided the use of a system as hereinbefore defined in a glass manufacturing process, and a method
- 20 of glass manufacture, in which molten glass is contacted with a system as hereinbefore defined.

Detailed description of the invention

- In accordance with an aspect of the invention there is provided a metal debonding coating composition. Essentially, such metal debonding coating composition will
- 25 comprise a ceramic coating material which will have sufficient chemical and thermal stability to render it useful in glass manufacturing processes. Suitably, the ceramic coating material comprises one or more oxides of titanium, aluminium, chromium, yttrium, zirconium or hafnium. In one embodiment the ceramic coating

material comprises high alumina. Preferably, the ceramic coating material comprises one or more oxides of yttrium, zirconium or hafnium. More preferably the ceramic coating material comprises one or more of yttrium oxide or zirconium oxide. The ceramic coating material may be a zirconium oxide, which is thermally
5 stabilised by the presence of yttria. Most preferably the ceramic coating material comprises yttrium oxide, and more especially comprises yttrium (III) oxide (yttria, Y_2O_3).

Additionally, the metal debonding coating composition comprises a carrier to render the composition in a suitable form for direct application to a substrate. The
10 carrier is used to provide the other constituents of the composition in the form of a slurry which allows for ease of application to a substrate. More especially, the carrier may be selected from the following, water, a water based carrier, a solvent, a polymer, an organic- based carrier, or an in-organic based carrier, or a mixture thereof. Particularly preferred carriers include water and solvents, or a mixture
15 thereof, and particularly suitable solvents include alkenes, alcohols or ketones. Most preferable the carrier is a solvent and is selected from one or more of acetone, isopropyl alcohol, propanol or ethylene. The most preferred selection of the one or more carrier will depend upon a number of factors, including the desired dry out rate of the composition and the desired viscosity of the composition, both
20 of which may be attuned for the method employed to apply the coating to the substrate of interest, for example, acetone may be used as the solvent carrier where a fast drying time is desirable, and ethyl alcohol may be employed where slower drying times are desirable.

The metal debonding coating composition may optionally comprise a dispersant.
25 This may be particularly advantageous where the carrier is water and the ceramic coating material would otherwise rapidly settle out of the carrier solution. The dispersant may be a suitable surfactant or rheology modifier. Suitable dispersants are known to the person skilled in the art of surface coatings.

Typically, the metal debonding coating composition will comprise between 0.5 and 50 weight % of the ceramic coating material, and more preferably, between 2 and 25 weight % of the ceramic coating material, in relation to the total metal debonding coating composition. Conversely, the metal coating composition will typically comprise between 50 and 99.5 weight % carrier, and more preferably 75 and 98 weight % carrier, based on the total weight of the metal debonding coating composition. Optionally, the metal debonding coating composition may comprise up to 2 weight % dispersant, based on the total weight of the metal debonding coating composition.

- 10 The metal debonding coating composition of the present invention has surprisingly been found to prevent complementary contacting metal surfaces from becoming bonded to each other when in use in a high temperature or high pressure environments, for example, such as in a glass product manufacturing process. More especially the application of the metal bonding coating composition has been found to prevent the bonding of coated metal surfaces in use at temperature in the region of 1500°C and even up to temperatures of 1900°C.

As such, in accordance with an alternative embodiment of the invention there is provided a method of applying a metal debonding coating composition comprising a ceramic coating material, as described above, to a substrate and the method comprises the steps of:

- a. providing a substrate having at least one metal containing surface, and
 - b. applying the metal debonding coating composition to the substrate, such that the ceramic coating material adheres to the at least one metal containing surface of the substrate.
- 25 Preferably the metal debonding coating composition is applied only to the at least one metal containing surface, however, application to the entire surface of the substrate (regardless of the surface composition) may allow for greater ease of application and manufacturing of accordingly coated substrates.

Generally, the substrate can be considered to be a work piece, and when in use said at least one metal containing surface of the work piece will be brought into contact with an at least one metal containing surface of a complementary work piece, in an environment where there is a likelihood of the work piece surfaces
5 which are in contact may become bonded together.

As discussed herein, a “system” comprises a first work piece (also referred to herein as a substrate) and a complementary work piece (also referred to herein as a complementary substrate). The first work piece has a PGM-containing surface and the complementary work piece has a metal-containing surface. The metal-
10 containing surface of the complementary work piece is also preferably PGM-containing. These surfaces can be brought together when the system is in use.

As used herein, “brought into contact” means that the PGM-containing surface of the first work piece and the metal-containing surface of the complementary work piece can be brought into a position where at least a portion of the surfaces are in
15 contact. This portion is referred to as the “contact surface” herein. Since at least one of the PGM- or metal-containing surfaces has a ceramic coating, it will be understood that the PGM- and metal-containing surfaces do not come into direct contact but are separated by the layer of ceramic coating material composition.

At least one of the work pieces has a ceramic coating on the PGM- or metal-
20 containing surface. In some embodiments the surfaces of both the first and complementary work pieces have a ceramic coating. Preferably, only one of the work pieces has a ceramic coating on the PGM- or metal-containing surface. In a preferred embodiment the first work piece has a ceramic coating on the PGM-containing surface, while the metal-containing surface of the complementary work
25 piece is uncoated. Most preferably, the first work piece has a ceramic coating on the PGM-containing surface, while the complementary work piece has a PGM-containing surface which is uncoated.

The following are examples of systems comprising a first work piece and a complementary work piece according to the invention, though the invention is not limited to these systems.

5 A first system includes a bushing assembly comprising a first work piece and a complementary work piece. The first work piece is typically a cylindrical lining for an opening (also known as a “bushing”), and the complementary work piece contacts the bushing. The two parts are brought into contact when the system is in use. A ceramic coating may be applied on at least a portion of the contact surface of the first and/or complementary work pieces.

10 A second system includes a stopper and a neck. A ceramic coating may be applied on at least a portion of the contact surface of the stopper and/or neck. In one embodiment the contact surface on the stopper has a ceramic coating while the contact surface of the vessel neck is uncoated. In another embodiment the contact surface on the vessel neck has a ceramic coating while the contact
15 surface of the stopper is uncoated.

A third system includes a crucible and a crucible lid. A ceramic coating may be applied on at least a portion of the contact surface of the crucible and/or crucible lid. In one embodiment the contact surface on the crucible has a ceramic coating while the contact surface of the crucible lid is uncoated. In another embodiment
20 the contact surface on the crucible lid has a ceramic coating while the contact surface of the crucible is uncoated.

A fourth system includes a first washer and a second washer. A ceramic coating may be applied on at least a portion of the contact surface of either or both washers. Preferably the contact surface of one washer has a ceramic coating
25 while the contact surface of the second washer is uncoated.

A fifth system includes a stirrer-plunger and a neck. A stirrer-plunger is a device which simultaneously stirs a liquid (e.g. molten glass) and oscillates up and down to force the liquid through an opening. A ceramic coating may be applied on at

least a portion of the contact surface of the stirrer-plunger and/or neck. In one embodiment the contact surface on the stirrer-plunger has a ceramic coating while the contact surface of the neck is uncoated. In another embodiment the contact surface on the neck has a ceramic coating while the contact surface of the stirrer-plunger is uncoated.

The following embodiments described in relation to the substrate (or work piece) also apply to the complementary substrate (or complementary work piece) unless stated otherwise.

Preferably, the substrate (or work piece) comprises at least one platinum group metal (PGM) selected from the following: ruthenium, rhodium, palladium, iridium, platinum, or an alloy thereof. More preferably the substrate comprises platinum, or an alloy thereof, and most preferably the substrate comprises a rhodium-platinum alloy. Suitably, substrates may be formed solely or entirely of platinum group metals (PGMs); PGM substrates are used in glass manufacturing processes due to their chemically inert nature and ability to withstand high temperatures without loss of shape or other types of disintegration. As such, preferably the substrate at least one metal surface comprises a PGM.

However, in the alternative, the at least one metal containing surface of the substrate may be provided by a metal, preferably a PGM as described above, which has been used as a layer to encase, or clad, a cheaper or lighter base material body to form a useful substrate for use. This will be described in more detail below. In addition, different PGMs containing alloys may be employed as the substrate, or as a layer, casing or cladding, to an alternative base material to form a substrate, with properties attuned to the particular manufacturing process in which they are used.

As such, in some embodiments the substrate may be formed from a base material, on to which the preferred PGM is applied, in a layer (via encasing, cladding or similar), to provide the at least one metal surface. More especially, the substrate may be formed from an alternative metal base material, which for example may be

cheaper than forming the substrate entirely from a PGM, and then this may be clad or coated with a PGM layer upon its surface; in this case the base material is preferably molybdenum. Alternatively, the substrate may be formed from a ceramic base material, and this may be clad or coated with a PGM layer upon its surface to provide the at least one metal surface. The said PGM layer may cover the entirety of the base material and hence provide a continuous metal surface, or alternatively, may be provided in a discrete or discontinuous layer, for example to the external surface of work piece only, or to a rim of a work piece only, to provide one or more of said at least one metal surface.

Additionally, the metal debonding coating composition may be applied to the at least one metal containing surface in a continuous or discontinuous layer. Where the metal debonding coating composition is applied as a discontinuous layer it is preferable that at least 50% of the metal containing surface is coated, more preferably 75 % of surface is coated, and even more preferably 80% of the surface is coated. Most preferably the composition is applied in a continuous layer, which coats substantially 100% of the metal surface, so as to delimit the surface sites which may permit metal debonding when the substrate is in use. As will be appreciated, it would be possible to provide one substrate surface with a continuous layer of metal debonding composition, and then provide the opposing and complementary substrate surface (when in use) with a discontinuous layer of the metal debonding composition below 50% of the surface being coated without loss of effective metal debonding, however, such an arrangement may require more onerous assembly of the substrates prior to use to, for example, to offset the coated areas, and so such an embodiment is less preferred.

Additionally, or alternatively, the metal debonding coating composition may be applied to the entire surface of the substrate (including those surfaces which may not be metal containing). In this case, all surfaces, and not only those which will be in contact with other metal surfaces, and at risk of bonding in use will have been coated. This method of application is particularly preferred for small work pieces, or those of intricate design, and may also minimise user error in the

placing of the work pieces when in use thus avoiding the accidental bonding of work pieces that have been incorrectly arranged.

It should be understood that the term surface can refer to an external surface, or an internal surface, and is intended to encompass any surface of a work piece or
5 substrate where metal bonding in use may be of concern.

Suitably the metal debonding coating composition may be applied by any suitable coating method. More especially, the metal debonding coating composition may be applied by brush, roller, dipping, spraying or by vapour deposition techniques such as chemical vapour deposition or physical vapour deposition. Most preferably
10 the metal debonding coating composition is applied by spraying. Preferred spraying methods include pressurised systems, utilising compressed air or chemical propellants, as these have been found to allow ease of application of the coating composition. However, the choice of application method will depend upon the size and intricacy of the substrate surface to which the coating
15 composition is to be applied. A suitable application method selection may be made on the basis of the knowledge of the skilled person.

Suitably the metal debonding coating composition is applied to provide a coating thickness of between about 10 microns (μm) to about 5 millimetres (mm) of the adhered ceramic coating material, and most preferably the metal debonding
20 coating composition is applied to provide a coating thickness of between about 100 μm to about 500 μm . However, the desired thickness of the coating may depend upon the environment in which the coated substrate work piece is to be used, the nature of the metal surface of the substrate to which the coating it to be applied, and the method which is employed to apply the coating. More especially,
25 where manual means such as brush or roller methods of application are employed a thicker coating may suitably be achieved, and where chemical vapour deposition methods are employed a thinner coating may suitably be achieved.

Optionally, once the metal debonding coating composition has been applied to the substrate, the coated substrate may be allowed to air dry, such that the coating composition carrier is substantially removed.

5 Additionally, or alternatively, once the metal debonding coating composition has been applied, the coated substrate may be cured at an elevated temperature. Curing the coated substrate ensures that the coating composition carrier is substantially removed. Curing provides additional improvements to the aforementioned air drying, as curing has been found to provide better adhesion of the metal debonding coating composition to the substrate to which it is applied;
10 this improves coating composition "drop off".

Suitably, curing at an elevated temperature is carried out at a temperature of about 450°C to 1000°C, more preferably at a temperature of about 500°C to about 750°C, and most preferably at a temperature of about 550°C to about 650°C. Preferably, the curing at an elevated temperature is carried out in an appropriately
15 sized furnace.

Suitably, the curing at an elevated temperature is carried out for a time duration of 0.5 hours to 4 hours, and more preferably curing is carried out for a time duration of 1.5 to 2.5 hours. However, suitably the total curing procedure may encompass a temperature ramp up phase, a dwell phase when curing is achieved, and a
20 temperature ramp down phase, in this case the total curing procedure may be carried out for a time duration of about 24 hours to about 48 hours, and preferably the total curing procedure is carried out for a time duration of about 36 hours. Suitably, the optional ramp up phase will utilise a rate of 100° per hour, and the optional ramp down phase will utilise a rate of 50°C per hour. The use of such a
25 total curing procedure is not necessary, and the coated substrate may be placed in a hot environment for curing without any detrimental effect being observed; similarly, once curing of the coating composition has occurred, the coated substrate may be removed from the furnace and allowed to air cool without any detrimental effect being observed.

- After the optional drying and curing step have been performed, the substrate is rendered in its final ready to use state with the desirable ceramic coating material adhered to the metal containing surfaces of the substrate. The metal debonding coating composition will now have had substantially all of the carrier removed, and
- 5 the adhered coating will comprise between 75 and 99 weight % of the ceramic coating material, as described above. This aspect will be further described in relation to the substrate product, below, where the metal debonding composition material which has adhered to the substrate rendered in its final "ready to use" state is referred to as the ceramic coating material composition, as the
- 10 composition will now necessarily comprise a majority of ceramic coating material, the carrier having been removed; this is as opposed to a composition comprising a majority of carrier which may be the case for the metal debonding coating composition prior to its application and adhesion to the substrate, as described above.
- 15 Optionally, the method may include an initial cleaning step, such that prior to coating the substrate with the metal debonding coating composition, the substrate surface to which the coating is to be applied is cleaned. The optional cleaning step ensures that the surface of the substrate to which the metal debonding coating composition is to be applied is dust and oil free, and this helps to ensure
- 20 that good adhesion of the metal debonding coating composition and the substrate surface is achieved, and any future "drop off" is minimised. The inclusion of this step is particularly preferred where the substrate is manufactured and then handled and/or transported prior to the applying the metal debonding coating composition.
- 25 According to a still further aspect of the invention, there is provided a substrate comprising ceramic coating material composition adhered to at least one metal containing surface. The substrate is as described above in relation to the method of applying the metal debonding coating composition above. In this case the ceramic coating material composition is derived from the application of the metal
- 30 debonding coating composition, described above, and has many similarities, save

for the fact that the majority, and preferably substantially all, of the carrier present in the metal debonding coating composition is removed in the ceramic coating composition which is adhered to the substrate as intended for use.

Suitably the ceramic coating material composition is adhered to the substrate at
5 least one metal containing surface to provide a coating thickness of between about 10 microns (μm) to about 5 millimetres (mm), more preferably to provide a coating thickness of between about 100 μm and 500 μm .

As described above in relation to the metal debonding coating composition, essentially, the ceramic coating material composition comprises a ceramic coating
10 material, and the ceramic coating material comprises one or more oxides of titanium, aluminium, chromium, yttrium, zirconium or hafnium. Preferably, the ceramic coating material comprises yttrium, zirconium or hafnium. More preferably the ceramic coating material comprises one or more of yttrium oxide or zirconium oxide, and most preferably the ceramic coating material comprises yttrium oxide,
15 more especially yttrium (III) oxide (yttria, Y_2O_3). In some particularly preferred embodiments the ceramic coating material will comprise yttrium oxide.

Suitably, the final substrate product is prepared from the method described above, and the final dried and/or cured coating material composition will comprise ceramic coating material in an amount of between 75 and 100 weight % of the total
20 adhered ceramic coating material composition; the presence of the carrier which is necessary to achieve application of the metal debonding ceramic coating composition having now been substantially removed, as described above. As such, the substrate of the present invention comprises a ceramic coating material composition adhered to the substrate which comprises ceramic coating material in
25 an amount between 75 weight % and 100 weight % of the total ceramic coating material composition, preferably the adhered ceramic coating material composition comprises ceramic coating material in an amount between 80 and 98 weight % of the total ceramic coating material composition, and more preferably the adhered ceramic coating material composition comprises ceramic coating material in an

amount between 90 and 98 weight % of the total ceramic coating material composition.

In a particularly preferred embodiment the ceramic coating material composition comprises 75 to 100 wt% of one or more oxides of yttrium, zirconium or hafnium,
5 preferably 80 to 98 wt% or 90 to 98 wt%.

In one embodiment the ceramic coating material composition comprises 75 to 100 wt% of yttrium oxide, preferably 80 to 98 wt% or 90 to 98 wt%

The ceramic coating material composition may optionally comprise a dispersant, as described in relation to the metal debonding coating composition, however,
10 preferably the dispersant is substantially removed and not present in the finished substrate product. When the dispersant is present, the adhered ceramic coating material composition may comprise dispersant at an amount of between 1 weight % and 25 weight % of the total adhered ceramic coating material composition, and preferably at an amount between 2 weight % and 10 weight %, and more
15 preferably at an amount between 5 weight % and 2 weight % of the total ceramic coating material composition. Ideally, the presence of the dispersant is kept as low as possible in the adhered ceramic coating material composition, and most preferably is not present in the final coated substrate product.

As described above in relation to the method embodiment, preferably, the
20 substrate comprises at least one platinum group metal (PGM) selected from the following: ruthenium, rhodium, palladium, iridium, platinum, or an alloy thereof. More preferably the substrate comprises platinum, or an alloy thereof, and most preferably the substrate comprises a rhodium-platinum alloy.

However, as described above, in the alternative, the substrate may comprise a
25 base material, which is encased, clad or coated by a layer comprising the preferred PGM. In this case, preferably the base material comprises an alternative metal, and most preferably comprises, or consists of, molybdenum, or the base

material comprises, or consist of, a ceramic. Suitable base materials will be known to the person skilled in the art.

The said PGM layer may cover the entirety of the base material and hence provide a continuous metal surface on the substrate, or alternatively, may be provided in a discrete or discontinuous layer, for example to the external surface of work piece only, or to a rim of a work piece only, to provide an at least one metal surface on the substrate.

Optionally, the substrate at least one metal containing surface may comprise the adhered ceramic coating material composition in a continuous or discontinuous layer which coats the said metal containing surface. Preferably at least 50% of the at least one metal containing surface is coated, more preferably 75 % of the at least one metal containing surface is coated, and even more preferably 80% of the at least one metal containing surface is coated. Most preferably the composition is applied in a continuous layer, which coats substantially 100% of the metal containing surface, so as to delimit the surface sites which may permit metal debonding when the substrate is in use.

In accordance with one embodiment of the present invention there is provided use of a system as hereinbefore defined, in a glass manufacturing process. The ceramic coating material composition is applied to the substrate by virtue of application of the metal debonding coating composition of the present invention, and has particular utility in preventing complementary metal surfaces on substrates, or work pieces, from becoming bonding together during use, as more fully described above. The present invention addresses a long felt want within this industry.

It will be appreciated that features described in relation to one aspect of the invention may be equally applicable in another aspect of the invention. For example, features described in relation to the substrate, may be equally applicable to the method of applying a metal debonding coating composition to a substrate, and the substrate product per se and *vice versa*. Some features may not be

applicable to, and may be excluded from, particular aspects of the invention. In particular, it will be appreciated that the ceramic coating material composition is derived from the metal debonding coating composition once carrier present in the metal debonding coating composition has been removed during the application
5 method, as such the aspects of the metal debonding coating composition apply equally to the ceramic coating material composition adhered to the substrate, save for the aspects concerning the carrier.

Description of the Drawings

Embodiments of the present invention will now be described, by way of example,
10 and not in any limitative sense, with reference to the accompanying drawings, of which:

Figure 1 schematic of spray gun application of metal debonding coating composition to the external surface of a substrate.

Figure 2 shows test samples where complementary faces are placed in contact
15 prior to exposure to heat and pressure.

Figure 3 shows the same test samples as in Figure 2, after exposure to heat and pressure.

Figure 1 shows a substrate 5 comprising a ceramic base material 9, and a platinum metal layer 11 in the form of a cladding to provide a continuous metal
20 surface on the external surface of the substrate 5 onto which a yttria only ceramic containing coating material layer 13 is being applied via a spray gun 17 application method.

The spray gun 17 contains a metal debonding coating composition in the form of a yttria ceramic coating material suspended in a solvent carrier to form a low
25 viscosity free flowing slurry, to ensure that the ceramic is in a form suitable for application by spraying. In this case the carrier is a solvent comprising acetone to allow for rapid air drying.

Figure 1 shows the metal debonding coating composition leaving the spray gun 17 as a finally dispersed spray 15. The spray gun 17 assembly also includes a compressed air line 19, the compressed air acts as a propellant to assist in producing a homogenous spray or appropriate droplet size to ensure the desired coating coverage, and ultimately a consistent thickness across the layer of ceramic coating material 13. Alternative methods of metal debonding coating composition application are envisaged as being useful.

Once the substrate 5 has been provided with a ceramic coating material layer 13 of sufficient thickness the coated substrate 5 is allowed to air dry for a short period of time, so that the coated substrate can be more easily handled. Following this brief air drying, the coated substrate 5 is then placed in a suitable oven and heated to 600°C for 2 hours; this allows the ceramic coating to cure and ensure the complete removal of the carrier material. In addition, the heating procedure included a ramp up procedure of 100°C per hour, and a ramp down procedure of 50°C per hour. The curing step results in the provision of a substrate product 5 having a yttria containing ceramic coating composition 13 adhered to an outer surface of the substrate 5. The substrate product 5 is now in a form suitable for use in a high temperature processing environment without experiencing detrimental metal to metal surface bonding during use.

Examples

To demonstrate that the present invention overcomes the problem of metal to metal bonding a simple comparative experiment was designed, as follows:

A platinum metal sheet was prepared to provide four identical pairs of metal surfaces, each pair represents a pair of substrates each having a complementary metal surface, and the two complementary surfaces are brought into contact with one another in a high temperature environment, typical of a glass manufacturing process, under conditions which would result in the pair of substrates becoming bonded at the contacting complementary surfaces.

One of the pairs of metal surfaces was left in an uncoated state to act as a control test sample. The remaining three pairs of metal surfaces had a surface coated with a potential metal debonding composition containing a) high alumina, HA, b) yttria, Y_2O_3 or c) boron nitride, BN. These three coated pairs of complementary metal surfaces provided three test samples for comparison with the control test sample. The pairs of surfaces in contact with one another are shown in Figure 2, for each of the test samples one of the contacting surface has had the potential metal debonding composition applied, the other contacting surface has no coating applied.

10 The four pairs of complementary metal surfaces were placed in contact with each other, to provide four comparative test samples, and subject to a load (achieved by sandwiching the four samples between bricks, the lower of which can be seen in Figure 2).

15 The four test samples, under load as provided by the uppermost brick, were then placed in a furnace for to be tested exposed for 60 hours at a temperature of $1400^{\circ}C$. The test samples were also exposed to a temperature ramp up procedure of $100^{\circ}C$ per hour and a ramp down procedure of $50^{\circ}C$ per hour. This simple test was designed to mimic the working environment which metal substrates would be exposed to in a glass manufacturing process.

20 In this simple comparative test the uncoated control test sample demonstrated that the two complementary metal surfaces bonded together and could not be separated. This is as was to be expected.

25 In addition, the provision of a coating composition comprising BN, was unable to prevent the relevant metal surfaces from becoming bonded together, as such BN is not a suitable coating material to provide an effective metal debonding coating composition for use in high temperature environments.

It was can also be seen, in Figure 3, that the sample where HA was applied to the metal surfaces did not perform satisfactorily. In this case, the two complementary

metal surfaces became somewhat bonded, resulting in the thin metal sheet being torn and damage to the underlying metal surfaces being observed once the complementary metal surfaces had been forced apart.

5 For the test sample in which the complementary metal surfaces were coated with yttria, no metal bonding was observed, and the pair of metal sheets were simple separated by hand, with no resistance, once the sample had cooled down. There was no observation of tearing or damage of the metal surfaces in this case.

10 It will be appreciated by persons skilled in the art that the above embodiments have been described by way of example only, and not in any limitative sense, and that various alterations and modifications are possible without departure from the scope of the invention as defined by the appended claims.

The present invention also includes the following embodiments:

1. A metal debonding coating composition comprising a ceramic coating material and a carrier, wherein the ceramic coating material comprises one or more oxides of titanium, aluminium, chromium, yttrium, zirconium or hafnium.
5
2. A metal debonding coating composition in according to embodiment 1, wherein the ceramic coating material comprises one or more oxides of yttrium, zirconium or hafnium.
3. A metal debonding coating composition according to embodiment 1 or 2,
10 wherein the ceramic coating material comprises yttrium oxide.
4. A metal debonding coating composition according to any preceding embodiment, wherein the carrier comprises water, a solvent, or a mixture thereof.
5. A metal debonding coating composition according to embodiment 4,
15 wherein the carrier comprises a solvent selected from one or more of acetone, isopropyl alcohol, propanol or ethylene.
6. A metal debonding coating composition according to any preceding embodiment, further comprising a dispersant.
7. A metal debonding coating composition according to any preceding
20 embodiment, comprising between 0.5 and 50 weight % of the ceramic coating material and between 50 and 99.5 weight % carrier, based on the total weight of the metal debonding coating composition.
8. A metal debonding coating composition according to embodiment 7,
25 comprising between 2 and 25 weight % of the ceramic coating material and between 75 and 98 weight % carrier, based on the total weight of the metal debonding coating composition.

9. A metal debonding coating composition according to any one of embodiments 6 to 8, comprising up to 2 weight % dispersant, based on the total weight of the metal debonding coating composition.

5 10. A method of applying a metal debonding coating composition comprising a ceramic coating material to a substrate, wherein the method comprises the steps of:

a. providing a substrate having at least one metal containing surface, and

10 b. applying the metal debonding coating composition to the substrate, such that the ceramic coating material adheres to the at least one metal containing surface of the substrate.

11. A method according to embodiment 10, wherein the substrate comprises at least one platinum group metal (PGM) selected from the following: ruthenium, rhodium, palladium, iridium, platinum, or an alloy thereof.

15 12. A method according to embodiment 11, wherein the substrate comprises platinum, or an alloy thereof, and most preferably the substrate comprises a rhodium-platinum alloy.

13. A method according to any one of embodiments 10 to 12, wherein said substrate at least one metal surface comprises a platinum group metal (PGM).

20 14. A method according to any one of embodiments 10 to 13, wherein the metal debonding coating composition may be applied to the at least one metal containing surface in a continuous or discontinuous layer.

25 15. A method according to embodiment 14, wherein the metal debonding coating composition is applied as a discontinuous layer and at least 50% of the at least one metal containing surface is coated.

16. A method according to embodiment 14, wherein Most preferably the composition is applied in a continuous layer, which coats substantially 100% of the at least one metal containing surface.
- 5 17. A method according to anyone of embodiments 10 to 16, wherein the metal debonding coating composition is applied by brush, roller, dipping, spraying or by a vapour deposition technique.
18. A method according to embodiment 17, wherein the metal debonding coating composition is applied by spraying.
- 10 19. A method according to any one of embodiments 10 to 17, wherein the metal debonding coating composition is applied to provide a coating thickness of between about 10 microns (μm) to about 5 millimetres (mm) of the adhered ceramic coating material,
- 15 20. A method according to embodiment 19, wherein the metal debonding coating composition is applied to provide a coating thickness of between about 100 μm to about 500 μm of the adhered ceramic coating material
21. A method according to any one of embodiments 10 to 20, wherein once the metal debonding coating composition has been applied to the substrate, the coated substrate may be allowed to air dry, such that the coating composition carrier is substantially removed.
- 20 22. A method according to any one of embodiments 10 to 21, wherein once the metal debonding coating composition has been applied, the coated substrate may be cured at an elevated temperature.
23. A method according to embodiment 22, wherein the curing at an elevated temperature is carried out at a temperature of about 450°C to 1000°C.
- 25 24. A method according to embodiment 23, wherein the curing at an elevated temperature is carried out at a temperature of about 500°C to about 750°C.

25. A method according to embodiment 24, wherein the curing at an elevated temperature is carried out at a temperature of about 550°C to about 650°C.

26. A method according to any one of embodiments 22 to 25, wherein the curing at an elevated temperature is carried out for a time duration of 0.5 hours to 4 hours.

27. A method according to embodiment 26, wherein the curing at an elevated temperature is carried out for a time duration of 1.5 to 2.5 hours.

28. A method according to any one of embodiments 10 to 27, further comprising an initial cleaning step

29. A substrate comprising ceramic coating material composition adhered to an at least one metal containing surface.

30. A substrate according to embodiment 29 is in the form of a refractory, bushing, die, stopper or stirrers, suitable for use in a glass manufacturing process.

31. A substrate according to embodiment 29 or 31, wherein the ceramic coating material composition is adhered to the substrate at least one metal containing surface to provide a coating thickness of between about 10 microns (µm) to about 5 millimetres (mm)

32. A substrate according to embodiment 31, wherein the ceramic coating material composition is adhered to the substrate at least one metal containing surface to provide a coating thickness of between about 100 µm and 500µm.

33. A substrate according to any one of embodiments 29 to 32, wherein the ceramic coating material composition comprises a ceramic coating material, and the ceramic coating material comprises one or more oxides of titanium, aluminium, chromium, yttrium, zirconium or hafnium.

34. A substrate according to embodiment 33, wherein the ceramic coating material comprises yttrium, zirconium or hafnium.

35. A substrate according to embodiment 34, wherein the ceramic coating material comprises yttrium oxide.

5 36. A substrate according to any one of embodiments 29 to 35, wherein the substrate comprises ceramic coating material in an amount of between 75 and 100 weight % of the total adhered ceramic coating material composition.

10 37. A substrate according to embodiment 36, wherein the substrate comprises ceramic coating material in an amount of between 90 and 98 weight % of the total adhered ceramic coating material composition.

38. A substrate according to any one of embodiments 29 to 37, comprising a ceramic coating material composition which further comprises a dispersant

15 39. A substrate according to embodiment 38, wherein the substrate comprises dispersant in an amount of between 1 weight % and 25 weight % of the total adhered ceramic coating material composition.

20 40. A substrate according to any one of embodiments 29 to 39, wherein the substrate comprises at least one platinum group metal (PGM) selected from the following: ruthenium, rhodium, palladium, iridium, platinum, or an alloy thereof.

41. A substrate according to embodiment 40, wherein the substrate comprises platinum, or an alloy thereof, and most preferably the substrate comprises a rhodium-platinum alloy.

25 42. A substrate according to embodiment 40 or 41, wherein the substrate comprises a base material, which is encased, clad or coated by a layer comprising said at least one platinum group metal (PGM) selected from the

following: ruthenium, rhodium, palladium, iridium, platinum, or an alloy thereof

43. A substrate according to embodiment 42, wherein said base material comprises molybdenum, or a ceramic.

5 44. A substrate according to any one of embodiments 29 to 43, wherein the at least one metal containing surface comprises the adhered ceramic coating material composition in a continuous or discontinuous coating.

45. Use of a substrate according to any one of embodiments 29 to 44, in a glass manufacturing process.

10 46. Use of a substrate in a glass manufacturing process according to embodiment 45, wherein the process is operated at temperature up to 1900°C.

15 47. Use of a substrate in a glass manufacturing process according to embodiment 45, wherein the process is operated at a temperature up to 1450°C.

Claims

1. A system comprising:

a first work piece having at least one platinum group metal (PGM) containing surface; and

5 a complementary work piece having at least one metal-containing surface;

wherein said at least one PGM-containing surface of the first work piece can be brought into contact with said at least one metal-containing surface of the complementary work piece when in use;

10 characterized in that a ceramic coating material composition is adhered to at least one of said surfaces.

2. A system according to claim 1, wherein the metal-containing surface of said complementary work piece is a PGM-containing surface.

3. A system according to claim 1 or claim 2, wherein the first work piece and
15 the complementary work piece are selected from:

a bushing assembly comprising a first part and a complementary part;

a stopper and a neck;

a crucible and a lid;

a first washer and a second washer;

20 a stirrer-plunger and a neck.

4. A system according to any one of claims 1 to 3, wherein the ceramic coating material composition is adhered to the at least one PGM-containing surface of the first work piece to provide a coating thickness of between about 10 microns (μm) to about 5 millimetres (mm).

25 5. A system according to claim 4, wherein the ceramic coating material composition is adhered to the at least one PGM-containing surface of the first work piece to provide a coating thickness of between about 100 μm and 500 μm .

6. A system according to any one of claims 1 to 5, wherein the ceramic coating material composition comprises a ceramic coating material, and the ceramic coating material comprises one or more oxides of titanium, aluminium, chromium, yttrium, zirconium or hafnium.
- 5 7. A system according to claim 6, wherein the ceramic coating material comprises yttrium oxide, zirconium oxide or hafnium oxide.
8. A system according to claim 6, wherein the ceramic coating material comprises yttrium oxide.
9. A system according to any one of claims 1 to 8, wherein the ceramic
10 coating material composition adhered to the at least one surface comprises ceramic coating material in an amount of between 75 and 100 weight % of the total adhered ceramic coating material composition, preferably of between 90 and 98 weight %.
10. A system according to any one of claims 1 to 9, wherein the ceramic
15 coating material composition comprises 75 to 100 wt% of one or more oxides of yttrium, zirconium or hafnium.
11. A system according to any one of claims 1 to 10, wherein the ceramic coating material composition comprises 75 to 100 wt% of yttrium oxide.
12. A system according to any one of claims 1 to 11, wherein the ceramic
20 coating material composition further comprises a dispersant.
13. A system according to claim 12, wherein the total adhered ceramic coating material composition comprises dispersant in an amount of between 1 weight % and 25 weight %.
14. A system according to any one of claims 1 to 13, wherein the first work
25 piece comprises at least one platinum group metal (PGM) selected from the following: ruthenium, rhodium, palladium, iridium, platinum, or an alloy thereof.

15. A system according to claim 14, wherein the first work piece comprises platinum, or an alloy thereof.

16. A system according to claim 14, wherein the first work piece comprises a rhodium-platinum alloy.

5 17. A system according to any one of claims 1 to 16, wherein the first work piece comprises a base material, which is encased, clad or coated by a layer comprising said at least one platinum group metal (PGM) selected from the following: ruthenium, rhodium, palladium, iridium, platinum, or an alloy thereof

10 18. A system according to claim 17, wherein said base material comprises molybdenum, or a ceramic.

19. A system according to any one of claims 1 to 18, wherein the PGM-containing surface of the first work piece comprises the adhered ceramic coating material composition in a continuous or discontinuous coating.

15 20. A system according to any one of claims 1 to 19, wherein the metal-containing surface of the complementary work piece is uncoated.

21. Use of a system according to any one of claims 1 to 20, in a glass manufacturing process.

20 22. Use according to claim 21, wherein the process is operated at temperature up to 1900°C.

23. Use according to claim 21, wherein the process is operated at a temperature up to 1450°C.

24. A method of glass manufacture, in which molten glass is contacted with a system as claimed in any of claims 1 to 20.

25. A method according to claim 24, wherein the process is operated at temperature up to 1900°C.

26. A method according to claim 24, wherein the process is operated at a temperature up to 1450°C.

Figure 1

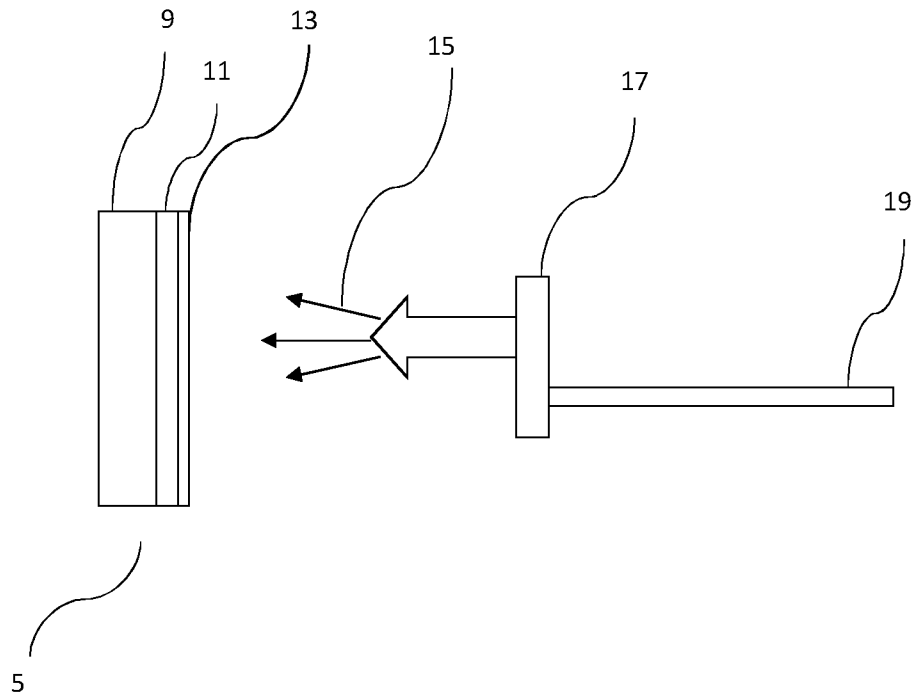


Figure 2

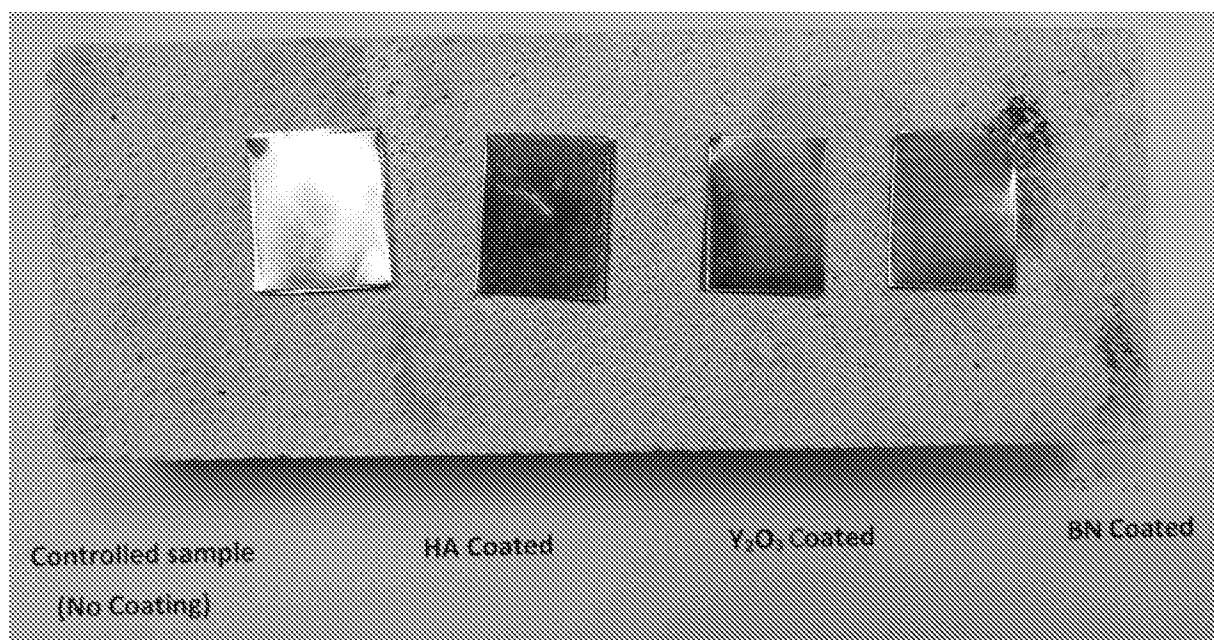
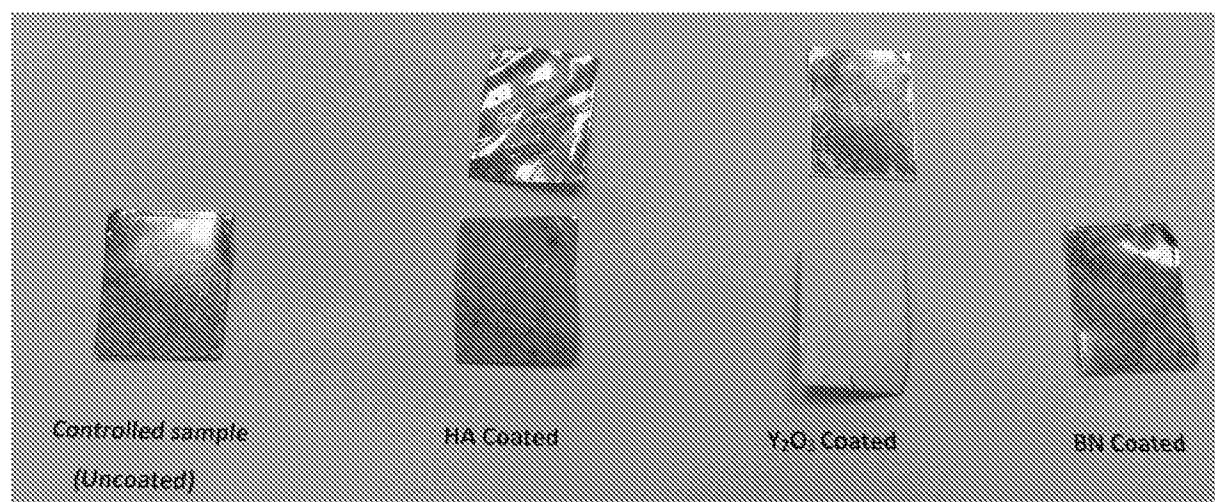


Figure 3



INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2019/051612

A. CLASSIFICATION OF SUBJECT MATTER
INV. C23C24/10
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C23C

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.
A	WO 2008/027482 A2 (CORNING INC [US]; GRZESIK DAVID M [US] ET AL.) 6 March 2008 (2008-03-06) the whole document	1-26
A	US 4 532 184 A (SCHUSTER GARY B A [US]) 30 July 1985 (1985-07-30) cited in the application the whole document	1-26



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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

"E" earlier application or patent but published on or after the international filing date

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

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

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"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

27 September 2019

Date of mailing of the international search report

11/11/2019

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2019/051612

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