

Description

This invention relates to a method of enhancing the purity of a body of fused quartz, e.g. vitreous silica, having opposed boundary surfaces, the method being of the kind disclosed in WO-A-8602919 which comprises maintaining the body at a temperature above 1000°C while a polarising potential is applied across the said boundary surfaces by means of electrodes at least one of which is in contact with the boundary surfaces so that at least some of the residual impurity ions are made to migrate away from one boundary surface towards the opposite boundary surface thereof and are subsequently discharged into the gaseous phase at the latter boundary surface. In particular the invention is concerned with an electrical purification method and articles purified by the method.

High purity vitreous silica (fused quartz) articles are commonly made by flame or electrical fusion of carefully refined powders derived from natural quartz crystal. With increasing attention being paid to residual impurities by certain industries, e.g. semiconductor and optical fibre manufacture, the level of purities sought is at times beyond that which can be achieved by conventional chemical and physical refinement techniques. There may even be an undesirable concentration of alkali ions, in articles manufactured from synthetic quartz or amorphous silica powders, either derived from the starting material or introduced accidentally as contamination in the manufacturing process.

For achieving very low levels of certain mobile metal ion impurities, notably ions of the alkali metals, e.g. lithium, sodium, potassium and copper, the application of an electrical polarising potential across the wall of a heated quartz article has been proposed (see WO-A-8602919 and JP-A-59169956). This can effect migration of the impurity ions away from one of the wall surfaces, and toward the opposite wall surface. The article may subsequently be cooled to ambient temperature while the polarising potential is still applied, in which case the impurities accumulating near the cathodic wall surface may be removed by machining or etching off a thin layer at that surface to leave the remaining mass of vitreous silica of higher average purity.

In one example included in WO-A-8602919, a method was described in which a vitreous silica crucible was inverted over an internal graphite mould and the crucible was rotated slowly while being heated with an oxy-propane burner. An electric potential of 4.5 kV was applied with the mould serving as negative electrode and the burner flame as positive electrode. Significant depletion of alkali metal ions was observed in the inner layers of the crucible, but while some coloration was observed in the flame due to the release of ions electrolysed from the crucible into the gas flame, significant amounts of alkali metal remained in the outer layers of glass.

The present invention represents an advance on the prior art and while it has several applications, it is particularly suited to the manufacture of fused quartz tubing, crucibles, and other hollow ware. The method of the invention may be applied to a finished tube or hollow ware, or in the course of drawing of the tube, or manufacture of the hollow ware or both during and after manufacture.

According to the present invention a method of the kind referred to of enhancing the purity of a body of fused quartz having opposed boundary surfaces, is characterised in that each of the electrodes makes electrical contact with the body via an at least partially ionised gaseous phase and in that at least one of the electrodes is used to heat the body.

Desirably the discharge of ions into the gaseous phase at said opposite boundary surface is continued to reduce the concentration of copper, lithium, potassium or sodium impurity ions in the body to a residual level which does not exceed 0.01 parts per million by weight.

Whereas in the past one or both of the electrodes used for electrolysing fused quartz has been a solid in contact with a surface of the fused quartz, it has now been found that it is possible to effect purification of a mass of heated fused quartz, for example a tube, by non-contact means using hot conductive gas flows to serve as the quartz contacting part of both positive and negative electrodes. This is particularly important in the purification of tubing for fibre optic applications, where any solid contact with the hot tube could cause unacceptable contamination or surface deformation.

It has furthermore been discovered that by using a hot conductive gas flow as the body-contacting part of the cathode, or negative electrode, and by ensuring that the cathodic surface of the mass of fused quartz is maintained at a sufficiently high temperature in a purging flow of gas, then it is possible to effect extensive volatilisation of the mobile impurity cations which would otherwise accumulate at the cathodic surface. Although the method according to the invention can be operated with the body of fused quartz at a temperature of 1000°C, it proceeds increasingly rapidly with higher temperatures, the preferred range being from 1500°C to 2100°C. The rate of movement of impurity ions towards the said opposite boundary surface is also dependent on the polarising potential applied and a potential difference of at least 10 V/mm thickness across the boundary surfaces is considered to be the minimum practical value.

The best known mobile impurities in vitreous silica are the ions of the alkali metals and of copper which may thus be substantially removed from a fused quartz article without the need for any solid contact with either surface of the article.

EP-A-0237431 describes a process and apparatus for the surface electrolysis of sheets of glass as they leave a float furnace, but in this case the electrodes are not used to heat the glass being electrolysed.

Brief Description of the Drawings

Figure 1 is a partly sectioned schematic view of one embodiment of apparatus for performing a method according to the invention of enhancing the purity of a fused quartz tube,

Figure 2 is a sectional view of another embodiment of apparatus for performing a method according to the invention of enhancing the purity of a tubular article of fused quartz, and

Figure 3 is a sectional view of a further embodiment of apparatus for performing a method according to the invention of enhancing the purity of a fused quartz crucible.

Description of Preferred Embodiments

Various methods according to the invention of enhancing the purity of bodies of fused quartz are illustrated by the following examples which should be read with reference to the appropriate one of the accompanying drawings.

Example 1 (see Figure 1)

A fused quartz tube 10 of outside diameter 25 mm and inside diameter 19 mm was mounted between the chucks 11,12 of a glass-working lathe. A wire 13 (e.g. of tungsten or molybdenum) was threaded through the tube bore and supported under slight tension along the tube axis by a spring 14. Gas fittings 15 and seals were provided in the tube bore so that argon gas (at a flow rate of 5 L/min) could be passed through the tube 10 while the latter was rotated in the lathe.

While thus rotating, the tube was heated by a metal oxy-hydrogen burner 16 (e.g. a semi-circular burner) to a temperature of 1600 °C, determined by the flow of gases and the rate of traverse of the burner in the axial directions of the tube.

While the burner was traversed along the tube at a rate of 50 mm/minute, a potential of 3.5 kV was applied between the wire 13 as anode (positive electrode) via graphite brushes 17 and the metal burner 16 as cathode (negative electrode). A corona discharge was observed within the tube bore around the wire 13 in the hot zone. The argon flow within the tube bore both protected the wire 13 and also provided a conductive path for the electrolysis current, (50 mA).

On application of the electrical potential a bright orange glow was observed in the burner flame which thus provided a conductive gaseous electrical contact with the exterior of the tube. Mobile metallic impurity ions were thus caused to diffuse through the fused quartz to the outer surface wall of the tube, where the hot gases stimulated vaporisation of the impurity ions, at the zone of impingement of the flame with the external surface of the tube.

The above treatment permitted a substantial up-grading of the purity of the tube material with respect to the following mobile metal ions, lithium, sodium, potassium and copper, as demonstrated by the analytical results below (ppm by weight).

	Typical Starting Tube	Similar Tube after Treatment
Li	0.34	< 0.01
Na	0.45	< 0.01
K	0.11	< 0.01
Cu	0.01	< 0.01

Example 2 (see Figure 2)

A hollow cylindrical ingot 20 of fused quartz having a wall thickness of 45 mm was lowered through a high temperature graphite furnace 21, as conventionally used for redrawing an annular ingot to tubing, operating at a temperature of 2100 °C. The interior 22 of the furnace was purged with nitrogen, and this gas

surrounded the ingot providing a gaseous conductive path between it and the graphite furnace.

In the course of the redrawing process, a graphite bobbin 23 was lowered on a graphite cord 24 down the axis of the annular ingot 20 through the furnace hot zone. An atmosphere of argon was maintained within the ingot, to preserve the graphite parts and to provide a conductive path for the electrolysis current.

A potential of 1000 volts was maintained between the graphite cord 24 as anode, and the graphite furnace 21 as cathode, and a current of 0.6 amps was caused to flow.

An electrolytic purification of the fused quartz occurred in the course of the above redrawing process, as is shown by the analytical figures given below. Once again the impurities are expressed in ppm by weight

	Tube without Electrolytic Current	Tube following Electrolytic Purification
Li	0.4	< 0.01
Na	0.54	< 0.01
K	0.20	< 0.01

Variations of the above process will be readily apparent to those skilled in the art.

Thus electrolytic purification in a lathe could be effected using either burner or plasma torch as heat source or gaseous electrode, alternatively a graphite or similar external furnace surrounding the tube in whole or in part could be employed.

The inner electrode could be replaced with a small internal burner, or plasma jet, or by alternative means of conduction, and the electrical polarity of the system may be reversed if required.

Again, the use of electrolytic purification in the course of redrawing of a larger ingot of fused quartz to a smaller sized product can be effected with alternative anode/cathode configurations, or the furnace may be replaced or supplemented by a flame or plasma heat source/electrode. Again the polarity of the system may be reversed if required.

Example 3 (see Figure 3)

A fused quartz crucible 30 having a wall thickness of 9 mm was inverted and placed over but not in contact with a hollow high purity graphite internal mould 31; the gap 32 between the mould 31 and the inner surface of the crucible 30 was uniformly about 5 mm.

The crucible and graphite were slowly rotated under an arrangement of ribbon flames 33 created by a water-cooled metal burner 34 fed with fuel gas and oxygen, and the crucible 30 was heated to a temperature of (about) 1500°C. A voltage of 2 kV was applied, between the burner 34 and the mould 31 such that the graphite mould 31 formed the anode and the metal burner 34 and its array of flames 33 formed the cathode of the electrolytic circuit. A current of 160 mA was caused to flow, and the flame was seen to glow bright orange.

The interior 35 of the mould 31 is filled with argon to serve as a protective atmosphere.

After this treatment, the crucible 30 was found to have a substantially reduced alkali content, as shown in the results below.

	Typical crucible untreated	Crucible after treatment
Li	0.4	< 0.01
Na	0.3	< 0.01
K	0.6	0.01
Cu	0.02	< 0.01
all in parts per million by weight		

Again, this Example demonstrates the efficiency of electrolytic purification, whereby both anodic and cathodic connections to the quartz are gaseous, and the mobile metal ion impurities may be volatilised at the cathodic surface.

The method of the invention operates conveniently at atmospheric pressure, but operation at higher or lower pressure is feasible. While argon represents a convenient conductive gas for use within a hollow tube or ingot being electrolysed, other gases may be used provided they yield a suitably conductive path under the conditions of temperature and pressure chosen for operation. In principle, any gas could be used to

comprise the gaseous electrode, but it is preferable to employ a gas which is readily used, non-hazardous, and does not react deleteriously with any components in the system. The so-called inert gases may be conveniently employed as can nitrogen or hydrogen. Other gases or gas mixtures may also be used.

As noted above, a combustion flame may likewise provide a useful source of conductive gas to act as one or both electrodes in the system. Such combustion flames may typically be generated by any appropriate fuel gas-oxidant combination. The combination in air, or preferably oxygen, of one or more of the fuel gases hydrogen, methane, ethane, propane, butane or acetylene, may be conveniently utilised in the present application.

Radial flow of electrolytic current, and therefore ion diffusion is obviously preferred, but depending on the geometry of the article being purified, other geometrical arrangements of electrode and workpiece may be used if required. An arrangement of particular interest is that of a quartz glass plate, whereby it is possible to achieve electrolytic purification of at least the central regions of a plate of fused quartz by traversing the plate between a pair of gaseous electrodes as defined above, for example a pair of oxy-hydrogen ribbon burners may be employed, both to heat the plate and to provide the necessary conductive gas flows.

Claims

1. A method of enhancing the purity of a body of fused quartz having opposed boundary surfaces, comprising maintaining the body at a temperature above 1000 °C while a polarising potential is applied across the said boundary surfaces by means of electrodes at least one of which is in contact with the boundary surfaces so that at least some of the residual impurity ions are made to migrate away from one boundary surface towards the opposite boundary surface thereof and are subsequently discharged into the gaseous phase at the said opposite boundary surface, characterised in that each of the electrodes makes electrical contact with the body via an at least partially ionised gaseous phase and in that at least one of the electrodes is used to heat the body.
2. A method as claimed in claim 1, characterised in that the discharge of ions into the gaseous phase at said opposite boundary surface is continued to reduce the concentration of copper, lithium, potassium or sodium impurity ions in the body to a residual level which does not exceed 0.01 parts per million by weight.
3. A method as claimed in claim 1 or 2, characterised in that the body is heated to a temperature in the range 1500 °C to 2100 °C by a flame, an electric arc, a plasma jet or a furnace.
4. A method as claimed in any one of the preceding claims, characterised in that the fused quartz body is a crucible, a hollow cylinder or a plate.
5. A method as claimed in any of claims 1 to 3, characterised in that the fused quartz body is a hollow cylinder and the purity enhancement is undertaken during conventional re-shaping of the hollow cylinder to form a body of differing diameter or cross-sectional area.
6. A method as claimed in any one of the preceding claims, characterised in that the body is maintained for a time corresponding to the thickness of the wall being polarised of at least 10 seconds/mm in the temperature range 1500 °C to 2100 °C and the effective polarising potential applied across the said boundary surfaces exceeds 10 V/mm thickness.
7. A method as claimed in any one of the preceding claims, characterised in that at least one of the gaseous electrodes is connected to electrical circuitry via a refractory conductor made from metal or carbon.
8. A method as claimed in any of the preceding claims, characterised in that the gaseous electrodes used to apply the polarising voltage are chosen from ionised helium, argon, neon, krypton, xenon, nitrogen or hydrogen or the flame produced by the combustion of hydrogen, methane, propane, butane or acetylene.



comprise the gaseous electrode, but it is preferable to employ a gas which is readily used, non-hazardous, and does not react deleteriously with any components in the system. The so-called inert gases may be conveniently employed as can nitrogen or hydrogen. Other gases or gas mixtures may also be used.

As noted above, a combustion flame may likewise provide a useful source of conductive gas to act as one or both electrodes in the system. Such combustion flames may typically be generated by any appropriate fuel gas-oxidant combination. The combination in air, or preferably oxygen, of one or more of the fuel gases hydrogen, methane, ethane, propane, butane or acetylene, may be conveniently utilised in the present application.

Radial flow of electrolytic current, and therefore ion diffusion is obviously preferred, but depending on the geometry of the article being purified, other geometrical arrangements of electrode and workpiece may be used if required. An arrangement of particular interest is that of a quartz glass plate, whereby it is possible to achieve electrolytic purification of at least the central regions of a plate of fused quartz by traversing the plate between a pair of gaseous electrodes as defined above, for example a pair of oxy-hydrogen ribbon burners may be employed, both to heat the plate and to provide the necessary conductive gas flows.

Claims

1. A method of enhancing the purity of a body of fused quartz having opposed boundary surfaces, comprising maintaining the body at a temperature above 1000 °C while a polarising potential is applied across the said boundary surfaces by means of electrodes at least one of which is in contact with the boundary surfaces so that at least some of the residual impurity ions are made to migrate away from one boundary surface towards the opposite boundary surface thereof and are subsequently discharged into the gaseous phase at the said opposite boundary surface, **characterised in that** each of the electrodes makes electrical contact with the body via an at least partially ionised gaseous phase and in that at least one of the electrodes is used to heat the body.
2. A method as claimed in claim 1, **characterised in that** the discharge of ions into the gaseous phase at said opposite boundary surface is continued to reduce the concentration of copper, lithium, potassium or sodium impurity ions in the body to a residual level which does not exceed 0.01 parts per million by weight.
3. A method as claimed in claim 1 or 2, **characterised in that** the body is heated to a temperature in the range 1500 °C to 2100 °C by a flame, an electric arc, a plasma jet or a furnace.
4. A method as claimed in any one of the preceding claims, **characterised in that** the fused quartz body is a crucible, a hollow cylinder or a plate.
5. A method as claimed in any of claims 1 to 3, **characterised in that** the fused quartz body is a hollow cylinder and the purity enhancement is undertaken during conventional re-shaping of the hollow cylinder to form a body of differing diameter or cross-sectional area.
6. A method as claimed in any one of the preceding claims, **characterised in that** the body is maintained for a time corresponding to the thickness of the wall being polarised of at least 10 seconds/mm in the temperature range 1500 °C to 2100 °C and the effective polarising potential applied across the said boundary surfaces exceeds 10 V/mm thickness.
7. A method as claimed in any one of the preceding claims, **characterised in that** at least one of the gaseous electrodes is connected to electrical circuitry via a refractory conductor made from metal or carbon.
8. A method as claimed in any of the preceding claims, **characterised in that** the gaseous electrodes used to apply the polarising voltage are chosen from ionised helium, argon, neon, krypton, xenon, nitrogen or hydrogen or the flame produced by the combustion of hydrogen, methane, propane, butane or acetylene.



Patentansprüche

1. Verfahren zur Steigerung der Reinheit eines Körpers aus Quarzglas mit einander gegenüberliegenden Begrenzungsflächen, bei dem der Körper auf einer Temperatur über 1000 °C gehalten wird, während über die Begrenzungsflächen ein polarisierendes Potential mittels Elektroden angelegt wird, von denen wenigstens eine mit den Begrenzungsflächen in Berührung steht, sodaß wenigstens ein Teil der verbliebenen Fremdionen zur Wanderung von einer Begrenzungsfläche zu der ihr gegenüberliegenden Begrenzungsfläche veranlaßt und dann in die Gasphase an der gegenüberliegenden Begrenzungsfläche abgegeben wird, dadurch gekennzeichnet, daß die Elektroden jeweils über eine teilweise ionisierte Gasphase in elektrischem Kontakt mit dem Körper stehen, und daß wenigstens eine der Elektroden zur Erwärmung des Körpers verwendet wird.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Abgabe von Ionen in die Gasphase an der gegenüberliegenden Begrenzungsfläche fortgeführt wird, um die Konzentration von Kupfer-, Lithium-, Kalium- oder Natriumfremdionen im Körper auf einen Restspiegel zu senken, der 0,01 Gewichtsprozent pro Million nicht überschreitet.
3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß der Körper auf eine Temperatur im Bereich von 1500 °C bis 2100 °C mittels einer Flamme, eines Lichtbogens, eines Plasmastrahls oder eines Ofens erhitzt wird.
4. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß es sich bei dem Quarzglaskörper um einen Tiegel, einen Hohlzylinder oder einen Teller handelt.
5. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß es sich bei dem Quarzglaskörper um einen Hohlzylinder handelt, und die Steigerung der Reinheit während einer herkömmlichen Umformung des Hohlzylinders zur Bildung eines Körpers mit einem anderen Durchmesser oder einer anderen Querschnittsfläche durchgeführt wird.
6. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der Körper eine der Stärke der Wandung, die polarisiert wird, entsprechende Zeit lang, nämlich wenigstens 10 Sekunden/mm, im Temperaturbereich von 1500 °C bis 2100 °C gehalten wird, und das über die Begrenzungsflächen angelegte wirksame polarisierende Potential größer ist als 10 V/mm Stärke.
7. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß wenigstens eine der Gaselektroden über einen hochschmelzenden Leiter aus Metall oder Kohlenstoff mit einer elektrischen Schaltungsanordnung verbunden ist.
8. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die zur Anlegung der polarisierenden Spannung verwendeten Gaselektroden aus ionisiertem Helium, Argon, Neon, Krypton, Xenon, Stickstoff oder Wasserstoff oder der durch Verbrennung von Wasserstoff, Methan, Propan, Butan oder Acetylen gebildeten Flamme gewählt werden.

Revendications

1. Procédé pour augmenter la pureté d'un corps de verre de silice ayant des surfaces limites opposées, comprenant le maintien du corps à une température supérieure à 1 000 °C pendant que l'on applique un potentiel polarisant entre lesdites surfaces limites, au moyen d'électrodes dont au moins l'une d'entre elles est en contact avec les surfaces limites, de telle sorte qu'au moins une partie des ions d'impureté résiduelle migre de l'une des surfaces limites vers la surface limite opposée à celle-ci et, par la suite, se décharge dans la phase gazeuse sur ladite surface limite opposée, caractérisé en ce que chacune des électrodes est en contact électrique avec le corps, par l'intermédiaire d'une phase gazeuse au moins partiellement ionisée, et en ce que l'on utilise au moins l'une des électrodes pour chauffer le corps.
2. Procédé selon la revendication 1, caractérisé en ce que la décharge d'ions dans la phase gazeuse sur ladite surface limite opposée est poursuivie pour réduire la concentration des ions d'impureté de cuivre, de lithium, de potassium ou de sodium dans le corps, à un niveau résiduel qui ne dépasse pas 0,01



partie par million en poids.

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3. Procédé selon la revendication 1 ou 2, caractérisé en ce que l'on chauffe le corps à une température dans la gamme de 1 500 °C à 2 100 °C par une flamme, un arc électrique, un jet de plasma ou un four.
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4. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le corps de verre de silice est un creuset, un cylindre creux ou une plaque.
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5. Procédé selon l'une quelconque des revendications 1 à 3, caractérisé en ce que le corps de verre de silice est un cylindre creux, et on réalise l'augmentation de la pureté au cours d'un remodelage conventionnel du cylindre creux, pour former un corps de diamètre différent ou de section droite différente.
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6. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le corps est maintenu pendant une durée correspondant à l'épaisseur de la paroi que l'on polarise, d'au moins 10 secondes/mm, dans la gamme de température de 1 500 °C à 2 100 °C, et le potentiel polarisant efficace, appliqué entre lesdites surfaces limites, dépasse 10 V/mm d'épaisseur.
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7. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que l'on connecte au moins l'une des électrodes gazeuses à un circuit électrique par l'intermédiaire d'un conducteur réfractaire fabriqué à partir de métal ou de carbone.
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8. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que l'on choisit les électrodes gazeuses, utilisées pour appliquer la tension polarisante, parmi l'hélium ionisé, l'argon, le néon, le krypton, le xénon, l'azote ou l'hydrogène, ou la flamme produite par la combustion d'hydrogène, de méthane, de propane, de butane ou d'acétylène.
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