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[54] **METHOD AND APPARATUS FOR FORMING AN ARTICLE OF HIGH PURITY METAL OXIDE**
12 Claims, 6 Drawing Figs.

[52] U.S. Cl. 239/422, 239/132.3, 239/424.5
[51] Int. Cl. F23d 11/16
[50] Field of Search 239/132.3, 291, 299, 424.5, 422

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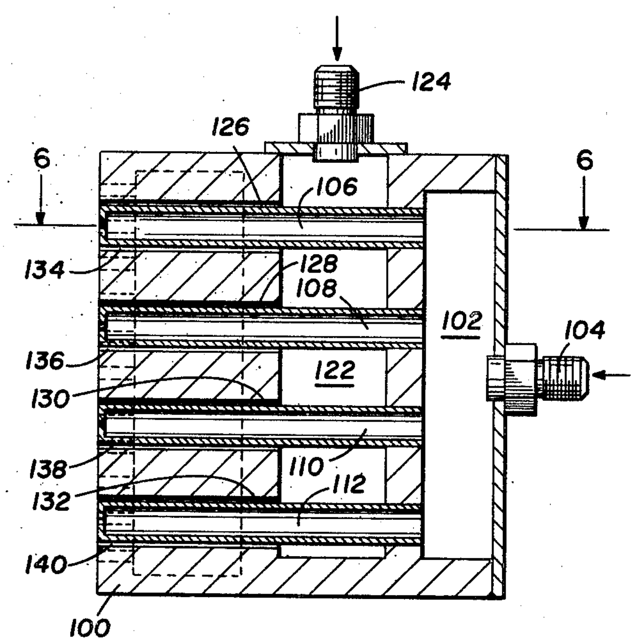
ABSTRACT: A torch flame resulting from the combustion of gaseous silicon tetrachloride and a mixture of hydrogen and oxygen is directed upon a mandrel in order to form a high purity silica article thereon. The torch includes a nozzle aperture for providing an output jet stream of silicon tetrachloride entrained in a carrier gas. A sheath of oxygen containing gases is streamed about the jet stream of silicon tetrachloride in order to prevent reaction immediately adjacent the face of the torch nozzle with a stream of combustible gas provided about the sheath of gas. When the torch is ignited, the resulting flame is directly applied to the mandrel wherein a layer of high purity silica is deposited thereon due to the vapor phase hydrolysis of the silicon tetrachloride.



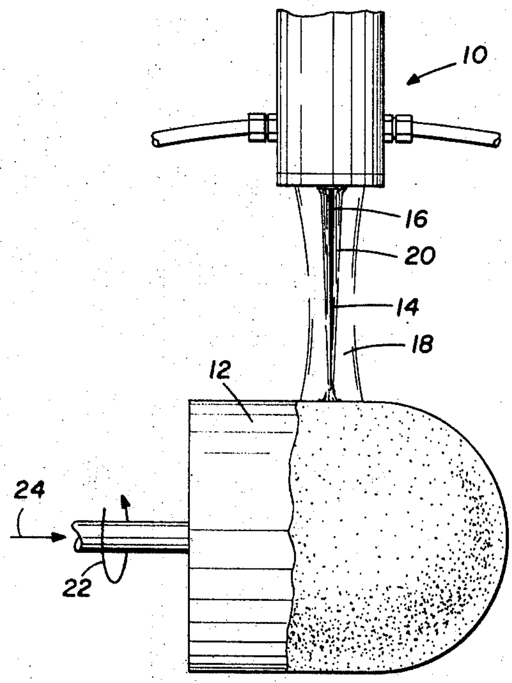


FIG. 1

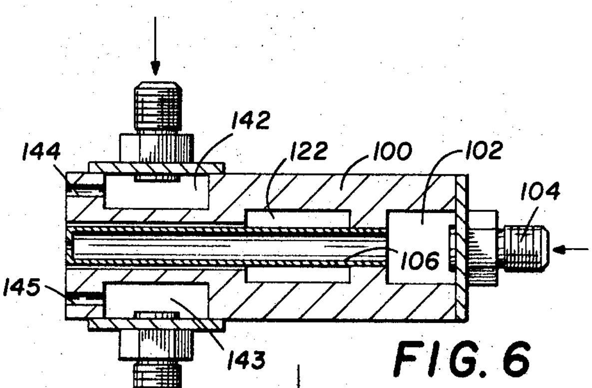


FIG. 6

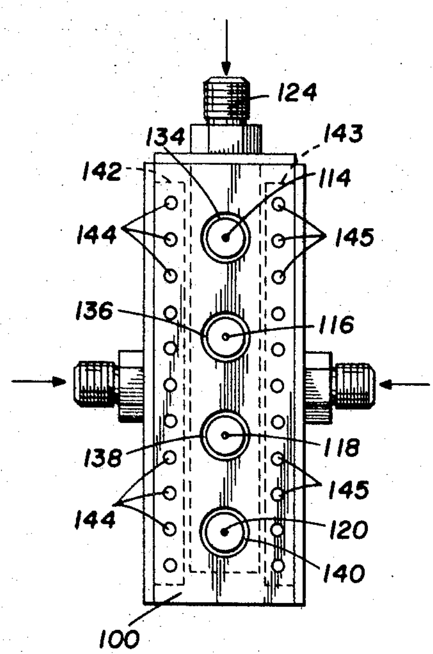


FIG. 5

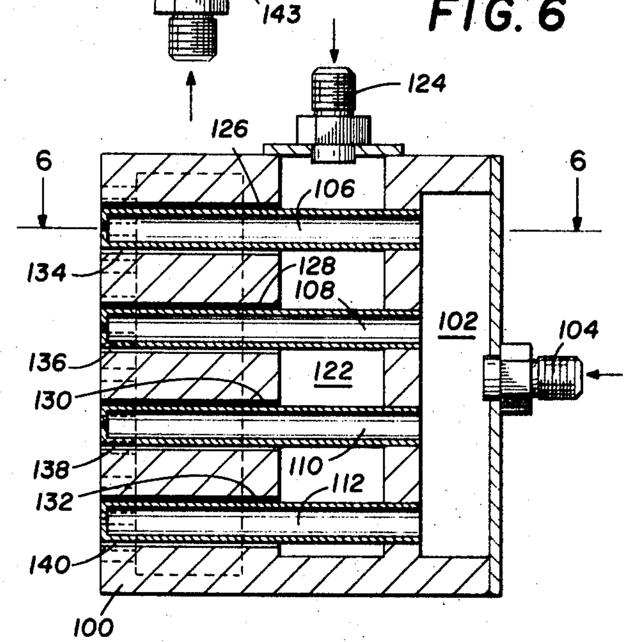


FIG. 4

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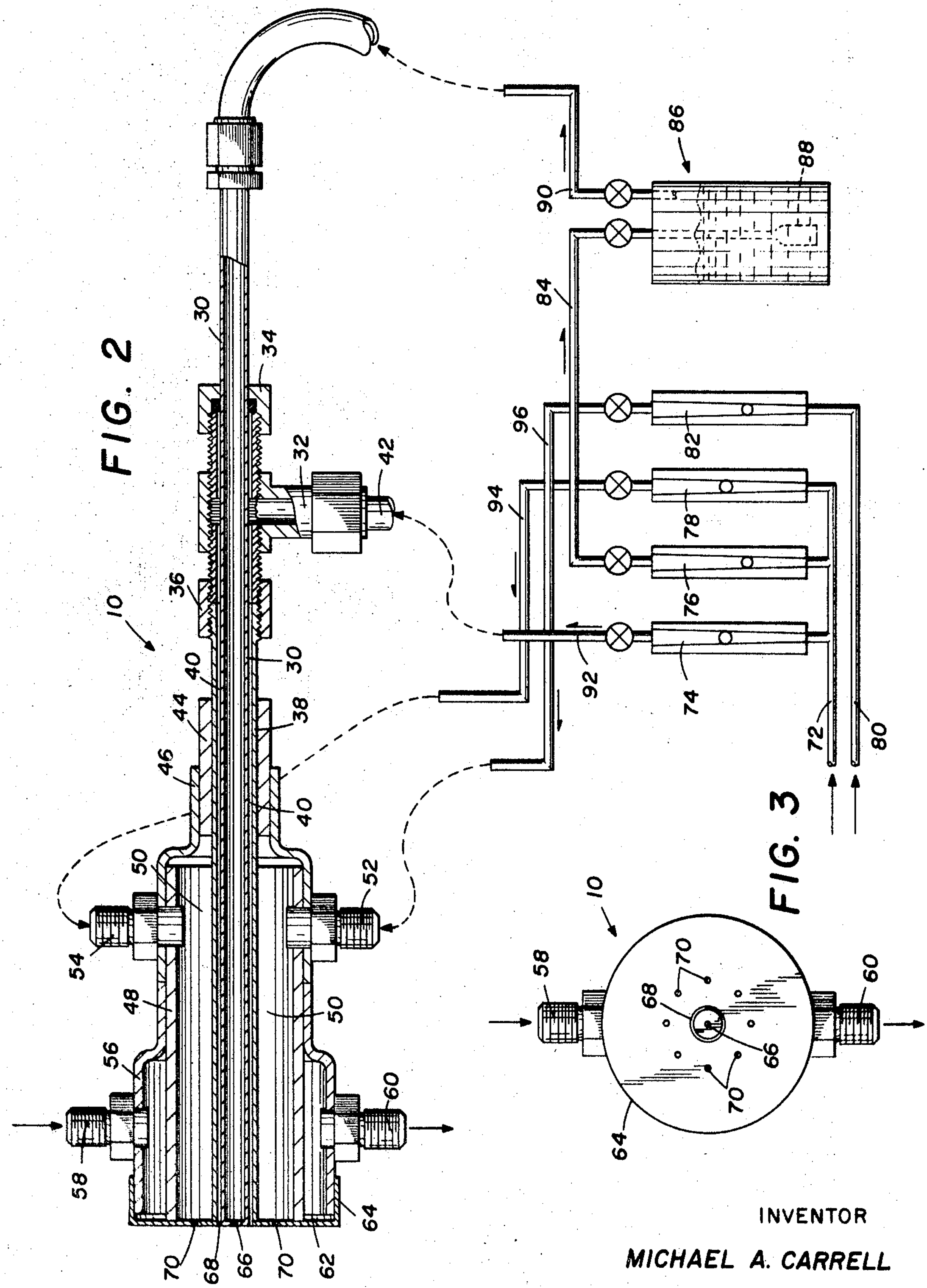

FIG. 2

FIG. 3

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METHOD AND APPARATUS FOR FORMING AN ARTICLE OF HIGH PURITY METAL OXIDE

This invention relates to the production of metal oxide by the decomposition of volatile metal chlorides, and more particularly to the deposition of metal oxide upon a substrate by the vapor phase hydrolysis by a flame of volatile anhydrous chlorides of metallic elements from groups III and IV of the periodic system, as for example, silicon tetrachloride, titanium tetrachloride, aluminum tetrachloride and tin tetrachloride.

In the formulation of certain semiconductor devices, monocrystalline silicon is "pulled" from a melt of silicon. Due to the extremely high temperatures required to provide a melt of silicon, it has been found that appreciable quantities of the material from which the crucible is constructed is lost within the melt. Hence, any impurities in the crucible enter into the pulled monocrystalline silicon. It has thus been found advantageous to construct the silicon melt crucible from very pure silica. It is also extremely important to provide a uniform "pull" from the silicon melt, and it is thus necessary that the crucible have very uniform sidewalls and a symmetrical configuration in order to prevent sudden changes in the level of the melt during pulling due to irregularities in the crucible configuration.

Various techniques have been heretofore devised for making articles from silica. For instance, U.S. Pat. No. 3,117,838, issued Jan. 14, 1964, discloses the utilization of a flaming torch for oxidizing a gas mixture including silane and a reactive gas to form molten silica and directing the molten silica onto a carbon form to grow a body of transparent silica. Further, U.S. Pat. No. 2,272,342, issued Feb. 10, 1942, discloses the production of a transparent article of silica by vaporizing silicon fluoride or silicon tetrachloride and decomposing the vapor in a flame. The flame is then impinged on a refractory core to deposit a layer of silica, whereupon the silica is vitrified to a transparent article by the application of high temperature. However, such previously developed techniques have not been completely satisfactory with respect to forming an extremely pure silica article having the desired uniform and symmetrical configuration, and having the necessary strength for use as a melt crucible.

It has been known that one can produce finely divided metal oxide from volatile metallic chloride by supplying a stream of the vaporized volatile metal chloride through a nozzle into a reactor and supplying oxygen and other gases to support combustion. The gas streams are then ignited in the reactor to decompose and oxidize the volatile metal chloride to form finely divided oxide which is withdrawn from the bottom of the reactor. In order to prevent obstruction of the nozzle due to buildup of crystals of the volatile metal chloride, it has heretofore been known to provide an alternate layer of relatively inert gas between the combustible supply of gas and the vaporized volatile metallic chloride. Examples of such systems are disclosed in U.S. Pat. No. 2,240,343, issued Apr. 29, 1941; U.S. Pat. No. 2,394,633, issued Feb. 12, 1946; and U.S. Pat. No. 2,823,982, issued Feb. 18, 1958.

In addition to the fact that such previously known burners have generally been useful only in a reaction chamber to form loose powdered oxide, such burners have often provided lower than desired efficiency in the production of oxide. One reason for this low efficiency is thought to be the fact that relatively large amounts of vaporized metallic chloride have been provided at high mass flow rates through large burner openings, thereby resulting in uneven contact of the different gas mixtures in certain regions in the flame. Further, such techniques have generally utilized oxidation processes rather than the hydrolysis of the volatile metal chloride. For these and other reasons, such burners have not been generally useful outside such reaction chambers for the direct application of silica upon mandrels where high deposition efficiency and even application of silica is required.

In accordance with the present invention, a volatile metallic chloride is vaporized and entrained in a carrier gas and then streamed from a jet nozzle. A stream of combustible gas is formed symmetrically about the jet stream, with interaction between the two streams being prevented in a preselected region adjacent the jet nozzle. The streams are ignited at a zone of interaction to form a flame which is directed upon a mandrel to form an article of high purity oxide directly thereupon.

In a more specific aspect of the invention, a torch is provided with a central passage therethrough for receiving gaseous silicon tetrachloride entrained in carrier gas. A nozzle aperture is defined in one end of the passage to provide an output jet stream of gaseous silicon tetrachloride entrained in the carrier gas. A sheath chamber defined in the torch includes an inlet for receiving an oxygen-containing gas and has an annular opening concentrically disposed about the nozzle aperture to provide a circular stream of oxygen-containing gas around the jet stream. A mixing chamber is disposed about the sheath chamber within the torch body and includes inlets for hydrogen and oxygen-containing gases. A plurality of output openings are disposed symmetrically around the annular sheath opening to provide streams of gaseous combustible mixture to allow the torch to be ignited and directed upon a mandrel for the deposition of high purity silica thereon.

For a more complete understanding of the present invention and for further objects and advantages thereof, reference may now be made to the following description taken in conjunction with the accompanying drawings, in which:

FIG. 1 illustrates somewhat diagrammatically the formation of a silica crucible upon a rotating mandrel with the present torch;

FIG. 2 illustrates an embodiment of the present torch;

FIG. 3 illustrates an end view of the nozzle of the torch shown in FIG. 2;

FIG. 4 illustrates a sectional side view of another embodiment of a torch according to the invention;

FIG. 5 is an end view illustrating the nozzles of the torch shown in FIG. 4; and

FIG. 6 is a sectional view taken generally along the section lines 6–6 in FIG. 4.

Referring to FIG. 1, the torch designated generally by the numeral **10** provides a flame for providing vapor phase hydrolysis of a gaseous volatile metal chloride to produce a metal oxide which is deposited upon a rotating mandrel **12**. In the preferred embodiment of the invention, silicon tetrachloride is decomposed to form silicon dioxide according to the following equation:

$$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$$

The flame produced from the torch **10** is shown diagrammatically as comprising a very hot central portion **14** wherein a vaporized silicon tetrachloride stream **16** reacts with a concentric stream of combustible gas **18** including a mixture of hydrogen and oxygen. The streams **16** and **18** interact at some distance below the nozzle of the torch **10** in a reaction zone which is spaced a short distance from the nozzle of the torch **10**. This spacing of the reaction zone from the torch nozzle is due to the provision of a stream of sheath gas **20** around the stream of silicon tetrachloride **16**, as will be subsequently described in greater detail.

The mandrel **12** is preferably constructed from graphite and may include a suitable hard metal coating over the surface thereof. The mandrel **12** is rotated in the direction of the arrow **22** and is translated in a direction of the arrow **24** while the torch **10** remains stationary. A silica article is deposited upon the mandrel as it translates past the stationary torch **10**. The rate of translation of the mandrel **12** is dependent upon the desired thickness of the silica article and upon parameters of the torch flame, such as flow rates of the various gases and the like. After the silica article has been deposited to the desired thickness upon the mandrel **12**, the article is removed and treated with various desired processing steps to provide a final product. It has been found that the articles have sufficient "green strength" to allow removal from the mandrel due to a slight degree of sintering of the silicon dioxide particles during deposition. In some instances, a separate conventional torch flame may be impinged on the article after deposition thereof to insure that sufficient green strength is provided. This method provides excellent silica crucibles with smooth wall surfaces and symmetrical configurations fur use in drawing semiconductor monocrystalline pulls.

FIG. 2 illustrates in greater detail the preferred embodiment of the present torch **10**. A stainless steel tube **30** extends through the length of the torch **10** to provide a passage for vaporized silicon tetrachloride entrained in a carrier gas. A T-connection **32** is connected about the tube **30** and is sealed to the tube **30** by member **34**. A member **36** fits over a stainless steel tube **38** to provide a seal between the end of tube **38** and the tube **30**. An annular sheath chamber **40** is thus defined between the tube **30** and tube **38**. An inlet portion **42** of the T-connection **32** is connected to a source of sheath gas, in this instance oxygen-containing gas, so that the sheath gas is passed into the sheath chamber **40**. One actual embodiment of the invention utilized a one-fourth inch diameter stainless steel tube **30** and a ⅝-inch diameter stainless steel tube **38**.

An annular spacer member **44** provides a fluid seal between the tube **38** and one end of a housing **46**. Housing **46** receives a tube **48** which defines an annular mixing chamber **50** about tube **58**. An inlet fitting **52** is connected to a source of hydrogen while an inlet fitting **54** is connected to a source of oxygen. Housing **46** includes a large diameter portion **56** which defines an annular cooling chamber about the tube **48**. An inlet fitting **58** is connected to a source of cooling fluid, such as cool water, and an outlet fitting **60** allows exhausting of the cooling fluid. In one practical embodiment of the torch **10**, the smaller diameter portion of the housing **46** was constructed of stainless steel, while the larger diameter portion **56** of the housing was constructed of brass to prevent corrosion thereof by the cooling fluid. In this embodiment of the torch, tube **48** was constructed from stainless steel and was provided with a diameter of 1⅛ inch. The entire length of the torch **10** in this embodiment thereof was approximately 9 inches.

The nozzle **62** is fitted over the end of the torch **10**. As shown in FIGS. **2** and **3**, the nozzle **62** comprises a circular member with bent flanges **64** for fluid-tight connection to the torch. A central nozzle aperture **66** is provided in the end of tube **30**. The end of tube **30** is received by an opening in nozzle **62** to define an annular sheath opening **68** which is concentrically disposed relative to the aperture **66** and has a substantially greater area than the aperture **66**. Nozzle aperture **66** has a substantially smaller area than the interior area of the tube **30**, such that a relatively high velocity jet of gas is provided from the nozzle aperture **66**. Gas flowing from the concentric sheath opening **68** substantially envelopes the jet of gas from the nozzle aperture **66** to prevent immediate reaction thereof, thereby reducing crystalline accumulation of the face of the nozzle member **62** and preventing obstruction thereof.

A plurality of apertures **70** are symmetrically disposed around the nozzle aperture **66** in a cylindrical configuration and communicate with the mixing chamber **50**. A combustible gas contained in the mixing chamber **50** flows out of the apertures **70** and reacts with the gas flowing from the aperture **66**. In a preferred embodiment of the torch, eight apertures **70** were provided, each having substantially the same area sa the nozzle aperture **66**. In this practical embodiment of the torch, diameters of .063 inch were found advantageous for aperture **66** and apertures **70**. For different operating conditions, greater or larger numbers of aperture **70** may be used.

Oxygen is supplied via conduit **72** to the inlet of three flowmeters **74**, **76** and **78**. A suitable source supplies hydrogen through a conduit **80** to a flowmeter **82**. The oxygen and hydrogen are dried prior to entering the flowmeters. Suitable valves are provided on the output of each of the flowmeters in order to allow regulation of the rate of flow of the hydrogen and oxygen to the e system. Oxygen is fed via a conduit **84** to a bubbler system designated generally by the numeral **86**. Bubbler system **86** comprises a container filled with liquid silicon tetrachloride. A diffusing element **88** bubbles the oxygen upwardly through the silicon tetrachloride, thereby entraining vapors of the silicon tetrachloride in the oxygen and passing outwardly through the conduit **90**.

Conduit **90** is connected to the tube **30** to provide a metered stream of vaporized silicon tetrachloride entrained in the oxygen carrier gas. Oxygen is also supplied through the flowmeter **74** via a conduit **92** to the inlet fitting **42** of the T-connection member **32**. Oxygen thus flows into the sheath chamber **40** and out the annular aperture **68** in the manner previously described. Oxygen is further supplied via conduit **94** to the inlet fitting **54** for passage into the mixing chamber **50**. Hydrogen is supplied through the flowmeter **82** via a conduit **96** into the inlet fitting **52** for mixing with the oxygen inside the mixing chamber **50**. A mixture of combustible gas is then fed outwardly through the aperture **70** in the manner described. Because the hydrogen and oxygen are mixed within the small chamber **50** within the torch, flashback in the present torch is limited to the interior of the torch itself.

FIGS. 4—6 illustrate another embodiment of the invention where a plurality of flames are provided. A metal block **10** has defined therein a generally rectangular chamber **102** including an inlet **104** for the admission of silicon tetrachloride vapors entrained in a suitable carrier gas.

Four tubular passages **106—112** extend from the chamber **102** to the opposite face of the body **100**. Relatively small nozzle apertures **114—120** respectively communicate with the passages to provide jet streams of the reactant gases in a similar manner to that previously described. A chamber **122** is formed in the general central region of the block **100** and includes an inlet **124** for a sheath gas such as oxygen. The chamber **122** includes four sheath passageways **126—132** for passing the oxygen-containing gas outwardly through annular sheath gas openings **134—140**.

A pair of chambers **142** and **143** are defined within the body **100** for respectively receiving a mixture of oxygen and hydrogen. The mixture of oxygen and hydrogen is then flowed outwardly through a plurality of apertures **144** and **145** for reaction with the gaseous silicon tetrachloride. When ignited, the torch provides four flames to provide an even application of silicon dioxide upon a mandrel in the manner previously described. Water cooled pipes may be disposed on the sides of the body in order to provide cooling thereof. The sheath of oxygen flowing from the annular apertures **134—140** prevent accumulation of crystals on the face of the nozzles and therefore prevent obstruction of the torch during usage thereof.

The following examples will further explain the present torches and the uses thereof, but should not be held to limit the true scope of this invention.

EXAMPLE 1

A torch constructed in accordance with FIGS. **2** and **3** was connected to a gas supply system similar to that shown in FIG. **2** and ignited. The diameter of the center nozzle aperture of the torch was .049 inch. A nonrotating mandrel constructed of graphite was disposed 4 inches from the nozzle of the torch and the flame issuing from the torch was impinged upon the graphite mandrel for 20 minutes. The temperature of the flame approximately one-fourth inch from the mandrel was in the range of 1,500° C. One liter per minute of oxygen and 1.56 liters per minute of silicon tetrachloride entrained in the oxygen was provided to the torch. To provide this flow of gas, the bubbler shown in FIG. **2** was maintained at a temperature of approximately 50° C. and at a pressure of 5 pounds per square inch. The percentage of silicon tetrachloride in the oxygen-carrier gas in this instance was 60.9 percent. One liter per minute of oxygen was fed into the sheath chamber of the torch to provide an output of sheath gas. 5.2 liters per minute of oxygen and 30 liters per minute of hydrogen were supplied to the mixing chamber of the torch to provide the combustible mixture to the flame. The resulting jet of gaseous silicon tetrachloride occurring at the center aperture of the torch was approximately 6.9×10^3 feet per minute. After 20 minutes of deposition, the actual deposition of silicon dioxide on the graphite mandrel was 35.4 grams. By comparing the actual deposition of the silicon dioxide with the theoretical computation of said 60.9 grams, a deposition efficiency of 46 percent was computed.

EXAMPLE 2

In use of the present torch, it was found that a percentage of silicon tetrachloride concentration in the carrier gas below about 75 percent provided excellent efficiency of deposition. Optimum efficiency was usually obtained at percentages of silicon tetrachloride below 60 percent of silicon tetrachloride in the carrier gas stream. For instance, a 20 minute deposition was provided in the manner described in example 1, with the exception that only .75 liters per minute of silicon tetrachloride was entrained in 1 liter per minute of oxygen. This was accomplished by maintaining a temperature of 39.6° C. upon the bubbler. 43 percent of silicon tetrachloride was entrained in the bubbler gas in this instance to provide a velocity at the bubbler nozzle aperture of 4.7×10^3 feet per minute. In this example, an actual deposition of 21.3 grams of silicon dioxide was deposited to provide a deposition efficiency of 57 percent.

EXAMPLE 3

It was found that for a particular construction of the torch and with a particular combination of gas flow rates, an optimum distance between the torch nozzle and the mandrel existed which provided increased deposition rates. For instance, an experiment was run utilizing essentially the same flow rates and other parameters of example 2, but with the distance between the torch nozzle and the mandrel being 5 inches. In this example, only 15.9 actual grams of silicon dioxide were deposited to provide a deposition efficiency of 43 percent. For the particular torch used, it was found that a mandrel distance in the range of 4 inches was desirable.

EXAMPLE 4

Good results were also obtained with use of the present torch by the utilization of a larger bubbler gas nozzle aperture at higher flow rates. For instance, a 20 minute run was conducted utilizing a nozzle having a nozzle aperture of a diameter of .063 inches and spaced 4 inches from a mandrel. A supply of oxygen at a rate of 2 liters per minute was provided to the bubbler which was maintained at 49° C. at a pressure of 5 pounds per inch. Vaporized silicon tetrachloride was entrained in the carrier gas at a rate of 2.88 liters per minute to provide a percentage of silicon tetrachloride in the entrained gas of 59 percent. A supply of oxygen at a rate of 1 liter per minute was supplied to the sheath chamber of the torch. A supply of oxygen at a rate of 5.2 liters per minute was supplied to the mixing chamber of the torch along with a supply of hydrogen at a rate of 30 liters per minute to provide the mixture of combustible gases. An output velocity at the nozzle aperture of 8×10^3 feet per minute was provided. A deposition of 68 grams of silicon dioxide was provided by the 20 minute run to provide a deposition efficiency of 48 percent.

The present invention thus provides a unique technique for forming high purity articles on mandrels by the direct application of oxides due to vapor phase hydrolysis by flame. The term "oxygen-containing gases" as used in the specification is meant to include pure oxygen. While the specification has been disclosed specifically with respect to the deposition of silicon dioxide by the decomposition of silicon tetrachloride, it will be understood that other volatile anhydrous chlorides of metallic elements from groups III and IV of the periodic system, such as for example, titanium tetrachloride, aluminum tetrachloride and the like could additionally be advantageously decomposed with the present technique.

Although specific embodiments of the present invention have been described, it will be understood that various modifications and changes will be suggested to one skilled in the art, and it is intended to encompass such modifications and changes which fall within the true scope of the invention as defined in the appended claims.

I claim:

1. A torch for decomposing a volatile metallic element by hydrolysis to directly form an oxide article on a surface comprising;

a. a torch housing including a passage terminating in a nozzle aperture for providing an output jet stream of said volatile metallic element entrained in a carrier gas;

b. means defining a first chamber disposed adjacent said passage within said torch housing for receiving a supply of a combustible gas and including nozzle openings symmetrically disposed to said nozzle aperture for providing a stream of combustible gas about said jet stream; and

c. means defining a second chamber disposed between said passage and said first chamber for receiving a supply of gas relatively inert to said volatile metallic element and including a sheath opening for providing a sheath stream of said inert gas between said jet stream and said stream of combustible gas sufficient when the torch is ignited to prevent residue from being formed on said nozzle aperture during operation.

2. The torch of claim 1 wherein the area of said sheath opening is substantially greater than the area of said nozzle aperture.

3. The torch of claim 1 wherein said volatile metallic element comprises silicon tetrachloride and said combustible gas comprises a mixture of oxygen and hydrogen.

4. The torch of claim 1 wherein said nozzle aperture is circular, said sheath opening is an annular opening concentrically disposed about said nozzle aperture, and said nozzle openings are circular and are disposed symmetrically about said annular opening.

5. The torch of claim 4 and further comprising eight nozzle openings disposed in a circle about said annular opening, each of said nozzle openings having generally the same area as said nozzle aperture.

6. The torch of claim 1 and further comprising a chamber enclosing said first chamber and having inlet and outlet means for circulation of a cooling fluid therethrough.

7. A torch for forming a silica article directly upon a mandrel by hydrolysis of silicon tetrachloride entrained in a carrier gas comprising:

a. a torch housing having a central passage therethrough with an inlet at one end for receiving gaseous silicon tetrachloride entrained in a carrier gas and having a nozzle aperture at the other end to provide an output jet stream of gaseous silicon tetrachloride entrained in a carrier gas;

b. a sheath chamber defined in said torch housing about said central passage including an inlet for receiving a relatively inert gas with respect to silicon tetrachloride and having an annular opening concentrically disposed about said nozzle aperture to provide a circular stream of said inert gas around said jet stream; and

c. a mixing chamber disposed about said sheath chamber including inlets for hydrogen and oxygen containing gases and a plurality of outlet openings disposed symmetrically adjacent said annular opening to provide streams of gaseous combustible mixture around said circular stream of said inert gas, whereby the flame resulting from ignition of said torch may be kept away from said nozzle.

8. The torch of claim 7 and further comprising a cooling chamber disposed about said mixing chamber having means for the circulation of cooling fluid therethrough.

9. The torch of claim 7 wherein the area of said annular opening is substantially greater than the area of said nozzle aperture.

10. A torch for direct formation of an oxide article on a mandrel by they hydrolysis of a volatile metal chloride comprising:

a. a torch housing including inlet means for receiving a supply of the vapor of said volatile metal chloride;

b. a plurality of nozzle apertures communicating with said inlet means for providing a plurality of output jet streams of said volatile metal chloride;

c. means for supplying a sheath of relatively inert gas around each of said jet streams; and

d. means for supplying a stream of combustible gas adjacent each said sheath of inert gas, whereby when said torch is ignited a plurality of flames will be provided for the direct formation of an oxide article on the mandrel.

11. The torch of claim **10** wherein each said sheath of inert

gas is supplied through an annular opening surrounding a nozzle aperture, and each said stream of combustible gas is supplied from an aperture spaced radially outwardly from said annular opening.

12. The torch of claim **11** wherein said nozzle apertures and annular openings are linearly disposed to one another, and said apertures for providing combustible gas are linearly disposed parallel to said nozzle apertures and annular openings.