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(54) OPTICAL FIBERS AND PROCESSES FOR THEIR PRODUCTION

(71) We, SUMITOMO ELECTRIC INDUSTRIES LTD., a Japanese Body Corporate, of 15 Kitahama 5-chome, Higashi-ku, Osaka, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to optical fibers and processes for their production.

Two conventional types of optical fiber are known. The first type of fiber is usually called a cladding type optical fiber which is composed of essentially a core of doped fused silica containing uniformly several % of a metal oxide to increase the index of refraction of the core and a cladding layer of pure fused silica surrounding the core. The second type of fiber is usually called a self focusing type optical fiber which is composed essentially of a fiber of which the distribution of the index of refraction over the cross section of the fiber varies radially and parabolically for self focusing the light beam.

In the cladding type of optical fiber, the light beam propagates in the core by reflecting itself repeatedly at the boundary surface between the core and the cladding layer and light beam diverges with the propagation distance and produces envelope delay distortion of optical signals.

Some roughness on the surface of the core of the cladding type optical fiber inevitably remains in spite of the polishing treatment carried out during the manufacturing process so that the light beam transmitted by reflection at the surface suffers a transmission loss due to this roughness.

In the self focusing type of fiber, there is the disadvantage that in the ion-exchange in the manufacturing process, it takes a very long time to get the necessary amount of ion diffusion, so that it is very difficult to accurately control the diffusing ions in the requisite amount.

According to the present invention there is provided a process for producing an

optical fiber, comprising depositing by vapour deposition, a layer of silica which contains a dopant capable of altering the refractive index of silica onto either the inside surface of a hollow rod of fused silica or the outside surface of a rod of either fused silica or doped silica, the contiguous portions of the said layer and the rod being of the same refractive index if the rod is of doped silica, and spinning or otherwise reducing the rod and the said layer to a fine solid fiber.

According to a modification of the process in which the layer is deposited on the outside surface of a solid rod, the rod is removed, the remaining deposited layer which is in the form of a tube being spun to a fine solid fiber.

Reference will now be made to the accompanying drawings, in which:

Figure 1(a) is a cross section of an optical fiber having a core of self focusing type in accordance with the present invention and two typical distributions of the index of refraction of such a fiber are shown in Figure 1(b) and Figure 1(c).

Figure 2 is a longitudinal section of the fiber of the present invention explaining the behaviour of the propagating light beam.

Figure 3 is a view explaining a process embodiment of the invention for depositing a layer of doped silica containing one or more oxides.

Figure 4 is a longitudinal section of a fiber manufactured by the method shown in Figure 3. Figure 4 also shows the distribution of the varied amount of TiO_2 contained in the deposited layer.

Figure 5 is a longitudinal section showing the spinning process from a pipe to a fine fiber.

Figure 6 is a side view showing another process embodiment of the invention for depositing a layer of doped silica containing one or more oxides.

Figure 7(a) is a longitudinal section of a rod having a deposited layer which has been prepared by the method of Figure 6.

Figure 7(b) shows the distribution of the varied amount of TiO_2 contained in the deposited layer shown in Figure 7(a) where a rod of pure silica is used. Figure 7(c) shows the distribution of the varied amount of TiO_2 contained in the deposited layer shown in Figure 7(a) where the rod is doped fused silica containing the same amount of TiO_2 as the amount of TiO_2 contained in the layer deposited around the outer surface of the rod.

Figure 8 is a longitudinal section of a pipe which has been made by removing the rod portion of the rod having a deposited layer as shown in Figure 7(a).

Figure 9 is a longitudinal section showing the spinning process from such a rod as shown in Figure 7(a) to an optical fiber.

Figure 10 is a longitudinal section showing the spinning process from such a pipe as shown in Figure 8 to an optical fiber.

Figure 11 is a curve showing the flow speed with respect to the deposition process time.

Figure 12 is a curve of the varied amount of TiO_2 contained in the layer deposited on a pipe with respect to the thickness of the deposited layer.

Figure 13 is the cross section of the pipe having a deposited layer.

The present invention will be explained in detail by referring to the drawings. Figure 1(a) is a cross section of an optical fiber and shows the distribution of the index of refraction over the cross section. In Figure 1(a), 1 denotes a cladding layer of fused silica, 2 a core which has such a distribution that the index of refraction over the cross section varies radially in accordance with a parabolic curve. The distribution curve of the index of refraction $n(r)$ as a function of radial distance r is given as shown in Figure 1(b) approximately by the following formula:

$$n(r) = n_0 (1 - \frac{1}{2} Ar^2)$$

Where n_0 is the index of refraction at the center of the core A is a constant.

Figure 1(c) shows the step-like distribution of the index of refraction which is similar with the above formula.

Figure 2 is a longitudinal section of the fiber shown by Figure 1(b) of the present invention explaining the behaviour of propagating light beam in the optical fiber. In the fiber having a distribution of index of refraction as shown in Figure 1(c) a light beam propagates similarly. In Figure 2, the same reference numerals shows the same portions as in Figure 1, and 3 denotes a light beam propagating in the core of the fiber. The light beam projected in such a fiber as shown in Figure 1 propagates along the central axis of the core in behalf of the

self focusing feature in the core and the light beam is not reflected on the surface between cladding layer and core for propagation in such a way that the light beam propagates by repeated reflection on the interface between cladding layer and core.

In accordance with a further feature of the invention, the core of the fiber is made by chemical vapor deposition method.

In the present invention, a deposition layer is provided on the inner surface of a pipe of fused silica or the outer surface of a rod of pure silica or of doped fused silica preferably containing some TiO_2 in accordance with the purpose of use preferably by means of oxidation or burning of a mixture of gaseous SiCl_4 and gaseous TiCl_4 . The rod or pipe having a deposited layer thus obtained is then heated and spun to a fine solid fiber.

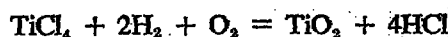
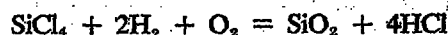
Such a deposition of silica containing a metal oxide dopant is generally provided by the oxidation of a gaseous mixture of a hydride or halide, carbonyl compound or organic compound of silicon and a similar compound of the metal.

As a high temperature furnace for use of chemical vapor deposition, an electric resistance furnace, hydrogen oxygen furnace, high frequency plasma torch or the like is preferably used.

Figure 3 shows an apparatus for depositing doped silica on the inner surface of a pipe of fused silica. In Figure 3, 4 denotes a container of SiCl_4 , 5 denotes a container of TiCl_4 , T_1 , T_2 are temperature of these containers 4, 5 respectively and H_1 , H_2 are the heaters for heating the container 4 and 5. V_1 , V_2 are the flow speeds of the carrier gas (oxygen) which is supplied to the containers 4, 5 respectively. 7 is a hydrogen oxygen burner for burning carrier gas V_1 , V_2 containing SiCl_4 and TiCl_4 for producing doped silica, whose chemical reaction is represented by the following formula. 8 is soot produced by the burning of carrier gas V_1 , V_2 . 9 is a pipe of fused silica near which the burner 7 is placed. The inner surface must be polished smooth and clean by mechanical polishing and HF acid etching or flame polishing.

The pipe 9 is rotatable around its axis.

In the manufacturing process of the present invention the materials SiCl_4 , TiCl_4 , H_2 and O_2 must be highly pure.



In the reaction at the burner 7, the more the temperature T_2 of the container 5 is elevated or the more the flow speed V_2 of the carrier gas coming into the container 5 is increased whilst the temperature T_1 of

the container 4 had the flow speed V_1 of the carrier gas coming into the container 4 are kept constant, the more the amount of TiO_2 that will be deposited with the silica. If the temperature T_1 of the container 4 is elevated or the flow speed V_1 of the carrier gas coming into the container 4 is increased, whilst the temperature T_2 of the container 5 and the flow speed V_2 of the carrier gas coming into the container 5 are kept constant, a greater amount of SiO_2 will be deposited with the TiO_2 .

Accordingly, the amount of TiO_2 contained in the deposited doped silica may be controlled accurately and easily by controlling the temperature of SiCl_4 or TiCl_4 containers and/or the flow speeds of the carrier gas of containers 4 or 5.

Figure 4 is a longitudinal section of a pipe having a deposited layer which has been produced by the method shown in Figure 3. In Figure 4, 9 denotes a pipe of fused silica, 10 a deposited layer which contains the varied amount of TiO_2 in the radial direction. The density of TiO_2 of the deposited layer 10 increases radially inwardly in accordance with a parabolic curve.

In the deposition process, it is preferable to make a layer of SiO_2 only on the surface of the pipe 9. If a layer of SiO_2 is prepared by deposition between the surface of the pipe 9 and the deposited layer containing TiO_2 , the deposited layer of SiO_2 serves to take away the harmful effect of roughness of the surface of the pipe 9 which inevitably remains even by polish-treatment of the pipe 9. In the deposition process, if the temperature of the burner 7 is increased to a high level, the soot melts and adheres to the surface of the pipe 9 in a vitreous state, but if the temperature of the burner 7 is not high enough to melt soot, the soot is deposited on the surface of the pipe 9 in a powder state. In the latter case, the deposited layer 10 of the powder state must be subsequently heated at a elevated temperature e.g. about 1450°C , in an oxygen rich atmosphere to sinter it.

Figure 5 is a longitudinal section explaining the process of spinning a pipe having a deposited layer to an optical fine solid fiber, the fiber having a core with a varied distribution of the index of refraction and a cladding layer of fused silica around the core.

In Figure 5, 1, 2 are the same portions as shown in Figure 1 and 9, 10 are the same portions as shown in Figure 4 and 11 is a heater for spinning the pipe 9. In Figure 5, the end portion is heated at a temperature about 1900°C and spun to a fine solid fiber to eliminate the hollow of the pipe.

The distribution of the index of refraction over the cross section of the core of the optical fiber thus obtained varies radi-

ally according to such a parabolic curve as shown in Figure 1, because the containing amount of TiO_2 in the deposited layer is controlled radially.

In order to enhance the light transparency of the fiber, the fiber may be annealed at a temperature of from 600°C to 1200°C in an oxygen rich atmosphere for a suitable period. By this annealing, the mechanical strength of the fiber is often decreased by a small amount. In this case, the mechanical strength of the annealed fiber may be improved by surface treatment by means of etching and polishing by HF acid solution.

Figure 6 shows another deposition method of the present invention. In Figure 6, 7 denotes a hydrogen oxygen burner, 21 is a pipe for supplying carrier gas which carries the SiCl_4 and TiCl_4 , 22 is a pipe for supplying hydrogen gas and 23 is a pipe for supplying oxygen gas, 8 is soot produced in the burner 7, 12 is a rod of pure silica installed so that it is rotatable around its axis. In Figure 6 doped silica soot 8 containing TiO_2 in a predetermined amount may be obtained by controlling the temperature of the containers containing the SiCl_4 and TiCl_4 and/or the supply of the carrier gases to the burner 7 for burning.

The rod 12 is rotated and a layer of doped silica is uniformly deposited on the surface of the rod. If the temperature of burner 7 is high, the deposited layer is in a vitreous state, but the temperature is not so high, the deposited layer is in a powder state. In the latter case, the deposited layer must be sintered by heat at high temperature e.g. about 1450°C in an oxygen rich atmosphere.

A rod having a deposited layer 14 produced by the method explained in Figure 6 is shown in Figure 7(a). Two kinds of the distribution of the index of refraction over the cross section of the rod having the deposited layer are shown in Figure 7(b) and 7(c).

The rod of Figure 7(b) is of the case where the rod 12 is a pure silica and doped silica layer 14 is deposited thereon. The rod of Figure 7(c) is of the case where the rod 12 is doped fused silica containing TiO_2 in the same amount as that contained in the portion, facing the rod 12, of the deposited layer 14.

In Figure 8, 14 shows a pipe of doped fused silica having a hollow 15 which is made of only a deposited layer by removing the rod portion. Such removing of the rod portion may be performed by the usual techniques used in the glass manufacturing field.

The pipe thus obtained may be polished by laser beam or by sapphire polishing, and washed by a solution of HF or flame polishing in order to make the inner surface of the pipe 14 smooth and clean. Subse-

quently, the rod and pipe thus obtained are spun to a fine solid fiber of a requisite shape and size at high temperature e.g. about 1900°C in an oxygen-rich atmosphere.

5 Figure 9 is a longitudinal section showing a process making a fiber from a rod as shown in Figure 7(a). In Figure 9, 11 is a heater, 12 is a rod of doped fused silica and 14 is a deposited layer. Figure 10 shows a view explaining the process for making a fiber from a pipe as shown in Figure 8. In Figure 10, the same reference numerals show the same parts of Figure 9.

15 The fiber obtained by the process mentioned above may be further heat-treated by annealing it at a temperature of 600°C—1200°C for a requisite period.

20 The fiber thus heat-treated has a distribution of index of refraction over the cross section of the fiber varied in accordance with a requisite curve.

In Figure 4, both the carrier gases whose flows are shown by V_1 and V_2 are oxygen gas. The flow speed of the carrier gas V_1 is 18 cc/min. The temperatures T_1 , T_2 of containers 4, 5 are kept at 30°C. The inner size and outer size of the pipe 9 are 6 mm and 10 mm respectively. The flow speed V_2 of the carrier gas is controlled in accordance with the curve shown in Figure 11.

30 Since the pipe 9 is rotated at a constant speed, a deposited layer containing the varied amount of TiO_2 with regard to the thickness of deposited layer is produced over the inner surface of the pipe 9.

35 The amount of TiO_2 of the deposited layer if graphed in a function of the thickness of the deposited layer x .

40 The curve of the function is shown in Figure 12. The relation between the thickness of the deposited layer x and the size of the pipe is shown by Figure 13.

45 The pipe having the deposited layer containing TiO_2 as shown by 12 is heated at a high temperature (about 1450°C) in an oxygen rich atmosphere for about one hour to sinter the powdered deposited layer to vitreous state.

50 The pipe is then heated in a furnace of hydrogen-oxygen gas burner at a temperature of about 1900°C from the bottom of the pipe and spun to a fine solid fiber which is an optical fiber having such a requisite distribution of the index of refraction over the cross section as shown in Figure 1. The optical fiber thus obtained is a cladding type optical fiber having a core in which a light beam is self focusing.

60 The fiber of this type has many excellent features including useful features of the self focusing type and the cladding type of fibers. In such an optical fiber, the transmitted light beam does not diverge and the phase difference of the wave front of the

light beam is cohered closely so that even image transmission is possible. As the light beam is focused in the axial direction, the beam propagates along and around the axis without perfect reflection at the boundary surface between core and cladding layer, the light transparency of the fiber being increased compared to the cladding type optical fiber.

70 In the manufacturing method of the present invention, as the amount of metal oxide in deposited layer is accurately and easily controlled, an optical fiber having any desired distribution curve of the index of refraction may be readily obtained.

80 As the deposited layer is made by oxidizing a halide, hydride or organic compound of silicon and a similar compound of a metal, the silica and the metal oxide in the deposited layer may be highly pure. As the rod or pipe used in the present invention is of highly pure silica or highly pure doped silica, the optical fiber made from these has little transmission loss because of the absence of impurities. Further, since a deposited layer of silica only is placed under the deposited layer of doped silica containing metal oxide so that the irregularities of the surface are effectively removed, the transmission loss of the optical fiber due to irregularity of the surface is reduced.

WHAT WE CLAIM IS:—

1. A process for producing an optical fiber, comprising depositing, by vapour deposition, a layer of silica which contains a dopant capable of altering the refractive index of silica onto the inside surface of a hollow rod of fused silica and spinning or otherwise reducing the rod and the said layer to a fine solid fiber.

2. A process for producing an optical fiber, comprising depositing, by vapour deposition, a layer of silica which contains a dopant capable of altering the refractive index of silica onto the outside surface of a rod of either fused silica or doped silica, the contiguous portions of the said layer and the rod being of the same refractive index if the rod is of doped silica, and spinning or otherwise reducing the rod and the said layer to a fine solid fiber.

3. A modification of the process, as claimed in claim 2, wherein the layer is deposited on the outside surface of a solid rod, the modification comprising removing the rod, the remaining deposited layer which is in the form of a tube, being spun to a fine solid fiber.

4. A process as claimed in any foregoing claim, wherein the layer is deposited by oxidising a mixture comprising the vapour of (a) at least one halide, hydride, carbonyl or organic compound of silicon and (b) at least one halide, hydride, carbonyl

quently, the rod and pipe thus obtained are spun to a fine solid fiber of a requisite shape and size at high temperature e.g. about 1900°C in an oxygen-rich atmosphere.

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The fiber obtained by the process mentioned above may be further heat-treated by annealing it at a temperature of 600°C—1200°C for a requisite period.

The fiber thus heat-treated has a distribution of index of refraction over the cross section of the fiber varied in accordance with a requisite curve.

In Figure 4, both the carrier gases whose flows are shown by V_1 and V_2 are oxygen gas. The flow speed of the carrier gas V_1 is 18 cc/min. The temperatures T_1 , T_2 of containers 4, 5 are kept at 30°C. The inner size and outer size of the pipe 9 are 6 mm and 10 mm respectively. The flow speed V_2 of the carrier gas is controlled in accordance with the curve shown in Figure 11.

Since the pipe 9 is rotated at a constant speed, a deposited layer containing the varied amount of TiO_2 with regard to the thickness of deposited layer is produced over the inner surface of the pipe 9.

The amount of TiO_2 of the deposited layer if graphed in a function of the thickness of the deposited layer x .

The curve of the function is shown in Figure 12. The relation between the thickness of the deposited layer x and the size of the pipe is shown by Figure 13.

The pipe having the deposited layer containing TiO_2 as shown by 12 is heated at a high temperature (about 1450°C) in an oxygen rich atmosphere for about one hour to sinter the powdered deposited layer to vitreous state.

The pipe is then heated in a furnace of hydrogen-oxygen gas burner at a temperature of about 1900°C from the bottom of the pipe and spun to a fine solid fiber which is an optical fiber having such a requisite distribution of the index of refraction over the cross section as shown in Figure 1. The optical fiber thus obtained is a cladding type optical fiber having a core in which a light beam is self focusing.

The fiber of this type has many excellent features including useful features of the self focusing type and the cladding type of fibers. In such an optical fiber, the transmitted light beam does not diverge and the phase difference of the wave front of the

light beam is cohered closely so that even image transmission is possible. As the light beam is focused in the axial direction, the beam propagates along and around the axis without perfect reflection at the boundary surface between core and cladding layer, the light transparency of the fiber being increased compared to the cladding type optical fiber.

In the manufacturing method of the present invention, as the amount of metal oxide in deposited layer is accurately and easily controlled, an optical fiber having any desired distribution curve of the index of refraction may be readily obtained.

As the deposited layer is made by oxidizing a halide, hydride or organic compound of silicon and a similar compound of a metal, the silica and the metal oxide in the deposited layer may be highly pure. As the rod or pipe used in the present invention is of highly pure silica or highly pure doped silica, the optical fiber made from these has little transmission loss because of the absence of impurities. Further, since a deposited layer of silica only is placed under the deposited layer of doped silica containing metal oxide so that the irregularities of the surface are effectively removed, the transmission loss of the optical fiber due to irregularity of the surface is reduced.

WHAT WE CLAIM IS:—

1. A process for producing an optical fiber, comprising depositing, by vapour deposition, a layer of silica which contains a dopant capable of altering the refractive index of silica onto the inside surface of a hollow rod of fused silica and spinning or otherwise reducing the rod and the said layer to a fine solid fiber.

2. A process for producing an optical fiber, comprising depositing, by vapour deposition, a layer of silica which contains a dopant capable of altering the refractive index of silica onto the outside surface of a rod of either fused silica or doped silica, the contiguous portions of the said layer and the rod being of the same refractive index if the rod is of doped silica, and spinning or otherwise reducing the rod and the said layer to a fine solid fiber.

3. A modification of the process, as claimed in claim 2, wherein the layer is deposited on the outside surface of a solid rod, the modification comprising removing the rod, the remaining deposited layer which is in the form of a tube, being spun to a fine solid fiber.

4. A process as claimed in any foregoing claim, wherein the layer is deposited by oxidising a mixture comprising the vapour of (a) at least one halide, hydride, carbonyl or organic compound of silicon and (b) at least one halide, hydride, carbonyl



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- or organic compound of the or each metal, the concentration of constituent (b) in the mixture being controlled so that the amount of the or each metal oxide in the deposited layer increases radially inwardly towards the centre of the rod or pipe.
5. A process as claimed in claim 4, wherein the mixture is produced by vaporising constituent (a) into a flow of a carrier gas to produce a first gas stream, vaporising constituent (b) into a flow of a carrier gas to produce a second gas stream, and mixing the two streams, the concentration of (b) in the mixture being controlled by controlling the relative amounts of (a) and (b) that are vaporised and/or the relative flow rates of the carrier gases.
6. A process as claimed in claim 5, wherein constituent (a) is silicon tetrachloride which is vaporised into a flow of oxygen to produce the first stream, and constituent (b) is titanium tetrachloride which is also vaporised into a flow of oxygen to produce the second stream, the mixture of the two streams being reacted with hydrogen to oxidise the silicon tetrachloride and titanium tetrachloride to, respectively, silica and titanium dioxide.
7. A process as claimed in any one of the foregoing claims, wherein the silica containing at least one dopant is deposited in the form of a vitreous layer.
8. A process as claimed in any of claims 1 to 6 wherein the silica containing at least one dopant is deposited in the form of a powder, the deposited powder then being sintered in an oxygen rich atmosphere.
9. A process as claimed in any one of the foregoing claims wherein the fiber is annealed at a temperature of from 600°C to 1200°C in an oxygen rich atmosphere.
10. A process as claimed in claim 9 wherein the surface of the annealed fiber is treated with a solution of hydrofluoric acid.
11. A process substantially as hereinbefore described with reference to and as shown in Figures 3 to 5 of the accompanying drawings.
12. A process substantially as hereinbefore described with reference to and as shown in Figures 6, 7a and 9 of the accompanying drawings.
13. A process as claimed in claim 6 substantially as hereinbefore described with reference to and as shown in Figures 6, 8 and 10 of the accompanying drawings.
14. An optical fiber which has been produced by a process as claimed in any one of claims 1 to 13.

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