ABSTRACT: The method of sintering amorphous of amorphous metal oxide, and in a preferred embodiment crucibles and tubing of fused silicon dioxide, by depositing a porous layer of amorphous metal oxide on a deposition surface, and thereafter partially sintering the edges of the metal oxide article to less than 90 percent of its theoretical density and substantially sintering the remainder of the metal oxide article to greater than 90 percent of its theoretical density. By only partially sintering the edge portions sufficient frictional forces are produced with the mandrel to exceed the surface tension forces created in the remainder of the metal oxide article by the higher sintering temperature thus preventing longitudinal contraction and crawling encountered in the prior art processes. For a silicon dioxide article, the edges of the mandrel are sintered at a temperature in the range of 1,250°C to 1,350°C; the remainder of the article is sintered at a temperature in the range of 1,450°C to 1,550°C. The partially sintered portion is then severed from the fully sintered portion to produce the desired article.
PREVENTION OF CRAWLING OF METAL OXIDE HOLLOW ARTICLES ALONG THE SUPPORT MANDREL DURING SINTERING

This invention relates to the production of metal oxide articles and, more particularly, to a technique for densifying and fusing articles of an amorphous metal oxide. Among the known methods for producing metal oxide articles, and especially silicon dioxide articles, is one by which a porous layer of an amorphous silicon dioxide is deposited on a surface by vapor phase hydrolysis of silicon tetrachloride and then sintered or densified. A method and apparatus for performing this method are disclosed in a copending application to Hearst J. Moltzan, Ser. No. 744,155, filed July 11, 1968 (TI-3326). In this method, vapor phase deposition of silicon tetrachloride is combined with a hydrogen and oxygen combustible gas stream, then ignited. The silicon tetrachloride is hydrolyzed to silicon dioxide and deposited on a deposition surface, usually a mandrel at least a part of which has a cylindrical configuration. To completely cover the surface of the mandrel, the mandrel is rotated and translated until a silicon dioxide article is formed.

The article thus formed comprises a porous layer of amorphous silicon dioxide. To be usable, the article must be sintered and densified. When the porous silicon dioxide article is inserted in a sintering furnace and elevated to a temperature of about 1,500°C, the silicon dioxide becomes a very viscous liquid and densifies to nearly its theoretical density. However, when the article becomes a viscous liquid, the surface tension forces on the article will cause it to contract and form a droplet or mass appearing much like that of a drop of water on a clean glass surface. These forces must be resisted in some manner. Various techniques are available in the art, among which is the use of a stepped deposition and sintering mandrel of the type disclosed in a copending application to R. Bruce Biddulph, Ser. No. 799,891, filed Feb. 17, 1969 (TI-3327).

These prior art methods, including the use of stepped mandrel configurations, are limited by the fact that, for example, when a mandrel of cylindrical configuration with end portions of abruptly reduced diameter of one-quarter of an inch are utilized to make silica tubing, the layer of silicon dioxide is deposited over the mandrel surface, including the stepped end portions. The mandrel with its deposit is then placed in a sintering furnace where the temperature is raised to about 1,500°C. The end portions of the silicon dioxide article tend to shrink over the stepped end portions of the mandrel and thus resist the tensile forces tending to contract the article. The drawback of this method, however, is that as the very viscous silica contracts over the stepped portion, it becomes very thin and often breaks, hence defeating the purpose of the stepped portion.

It would be, therefore, desirable to provide a method of sintering and densifying a metal oxide article, specifically a silicon dioxide article, to eliminate the problems associated with present densification methods. It is desirable to eliminate the tendency of the silicon dioxide to break away from a stepped mandrel. It is also desirable to develop a technique whereby a cylindrical unstepped mandrel can be utilized.

To overcome the disadvantages of the prior art and to provide a novel technique for sintering metal oxide articles, this invention provides a method for manufacturing a metal oxide article which tends to contract when it is heated to a temperature sufficiently high to fuse and densify the metal oxide, which method comprises depositing a porous layer of amorphous metal oxide on a deposition mandrel, thereafter partially densifying the edge portion of the article while substantially fully densifying the remainder of the article.

In a preferred embodiment, a silicon dioxide article is produced by hydrolysing silicon tetrachloride at a temperature in the range of 1,250°C to 1,350°C, and heating the remaining portion of the article to a temperature of at least 1,250°C, and then sintering and densifying the remainder of the article at a rate of at least 1,500°C.

The invention will be more easily understood by reference to the attached drawings wherein:

FIG. 1 is a cross-sectional partially schematic representation of a vapor phase hydrolysis torch depositing a metal oxide on a stepped mandrel to form a tubular shape;
mandrel 108 is rotated in the direction shown by arrow 106. A saw 110, preferably of circular configuration and having a cutting edge sufficiently hard to penetrate the metal oxide article 112, is rotated in the direction of the arrow 114. The saw and mandrel, rotating on parallel axes are brought together so that the partially sintered portion 116 of the article 112 is severed from the main portion of the article 112 along a plane 118. In this figure a crucible shaped article has been shown. It is to be readily understood, however, that if an article such as that shown in FIG. 6 is produced, both end portions 78 will be severed from the main body portion of the tubular-shaped article 76.

To better explain the procedure of this invention, an exemplification of a preferred mode of carrying it out follows.

A porous layer 2 inches thick of amorphous silicon dioxide is deposited on a stepped mandrel by vapor phase hydrolysis of silicon tetrachloride in the manner described in conjunction with FIG. 1. The mandrel is 14 inches long, cylindrical in shape, and has a diameter through its major portion of 350 inches. The stepped end portions of the mandrel are cylindrically shaped having a diameter of 3 7/16 inches and a height or length of three-quarters of an inch. The mandrel and deposit are removed from the deposition enclosure and inserted in a sintering furnace. The density of the oxide layer prior to sintering is in the range of 8 to 15 percent of the theoretical density of silicon dioxide.

A radiofrequency induction heater is utilized to bring the temperature of the mandrel and oxide layer from the ends thereof to points 2 inches longitudinally inward up to about 1,300°C. The remaining 10-inch central portion is maintained at a temperature of about 1,500°C. After 30 minutes at the peak temperature of 1,500°C, the mandrel is removed from the sintering furnace and cooled. The density of the middle 10 inches of the silicon dioxide article is greater than 99.5 percent of theoretical. The average density of the 2-inch end portions is about 85 percent of theoretical. The silica article conforms to a shape very similar to that illustrated in FIG. 6. The fully densified portion is then severed from the partially densified end portions by the procedure described in conjunction with FIG. 9.

The above procedure is repeated except that the entire silicon dioxide article is sintered at a temperature of 1,500°C for 30 minutes. The silicon dioxide article pulls away from the stepped end portions of the mandrel and forms a toroidally shaped article having a density greater than 99 percent of theoretical. For practical purposes, the article is unusable.

Although the foregoing invention has been described in conjunction with a preferred embodiment, it is to be understood that various modifications of this invention can be made without departing from the spirit of the invention. The scope of the invention is intended to be limited only by the appended claims.

What is claimed is:

1. In the method of making a fused metal oxide article wherein the oxide is selected from the metals of groups IIIA, IIIA, IVA, IIIIB, IVB, and VB of the Periodic Table which form an oxide and which upon reaching a temperature sufficient to fuse the oxide tend to contract comprising the steps of:

a. Depositing a porous layer of the amorphous oxide onto a refractory mandrel by vapor phase hydrolysis of the metal halide in the presence of an ignited combustible gas stream;

b. Sintering the porous layer while on the mandrel to fuse and densify the oxide layer to near its theoretical density; wherein the improvement comprises; heating the edge portions of the oxide layer to a first temperature while heating the remainder of the oxide layer to a second temperature higher than said first temperature and sufficient to cause it to fuse and densify to near theoretical density, said first temperature being controlled so that the edge portions only partially densify and maintain sufficient frictional forces with the mandrel to prevent longitudinal contraction of the metal oxide layer.
The method of claim 1 wherein the metal oxide is silicon dioxide.

The method of claim 3 wherein a porous layer in the shape of a cylinder is deposited, the method including partially densifying the end portions of the cylindrical layer and substantially fully densifying the portion intermediate the ends to an extent greater than the end portions.

The method of claim 3 wherein the end portions are densified to less than 85 percent of their theoretical density.

The method of claim 4 wherein the intermediate portion is densified to greater than 90 percent of its theoretical density.

The method of claim 4 wherein the intermediate portion is densified to greater than 99 percent of its theoretical density.

The method of claim 1 wherein the metal halide is silicon tetrachloride and is hydrolyzed to silicon dioxide.

The method of claim 7 for manufacturing a fused silicon dioxide article wherein the edge portion of the article is partially densified at a temperature of from 1,250° to 1,350° C. and the remainder of the article is densified at a temperature of from 1,450° to 1,550° C.

The method of claim 8 including the step of severing the partially densified portion of the article from the fully densified portion of the article.

The method of claim 8 wherein the edge portion of the article is densified to less than 90 percent of its theoretical density.

The method of claim 10 wherein the edge portion is densified to less than 85 percent of its theoretical density.

The method of claim 8 wherein the remainder of the article is densified to greater than 90 percent of its theoretical density.

The method of claim 12 wherein the remainder of the article is densified to greater than 99 percent of its theoretical density.

The method of claim 8 wherein the porous silicon dioxide layer is deposited on a mandrel having generally a cylindrical configuration, the end portions of which have an abruptly reduced diameter to form a mandrel having stepped end portions.

The method of claim 14 wherein the edge portion of the silicon dioxide article adjacent the stepped portion of the mandrel is partially sintered and the portion of the article intermediate the stepped portions of the mandrel is fully sintered.

The method of claim 8 wherein the porous silicon dioxide layer is deposited on a mandrel having a generally cylindrical configuration, one end portion of which has an abruptly reduced diameter to form a stepped portion, the other end of which is smoothly rounded having generally the shape of a segment of a spheroid.

The method of claim 11 wherein the portion of the article so formed adjacent the stepped portion is partially sintered and the remainder of the article is sintered.