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METHOD FOR MAKING DUCTED REFRACTORY ARTICLES

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This invention relates to powder metallurgy, and more particularly to a method for forming continuous ducts or passages in articles fabricated by powder metallurgy.

Most metal powders, such as iron, iron-copper, copper and copper-tin, as well as brass and carbon steel can be formed by powder metallurgy processes. These metal powders may be molded and sintered to form articles. The literature describes techniques used to form ducts or passages in sintered metal bodies by employing cores of a low melting alloy. During the sintering process, the core metal melts and either flows out of the body through the passage, or it is dispersed in the pores of the sintered metal body. One disadvantage of forming passages by this process is that the lower melting core alloy contaminates the body, which may cause it to have undesirable properties.

Refractory metals, such as tungsten, tantalum, zirconium, hafnium and niobium, have very high melting points. These metals are commonly combined with carbon, boron or oxygen to form very hard, refractory compounds which have melting points above 2500° C. Since most of these refractory compounds are temperature resistant, most of them are not amenable to conventional, commercial sintering techniques. Articles may be formed from these refractory compounds, however, by compacting them in powder form at a high temperature by a process known as hot forming or hot pressing. Very hard, heat resistant powder metal articles have been developed using this technique. Often, it is desirable to provide passages or ducts in these hot pressed refractory articles. Forming the passages by melting out rods or cores is objectionable because the core metal infiltrates the pores in the articles. Similarly, the presence of low melting metals in the pores of these refractory metal articles may seriously affect the hardness and heat resistance of the the articles.

Powder metallurgy processes exist for varying the density of articles. Sintering processes can be used to produce articles that are so porous that the matrix occupies only a relatively small percentage of the total volume. On the other hand, high density powder metal articles, including hot pressed refractory articles, may be formed having densities close to the theoretical limit. The method of forming passages by using a low melting metal core cannot always be carried out successfully in the high density powder metal articles, since the core metal tends to react with or contaminate the matrix at the contact points.

For refractory carbides, attempts to produce passages or ducts through powder metal articles by means of combustible metallic or organic wires, rods or other geometries have not been successful. This is due to restricted opportunities for the decomposition products to leave the potential pore site. Often, non-volatilized, unburned residue associated with the pore forming component remains in the article where it blocks the passage.

Accordingly, it is an object of this invention to provide a method for forming passages within powder metal articles.

It is a further object of this invention to provide a method for forming passages of predetermined size and position within the powder metal articles.

It is a still further object of this invention to provide a method for forming passages in powder metal articles, while obtaining article densities up to 85 percent of theoretical.

Another object of this invention is to provide a method for forming ducted refractory articles of dense carbides, with only minimal chemical contamination of the articles.

These objects are accomplished in accordance with a preferred embodiment of the invention by supporting a tube in a predetermined position in a mold cavity. The tube is preferably formed of an organic material, such as polyethylene. The opposite ends of the tube extend out of the mold cavity. The mold cavity is then filled with desired powder, which is preferably compacted around the tube. The article is then heated to a high temperature under moderate pressure in a combined sintering-hot pressing process. The pressure-sintering temperatures are sufficiently high to burn away the tube, leaving a continuous passage through the article. Temperatures in excess of 2000° C., pressures as high as 500 pounds per square inch are preferably employed, depending on the characteristics of the organic pore-former. The full advantages of this method are best realized when the least pressures permissible are used.

This method can be used to form passages either in dense powder metal articles, or in more porous powder metal articles. The use of hollow organic tubes for forming the passages in accordance with the invention eliminates residue in the passages because the flow of gas through the tube during combustion promotes complete combustion of the tube and carries away solid residue.

In order to achieve the desired gas flow through the hollow tubes during combustion, it is usually necessary to arrange the tubes in the article in such a way that the opposite ends of the tube are in communication with the outside surface of the article. The ends of the tubes may be spaced interiorly of the surface of the article, provided the ends are sufficiently close to the surface of the article to permit the decomposition gases to flow out of the pore sites.

The combustible organic tubing that is used in carrying out the process of this invention may have an external diameter as small as 0.010 inch. The internal diameter is correspondingly smaller and conventional capillary tubing has been found to produce satisfactory results. Although polyethylene is preferred because it produces a minimum of carbonaceous material when decomposed, other synthetic resins, such as polystyrene and nylon, and other organic materials which decompose completely and have low ash producing tendencies upon combustion have also been used. In powder metal articles, even of high porocity, incomplete decomposition of wires and rods may cause the residue to block the passages when the length to diameter ratio of the passages exceeds 30.

As an example, a length of polyethylene tubing of 0.024 inch outside diameter and 0.011 inch inside diameter was positioned in a mold which was partially filled with niobium carbide powder. The remainder of the mold was then filled with the powder. A constant pressure of 300 pounds per square inch and a temperature of approximately 2500° C. were employed in hot pressing the powder. The polyethylene tubing burned during the process and only a trace of carbonaceous by-product remained. A continuous duct was formed in the powder metal article in place of the polyethylene tubing.

Either a single tube or a plurality of tubes may be molded in the refractory article. The tubes may be supported in a suitable jig and the metal powder may be deposited in the mold around the tubes. Another method is to alternate layers of metal powder with layers of tubing within the mold. The tubing may be arranged in the desired pattern and joined together by cementing or fusion to form one layer of the article. Each successive layer of powder is tamped to completely surround each successive layer of oriented tubing. This process is repeated until the mold is filled with alternate layers of metal powder and tubes.

In order to carry out the method, it is necessary to heat the molded article to a temperature sufficiently high to assure the complete combustion of the tubing. For example, when polyethylene tubing is used, the temperature should exceed 500° C., since exposure of an organic material to a temperature of 500° C. causes complete combustion. However, the pressure-sintering is best carried out at a temperature above 1000° C. Pressure-sintering of carbides, oxides and other refractory metal compounds requires temperatures above 1400° C. The pressure during sintering or hot pressing preferably is between 100 p.s.i. and 500 p.s.i. Excessive pressure may cause the tubes to collapse. Depending on the organic pore-former used, the maximum pressure successfully used in fabricating pore diameters between 10 mils and 200 mils has been 750 p.s.i.

The method of this invention is particularly suitable for hard, dense refractory materials, in which passages cannot be machined. Examples of such refractory materials are silicon carbide, titanium carbide, zirconium carbide, niobium carbide and hafnium carbide. With variations this method can also be applied to analogous borides or oxides. These metal and metalloceramic carbides, borides and oxides preferably have a density of 80 to 85 percent or more of their theoretical density and a hardness of seven or more on the Mohs' scale. These materials have good refractory properties and may be used for rocket nozzles, for example, where the material must simultaneously withstand very high temperatures and high pressures.

Various articles may be constructed utilizing the method of this invention. For example, hollow cylinders may be formed with radially oriented ducts or pores by placing the tubing in a suitable mold with the tubing oriented radially and perpendicular to the central axis. A rocket nozzle may likewise be constructed by placing organic tubes in a radial plane and spaced apart at equal angular positions. A plurality of planes of tubing may be spaced axially along the nozzle. When the nozzle is heated to a high temperature, the tubes are burned, leaving radial passages. These passages may be used to supply coolant fluid to the interior of the nozzle to cool the surface of the nozzle.

One important use of the method of this invention is in making powder metal articles of metal carbides, such as tungsten carbide, silicon carbide, tantalum carbide, zirconium carbide, hafnium carbide, and niobium carbide. These metal carbides exhibit good mechanical properties at temperatures as high as 3000° C. To obtain the maximum strength and hardness, articles are formed by hot pressing these carbide powders at pressures to about 5000 pounds per square inch. This process results in the formation of an article having a density of as much as 99 percent of the theoretical density. Passages can be formed in these articles by using organic tubing in accordance with this invention. However, the maximum pressure that may be used while forming ducts or pores in accordance with this invention is of the order of 750 pounds per square inch for tubing of 10 mils to 200 mils. The maximum density obtainable with this process is about 85 percent of the theoretical density. Since the residue, if any should remain, is carbonaceous, it will not contaminate the carbide of which the article is formed. Therefore, small diameter passages can be formed in these refractory materials without affecting the properties of the article.

In carrying out the method of this process with tungsten and other metals which are capable of combining with carbon to form metal carbides, an additional step may be required to assure that the ducted article is composed entirely of the free metal. When the organic tube forming the duct or passage burns, the carbon residue may combine with the free metal in the article and form a metal carbide. This problem may be overcome by heat treating the article in a reducing atmosphere. For example, if tungsten powder is molded around a tube of polyethylene, and the article is hot pressed in accordance with the method of this invention, the carbon residue of the tube may combine with the metal to form tungsten carbide. The tungsten carbide may be eliminated by subjecting the article to heat treatment in a hydrogen atmosphere furnace for a sufficient period of time to remove the tungsten carbide impurity.

An important advantage of the method of this invention is that relatively long fluid passages having a small diameter may be formed in powder metal articles, particularly dense, hard articles. The passages may be arranged in a predetermined pattern and tubing may be selected to produce passages of the desired diameter. Since the tubing is completely decomposed during the sintering of the metal powder, the passages are free of obstructions. Apparently, the products of combustion are conducted out of the passage through the hole through the center of the tube.

While this invention has been described in one embodiment, it is recognized that variations and changes may be made therein without departing from the invention as set forth in the claims.

I claim:

1. A method of making ducted articles by powder metallurgical techniques which comprises the steps of arranging at least one combustable organic tube in a predetermined pattern, interspersing loose particles of refractory metal-containing powder around said tube, subjecting said tube and said powder to the simultaneous application of temperature and pressure, said temperature being sufficiently high to cause complete combustion of said tube and cohesion of said powder without the melting thereof and said pressure being less than that required to collapse said tube.

2. The method according to claim **1** wherein said powder is selected from the group of powders consisting of tungsten, silicon, tantalum, zirconium, hafnium, niobium and the carbides, borides and oxides thereof.

3. The method according to claim **1** wherein said pressure ranges between 100 p.s.i. and 750 p.s.i.

4. The method according to claim **1**, wherein the article is heated to a temperature greater than 500° C.

5. The method according to claim **1**, wherein the tubing is formed of polyethylene.

6. The method according to claim **1**, wherein the tubing is formed ofa synthetic resin.

7.The method according to claim **1**, wherein said powder metal article has a density 50–85 percent of its theoretical density.

8. The method according to claim **1**, wherein said passage has a length to diameter ratio greater than 30.

9. The method according to claim **1**, wherein the refractory metal containing powder is selected from the group consisting of tungsten carbide, silicon carbide, tantalum carbide, zirconium carbide, hafnium carbide and niobium carbide.

10. The method according to claim **1**, wherein said metal is a metal capable of combining with carbon to form a metal carbide impurity, and including the additional step of heating the article in a reducing atmosphere whereby the metal carbide impurity is removed.

11. The method according to claim **10**, wherein said metal is tungsten.

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