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(54) Boric oxide or boric acid sintering aid for sintering ceramics

(57) A liquid sintering aid for densifying ceramic material is selected from solutions of H_3BO_3 , B_2O_3 and mixtures of these solutions. In sintering ceramic articles, e.g. silicon carbide, a shaped green body is formed from a particulate ceramic material and a resin binder, and the green body is baked at a temperature of 500 to 1000°C to form a porous body. The liquid sintering aid of B_2O_3 and/or H_3BO_3 is then dispersed through the porous body and the thus treated body is sintered at a temperature of 1900 to 2200°C to produce the sintered ceramic article.

GB 2 012 309 A

SPECIFICATION

Liquid sintering aid and methods of producing sintered ceramic articles using such aid

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The present invention relates to the use of liquid sintering aid in processes involving sintering of ceramic materials to produce dense, hard articles having industrial uses. Although the present invention will be specifically discussed in regard to compositions containing silicon carbide as the ceramic material, it will be understood that other sinterable carbides, for example, titanium carbide, may be utilized as the ceramic material.

10 Silicon carbide has long been known for its hardness, strength and excellent resistance to oxidation and corrosion. Silicon carbide has a low coefficient of expansion, good heat transfer properties, and maintains high strength at elevated temperatures. In recent years, the art of producing high density silicon carbide materials by sintering silicon carbide powders has been developed. High-density silicon carbide materials find utility in the fabrication of components for turbines, heat exchange units, pumps, and other equipment or tools that are exposed to severe corrosion or wear, especially in operations carried out at high temperatures.

Ceramic bodies or compacts may be formed or shaped by various casting or molding processes. Forming or shaping processes known in the art, such as cold pressing, isostatic forming, slip casting, extrusion, injection or transfer molding or tape casting, may be utilized. The shaped ceramic body is subsequently sintered between about 1900°C and 2200°C to form a dense, hard article.

In order to obtain high-density and high-strength silicon carbide ceramic materials, various additives have been utilized. For example, a method of hot pressing silicon carbide to densities in order of 98 percent of theoretical by addition of aluminium and iron as densification aids is disclosed by Alliegro, et al, J. Ceram. Soc., Vol. 39, No. 11, Nov. 1956, pages 386 to 389.

They found that a dense silicon carbide could be produced from a powder mixture containing 1 percent by weight of aluminium. Their product had a modulus of rupture of 54,000 psi at room temperature and 70,000 psi at 1371°C. More recently, the use of boron or beryllium as sintering or densification aids has been developed. Such aids are usually added to the ceramic material powder in amounts ranging between about 0.3 and about 5.0 percent by weight of boron or beryllium. The sintering aid may be in the form of elemental boron or beryllium or in the form of boron- or beryllium-containing compounds. Boron is the preferred additive for reasons of handling and performance. Boron is commonly utilized in the form of boron carbide. Examples of boron containing silicon carbide powders may be found in U.S. Patents 3,852,099; 3,954,483; and 3,968,194.

Sinterable powders also contain excess or uncombined carbon. Excess carbon in amounts of from about 1.0 to about 4.0 percent by weight are commonly used. The excess carbon required for sin-

tering may be in the form of carbon remaining in the article from a previous processing step or may be added in the form of a carbon source material which would yield the desired amount of excess carbon as the article is sintered. Excess carbon facilitates sintering and is beneficial in reducing the amounts of various oxide impurities in the starting ceramic material that otherwise would remain in the finished product.

In accord with the present invention, the sintering aid utilized to densify ceramic materials is employed in liquid form. The source of boron, or sintering aid, of the present invention is selected from solutions of H_2BO_3 , B_2O_3 or mixtures thereof. Although the solvent may be any liquid in which H_2BO_3 or B_2O_3 are soluble, water or alcohols are preferred because of their availability and cost.

The liquid sintering aid is suitably added to a shaped, porous ceramic body prior to sintering. In one mode of the invention, the sintering aid and a source of carbon are added together in liquid form. In such mode, the sintering aid may be dissolved in the carbon source, or the sintering aid and the carbon source may be dissolved in a common solvent, for example, water or alcohol.

The ceramic starting material is initially prepared in finely divided form. Preferably, the particles have an average size of from about 0.10 to about 2.00 microns, with a maximum of about 5.00 microns. Although size is a critical parameter, surface area is also of relevant consideration in determining the suitable material. Accordingly, the particles preferably have a surface area of from about 1 to about 100 m^2/g . Within this range, it is more preferred that the surface area of particles range between about 5 and about 20 m^2/g .

Silicon carbide is a preferred ceramic starting material. The silicon carbide may be alpha or beta phase, or may be amorphous. At the present time, the alpha (non-cubic) crystalline phase of silicon carbide is most economically obtained. The present compositions may contain substantially entirely, e.g. 95 percent or more by weight, silicon carbide of the alpha phase, or may contain mixtures of the various forms of silicon carbide. For example, mixtures which are predominantly alpha phase (greater than 50 percent) are aptly suited to use. The ceramic material may contain minor amounts of impurities without deleterious effect. Generally, a purity of at least about 95 percent is required and a higher purity desired.

In accord with the present invention, the sintering aid, or a combination of sintering aid and carbon source material, are added to a shaped porous ceramic body after baking and prior to sintering. Such bodies are produced by molding or casting processes wherein a green body is formed, baked, and subsequently sintered. The addition of sintering aid or a combination of sintering aid and carbon source material after baking and just prior to sintering is particularly advantageous in injection molding and slip casting processes. In present practice, the ceramic starting material is initially mixed with a variety of additives, e.g. sintering aids, carbon source material, resin binder materials, mold release

agents, and additives to lower the viscosity of the mixture. It has been found that the sintering aid and/or the carbon source material frequently has a deleterious effect on the binding, release or flow properties of the mixture. The elimination of the sintering aid, or the sintering aid and the carbon source material, facilitates the forming process and greatly increases the number of useful binder resins and processing additives that may be utilized in such mixtures.

The sintering aid of the present invention is added to the baked green body in amounts which will provide from about 0.3 to about 5.0 percent by weight of boron, and, within this range, from about 0.5 to about 4.0 percent are aptly suited to use. When amounts of boron below about 0.3 percent by weight are used, sintering is generally not effectively carried out. When amounts of boron above about 5.0 percent by weight are included, densification is not noticeably improved and may be adversely affected by the inclusion of excessive amounts of boron. The strength of the present solutions of sintering aid is adjusted to provide a boron source substantially uniformly dispersed throughout the porous body that, upon sintering, will yield boron within the foregoing ranges. The sintering aid solution may be made relatively strong, and, after saturating or impregnating the porous area, the excess may be allowed to drain off. The amount of boron added may be determined by a simple weighing of the body before and after impregnation or dispersion of the sintering aid and calculating from the added weight.

The present invention also contemplates the use of a combination of sintering aid and a source of excess carbon in liquid form. Suitably, the sintering aid may be dissolved in the excess carbon source material, or both the sintering aid and the excess carbon source material may be dissolved in a common solvent. Excess or combinable carbon in amounts between about 0.05 and about 5.0 percent of the ceramic material are useful to facilitate sintering, and, within this range, amounts of from about 1.0 to about 4.0 percent by weight are especially useful. The carbon source may be any carbonaceous material in which the sintering aid is miscible, without an adverse reaction, or which is miscible in a common solvent with the sintering aid. Sugars, such as sucrose and dextrose, corn syrup, furfuryl alcohol, furfuryl, tetrahydrofurfuryl alcohol, phenolic resins, polyphenylene resins, and furan resins are typical useful carbon source materials. Usually, the char or carbon value of carbon source materials ranges from about 15 to about 80 percent by weight. The appropriate amounts of sintering aid and carbon source material may thus be easily calculated. It is postulated that the present sintering aid undergoes reduction during sintering. The amount of carbon source material may be adjusted to provide both the amount of carbon required for such reduction and the amount of excess carbon required for sintering.

The liquid sintering aid of the present invention may be prepared by simply dissolving H_3BO_3 , B_2O_3 , or mixtures thereof, in an appropriate solvent. It will be understood that the formula designations H_3BO_3 and

B_2O_3 , boric acid and boron oxide, shall be read to be inclusive of hydrates of H_3BO_3 and B_2O_3 . The solvent may be any liquid in which H_3BO_3 or B_2O_3 are soluble, suitably the solvent is water or alcohol. The sintering aid of the present invention is added to a porous body to provide from about 0.3 to about 5.0 percent and, preferably, within that range, from about 0.5 to about 4.0 percent by weight boron to the body. The strength of the solution of sintering aid is adjusted to facilitate a substantially uniform dispersion of a boron source throughout the body.

The sintering aid of the present invention may be dissolved in a source of carbon to provide a liquid combination of sintering aid and carbon source material. Suitable sources of carbon useful in this mode are those in which the sintering aid is soluble. Especially suited are alcohols such as furfuryl alcohol and tetrahydrofurfuryl alcohol. Excess or combinable carbon is utilized in the range of from about 0.05 to about 5.0 percent by weight, and, preferably, from about 1.0 to about 4.0 percent by weight of the porous body to facilitate sintering. Generally, carbonaceous materials yield between about 15 and about 80 percent by weight free or combinable carbon upon destruction by heating. In this mode of the invention, an appropriate amount of sintering aid is dissolved, suitably by mixing, in an appropriate amount of carbon source material to provide excess carbon within the desired range.

The sintering aid of the present invention and the carbon source material may be dissolved in a mutual solvent to form a combination liquid sintering aid and carbon source material. In this mode, water is aptly suited to use as the mutual solvent. Examples of water-soluble carbon source materials that may be employed are sugar, such as sucrose and dextrose, corn syrup, and alcohol, such as furfuryl alcohol. Alcohols may also be used as the mutual solvent. Ethyl, methyl, propyl, and isopropyl alcohols are eminently useful. Phenol-formaldehyde resins are particularly adapted to use as the carbon source material when short chain alcohol is used as the common solvent. The sintering aid and carbon source material are dissolved, suitably by mixing, in the common solvent to provide a combination liquid sintering aid and carbon source material.

In carrying out the method of the present invention, the liquid sintering aid or combination liquid sintering aid and carbon source material are dispersed in a baked green body, and subsequently the body is sintered to produce a dense, hard ceramic article.

The process used to form or shape the green body is not critical to the present invention. Generally, in such processes, the particulate ceramic starting material is initially mixed with a resin binder material and other appropriate additives, for example, mold release agents, lubricants, viscosity aids, and excess carbon sources. The mixture is then molded or shaped by known art processes such as cold pressing, isostatic forming, slip casting, tape casting, injection or transfer molding. The shaped green body is baked, usually at temperatures between about 500°C and about 1000°C and, more commonly between about 700°C and about 900°C. The result o:

the baking step is a product having an open pore structure which is particularly adapted to be treated with the liquid sintering aid or combination sintering aid and carbon source material of the present invention. The sintering aid or combination sintering aid and carbon source material may be dispersed substantially uniformly throughout the baked body by impregnating the body, by applying pressure, or capillary action of the pores. The preferred method, however, is by vacuum filling. In such method, a vacuum is drawn on the body, and the liquid sintering aid or combination liquid sintering aid and carbon source material is fed into the evacuated body. After dispersion of the sintering aid, or combination sintering aid and carbon source material, the impregnated body is sintered at temperatures between about 1900°C and 2200°C to produce a dense, hard article or body.

It will be appreciated that the invention is not limited to the specific examples and embodiments of sintering aids and sintering methods, and that various modifications may be made within the ordinary skill of the art, without departing from the spirit and scope of the invention.

25 CLAIMS

1. A method of producing a sintered ceramic article which comprises the steps of:
 - a) forming a shaped green body comprised of a particulate ceramic material and a resin binder,
 - 30 b) baking said green body at a temperature of from about 500°C to about 1000°C to form a porous body,
 - c) dispersing a liquid sintering aid selected from the group of H_3BO_3 , B_2O_3 and mixtures thereof,
 - 35 through said porous body,
 - d) sintering said treated body at a temperature of from about 1900°C to 2200°C to produce a sintered ceramic article.
2. A method as claimed in claim 1 wherein the said ceramic material is silicon carbide.
3. A method as claimed in claim 1 or 2, wherein the liquid sintering aid is a solution of H_3BO_3 .
4. A method as claimed in claim 3 wherein the liquid sintering aid is an aqueous solution of H_3BO_3 .
- 45 5. A method as claimed in claim 1 or 2, wherein the liquid sintering aid is an aqueous solution.
6. A method as claimed in claim 1 or 2 wherein the liquid sintering aid is an alcohol solution.
7. A method as claimed in any one of claims 1 to 50 6, wherein sufficient liquid sintering aid is dispersed in said baked green body to add between about 0.3 and about 5.0 percent by weight of boron.
8. A method as claimed in claim 1 wherein the liquid sintering aid includes a source of carbon.
- 55 9. A method as claimed in claim 1 wherein the liquid sintering aid is in solution with a source of carbon.
10. A method as claimed in claim 9 wherein the liquid sintering aid includes a source of carbon as a 60 solvent.
11. A method as claimed in claim 9 wherein the solution is aqueous.
12. A method as claimed in claim 9 wherein the solution is alcoholic.
- 65 13. A method as claimed in any one of claims 1 to

12 wherein the liquid sintering aid is dispersed within said green body by vacuum filling.

14. A method as claimed in any one of claims 1 to 12, wherein the liquid sintering aid is dispersed 70 within said green body by capillary action.

15. A method of producing a sintered ceramic article substantially as hereinbefore described.

16. A sintered ceramic article when produced by the method of any one of claims 1 to 15.

75 17. A liquid sintering aid for densifying ceramic materials selected from the group of alcoholic solutions of H_3BO_3 , B_2O_3 , and mixtures thereof.

18. A sintering aid as claimed in claim 17 which is a solution of H_3BO_3 .

80 19. A sintering aid as claimed in claims 17 or 18 that includes a source of carbon.

20. A sintering aid as claimed in claim 17 wherein said sintering aid is in solution with a source of carbon.

85 21. A sintering aid as claimed in claim 20 wherein the solvent is furfuryl alcohol.

22. A liquid sintering aid substantially as hereinbefore described.

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