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(19)

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(54) DENSE CERAMIC ARTICLES

(71) We, THE PLESSEY COMPANY LIMITED, a British Company of 2/60 Vicarage, Lane, Ilford, Essex, 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 the manufacture of articles of substantially pure dense ceramic materials.

Articles of substantially pure dense ceramic materials are in demand for use in arduous environments. For example, it is known to make the gas turbine blades of substantially pure dense ceramic materials. Silicon nitride is a ceramic which is very suitable for use in arduous environments because it possesses outstanding high temperature properties. However, difficulty is experienced in making articles of substantially pure dense silicon nitride, because silicon nitride—unlike the majority of ceramic materials—is not amenable to sintering. Consequently two methods have been developed for making articles of silicon nitride. In the first method, a silicon compact is made (for example from powdered silicon and a volatile binder) which closely resembles the desired article, the compact subsequently being nitrided to yield a porous silicon nitride body of the desired form. In the second method, powdered silicon nitride is hot pressed into a dense billet, from which the article is subsequently formed by machining or hot forging. The second method suffers from the disadvantage that the dense billet can only be formed from the powder if an additive, commonly magnesium oxide, is present. The disadvantage is two fold. Firstly, the additive gives rise to residual fluxes which are inimical to the development of optimum high temperature properties. Secondly, some at least, of the additive almost inevitably survives in the article as an impurity.

According to the invention there is provided a method of manufacturing an article of substantially pure dense ceramic material, which includes the following three stages: firstly, mixing a powder of the substantially pure ceramic material with an additive which promotes densification and is capable of nuclear transmutation into a gas when exposed to radiation, and hot pressing the mixture to form a billet of dense ceramic material in which at least some of the additive survives as an impurity; secondly, irradiating the billet to convert the surviving additive by nuclear transmutation into a gas which is held captive in the billet; and thirdly, subjecting the billet to a hot forging operation, during which the captive gas escapes and an article of substantially pure dense ceramic material is forged from the billet.

The method is primarily intended for use when the ceramic material is silicon nitride, but the advantages of the method are equally obtainable with other ceramic materials. The method will be discussed with reference to silicon nitride.

Substantially pure silicon nitride is mixed with an additive. The additive is a material which both promotes densification and is capable of nuclear transmutation when exposed to radiation, and yields a product which is a gas of low atomic weight which remains behind dispersed in the silicon nitride. The additive is used in powder form. Suitable additives are lithium or its compounds such as lithium oxide, lithium nitride or lithium silicide, employed either separately or in combination. Beryllium and its compounds may also be used, but discussion will be confined to lithium.

The powders are mixed together, and the mixture is placed in a graphite die which has been coated with boron nitride or other suitable compound as a separating agent. The mixed powders are then hot pressed in the dies, in the manner already known in relation to other additives such as magnesium oxide. The hot pressing yields a billet of dense silicon nitride which is very impure at the surface. The surface impurities are mainly the separating agent e.g. boron nitride, and silicon carbide formed by interaction of the silicon nitride with the carbon of the graphite die. The impure surface is removed by grinding in the known way, leaving a slightly smaller billet of dense silicon nitride, which however is impure. The impurity is that proportion of the densifying additive which did not escape during the hot pressing. The impurity is distributed throughout the billet. In the known process, the impurity is magnesium or a magnesium compound.

In the present example, the impurity is lithium or a lithium compound. The dense impure billet is now irradiated. The irradiation may take the form of bombardment by protons or bombardment by neutrons. In either event the lithium is transmitted into helium. Helium, being a gas of low atomic weight, is readily absorbed into the silicon nitride, in which its atoms are temporarily held captive.

The irradiated billet is now rapidly hot forged into the desired article. During the forging, the captive gas escapes, leaving an article of substantially pure dense silicon nitride. As pure silicon nitride cannot be forged, it is essential that the desired article be formed by the time the last of the gas escapes. As the gas escapes quickly, the forging must be rapid, for example, within ten minutes. Forging should preferably take place between 1000°C and 1850°C, and the pressure should not exceed 1 1/2 tons per square inch.

The quantity of lithium or of a lithium compound which is mixed with the silicon nitride powder must be such that; immediately prior to irradiation lithium is present in the dense billet to the extent of at least 5 parts per million and not more than 5 per cent by weight.

The irradiation may be represented by the formula:—

$$^{7}_{3}Li+^{1}_{1}H=2^{4}_{2}He$$

assuming bombardment by protons. However, this process will involve large and expensive apparatus and it is, therefore, preferable to use isotopically enriched lithium. In this case, the irradiation involves bombardment by neutrons, and the formula:—

$$^{6}_{3}Li+^{1}_{0}n=^{3}_{1}H+^{4}_{2}He$$

If beryllium were used, bombardment would need to be carried out in two stages, the first stage could, for example, be effected by using deutrons in which case the formula would be:—

$$^{9}_{4}Be+^{2}_{1}H=^{7}_{3}Li+^{4}_{2}He$$

In the second stage the lithium formed during the first stage is transmitted into helium by bombardment with protons, in which case the formula would be:—

$$^{7}_{3}Li+^{1}_{1}H=2^{4}_{2}He$$

WHAT WE CLAIM IS:—

1. A method of manufacturing an article of substantially pure dense ceramic material which includes the following three stages: firstly, mixing a powder of the substantially pure ceramic material with an additive which promotes densification and is capable of nuclear transmutation into a gas when exposed to radiation, and hot pressing the mixture to form a billet of dense ceramic material in which at least some of the additive survives as an impurity; secondly, irradiating the billet to convert the surviving additive by nuclear transmutation into a gas which is held captive in the billet; and thirdly, subjecting the billet to a hot forging operation during which the captive gas escapes and an article of substantially pure dense ceramic material is forged from the billet.

2. A method as claimed in claim 1 wherein the ceramic material is silicon nitride.

3. A method as claimed in claim 2 wherein the additive is provided by lithium, or beryllium, or compounds of lithium or beryllium, and wherein when the additive is lithium or its compounds, the quantity which is mixed with the silicon nitride is such that, prior to irradiation lithium is present in the dense billet to the extent of at least 5 parts per million and not more than 5 per cent by weight.

4. A method as claimed in claim 5 wherein the additive is provided by lithium oxide, lithium nitride or lithium silicide either singly or in any combination and wherein the quantity of the lithium additive which is mixed with the silicon nitride is such that, prior to irradiation lithium is present in the dense billet to the extent of at least 5 parts per million and not more than 5 per cent by weight.

5. A method as claimed in any one of the claims 3 or 4 wherein the irradiation of lithium or its compounds is effected by proton or neutron bombardment.

6. A method as claimed in any one of the claims 2 to 5 which includes the steps of mixing substantially pure silicon nitride powder with an additive which promotes densification and is capable of nuclear transformation into a gas when exposed to radiation; hot pressing the mixture in a graphite die which is coated with a separating agent such as boron nitride, to form a billet of dense silicon nitride, interaction of the silicon nitride with the

carbon of the graphite die forming surface impurities of the separating agent and silicon carbide; removing the impure surface of the billet to form a dense silicon nitride billet in which at least some of the additive survives as an impurity; and subjecting the billet to the said irradiation and hot forging stages.

7. A method as claimed in claim 6 wherein the additive is lithium, and the quantity of the lithium additive which is mixed with the silicon nitride is such that, prior to irradiation, lithium is present in the dense billet to the extent of at least 5 parts per million and not more than 5 per cent by weight, and wherein the irradiation is effected by either proton or neutron bombardment, the lithium being transmitted into helium and wherein the hot forging is effected at a temperature in the range 1000°C to 1850°C and at a pressure of 1 1/2 tons per square inch.

8. A method of manufacturing an article of substantially pure dense ceramic material according to claim 1 substantially as hereinbefore described.

9. An article of substantially pure dense ceramic material produced by the method as claimed in any one of the preceding claims.

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