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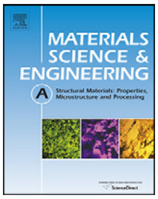

Dense and near-net-shape fabrication of Si_3N_4 ceramics

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ABSTRACT

With silicon nitride significant progress has been made in order to search for fully dense, strong, reliable structural ceramics to find wide use in applications at high temperatures which are allowing new and innovative solutions to component design problems. Taking into account that more and more ceramic components based on Si_3N_4 are being used in the aerospace and automobile industries, it is a great challenge to fabricate such complex-shaped components with high reliability and with defect-free microstructures such as pores, inclusions or any other inhomogeneity at acceptable costs. On the other side, the high hardness of Si_3N_4 ceramics is almost always cost prohibitive to shape components by hard machining. It is therefore great effort exhibited in the development of near-net-shape fabrication processes that can produce complex-shaped components with a minimum of machining as well as to minimize the number and size of microstructural defects within design limits. In this review, the fabrication of near-net-shape Si_3N_4 ceramics is given in detail. All kinds of these techniques (injection molding, gelcasting, robocasting, mold shape deposition, rapid prototyping) and their advantages and disadvantages are explained.

1. Introduction

Structural ceramics based Si_3N_4 have been explored since the late 1960s [1] emphasizing Si_3N_4 based materials primarily for use in high temperature, structural applications such as heat engines. Taking into account their unique combination of properties, silicon nitride and related materials have probably become the most thoroughly characterized non-oxide ceramics with wide applications including heat exchangers, turbine and automotive engine components, valves and cam roller followers for gasoline and diesel engines and radomes on missiles as well as insulators, electronic substrates, high Tc superconductors, tool bits, wear surfaces, to name a few [2,3–17]. The market for these applications is very high; there are still several difficulties that must be overcome before the full potential of structural ceramics based silicon nitride is realized. The sintering of silicon nitride is very difficult because of the low self-diffusivity of this covalent material [13–20,21–30]. Doping pure Si_3N_4 with of some oxides provides the formation of intergranular liquid phase which aids the further densification of the silicon nitride during different sintering routes [3–7,13–31]. These oxides, however, remain as grain boundary glassy phase, which deteriorate the high temperature properties of the ceramics such as creep and high temperature strength [17,32,33]. Considering this, it is very important to stress that the recent advances in improving properties are mainly attributed to improved processing techniques, purer raw materials and the use of gas pressure sintering or HIP techniques in order to reduce critical flaw size [33].

It is a common practice to densify Si_3N_4 by alternative techniques and/or supplementary means such as nitridation of silicon powder or with the application of pressure in order to assist the sintering process. These techniques can be summarized: i) Reaction Bonding Silicon Nitride (RBSN), ii) Hot Pressing Silicon Nitride (HPSN), iii) Sintering Silicon Nitride (SSN), iv) Sintering Reaction Bonding Silicon Nitride (SRBSN), v) Hot Isostatic Pressing Silicon Nitride (HIPSN), vi) Hot Isostatic Pressing Reaction Bonding Silicon Nitride (HIPRBSN), vii) Hot Isostatic Pressing Sintered Silicon Nitride (HIPSSN) and viii) Hot Isostatic Pressing Sintered Reaction Bonded Silicon Nitride (HIPSRBSN) [20,22–34]. It is very difficult to produce pure dense silicon nitride ceramics by means of conventional sintering (simple heating of powder compacts) due to the high degree of covalent bonding between silicon and nitrogen [35]. The principal reason for this is that the diffusion of silicon (at 1400 °C $D_{Si} \approx 0.5 \times 10^{-19}\ m^2\ s^{-1}$) and nitrogen (at 1400 °C $D_N \approx 6.8 \times 10^{-10}\ m^2\ s^{-1}$) in the volume or at the grain boundaries of Si_3N_4 is extremely slow [36]. Taking into account that the densification by sintering requires mass transport via volume or grain boundary diffusion and since such diffusion is a thermally activated

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process, a higher sintering temperature would result in a highly dense material but at high temperatures Si_3N_4 starts to dissociate [35,37].

Many different sintering techniques have been developed since the material properties strongly depend on the fabrication method and the silicon nitride cannot be considered as a single material [38]. As was previously outlined, the most common sintering methods used to consolidate Si_3N_4 based ceramics [20] are: i) Reaction bonding (RBSN), ii) Hot pressing (HPSN), iii) Hot isostatic pressing (HIPSN), iv) Sintering (SSN), v) Gas pressure sintering (GPSN) and vi) Sintering reaction bonding (SRBSN). On the other hand, in order to manufacture Si_3N_4 ceramics for application in heat engines, development of near-net-shape fabrication methods is critical [39]. Recognizing this need, several companies in the United States, Europe and Japan have invested significant resources to develop injection molding, gelcasting of silicon metal, and slip casting for fabrication of complex cross-section structural ceramic parts [40]. Among the shapemaking techniques, slip casting is believed to be a method appropriate for prototypes, whereas injection molding is ideally suited for high-volume, cost effective production of complex parts [28,41]. Nowadays, robocasting is a new freeform fabrication technique for dense silicon nitride ceramics [42]. This colloidal method has shown its potential to improve the strength and reliability of high-performance ceramics. Ceramic components with simple or complex shapes can be rapidly produced from a computer aided-design (CAD) drawing directly to a finished component that requires little or no machining after fabrication [42,43].

More complex techniques for manufacturing silicon nitride ceramics have been used to produce reliable parts. Injection molding, slip casting, robocasting aqueous, gelcasting, are some of them [42,44,45]. The fabrication techniques to obtain near-net-shape Si_3N_4 ceramics as well as their advantages and disadvantages are given in detail.

2. Manufacture of silicon nitride powders

Some studies on the sintering of silicon nitride powders to dense bodies have shown the great importance of surface composition: the nature and amount of sintering aids (such as Al_2O_3, Y_2O_3, Yb_2O_3, ZrO_2, etc.) at high temperatures (1750–2000 °C) [3–9] depended on the surface oxygen content of the powders [6]. However, the sintering of silicon nitride ceramics without additives is an important approach to reducing impurity phases in the densified bodies achieving Si_3N_4 ceramics with the intrinsic properties of the materials. Ceramics free of aids sintered under high pressures exhibited improved mechanical properties at high temperatures compared to those sintered with additives [8,9].

These materials tend to be expensive due to the high cost of the silicon nitride powder used to produce them. Therefore, the reduction of cost has been recognized as a major factor for the introduction of silicon nitride ceramics into the marketplace with a broad range of properties to replace the stainless steels, super alloys, tungsten carbides and some ceramics such as Al_2O_3 and ZrO_2 in automotive, aerospace, metal processing and forming, mineral processing, machining, oil field services, petrochemical, semiconductor processing industries, etc. [10–12].

As indicated a number years ago [3], there is a great advantage to processing ceramics from powders with an idealized set of physical and chemical characteristics [46] as follows: i) small size less than 1 μm, ii) narrow size distribution, iii) equiaxed morphology tending towards spherical, no agglomeration, or very weak agglomerate bonds which can be broken during processing and iv) high degree of chemical and crystal purity. With these characteristics, it is possible to obtain advantages such as reduction of sintering times and temperatures, reduction of grain size and distribution, higher sintered densities with the use of low pressures and reduction or sintering aids, etc., all of which lead to obtain excellent properties [47–51]. There has been considerable interest in developing ceramic materials for use in advanced heat engines. Therefore, possessing low density and excellent thermomechanical properties, ceramics materials provide a means for producing heat engines with very efficiency ceiling far above what is presently possible with today's super alloys. Silicon nitride (Si_3N_4), has received considerable attention due to its high decomposition temperature (approximately 1880 °C) as well as excellent creep properties [3,52,53]. Today, commercially available Si_3N_4 powders are prepared by means of various routes, already in use for production on a technical scale because these powders are the starting point for dense materials, namely:

2.1. Silicon nitridation

Chemically pure Si powder (particle diameter <10 μm) is nitrided in an atmosphere of NH_3, N_2/H_2 or N_2 as follows:

$$3Si + 2N_2 \underset{1746-1996\,^{\circ}C}{\longrightarrow} Si_3N_4 \qquad (1)$$

under controlled furnace conditions such as bed-depth [54]. The nitriding process results in Si_3N_4 lumps which are crushed and milled. The reaction (1) is the high temperature reaction of silicon powder with a nitrogen and it is a reaction strongly exothermic with $\Delta H^{\theta} \sim 733\ \mathrm{kJ\,mol^{-1}}$. It is important to stress that the density of silicon is $2329\ \mathrm{kg\,m^{-3}}$ and that of silicon nitride is $\sim 3185\ \mathrm{kg\,m^{-3}}$, so that a volume expansion of 21.7% occurs during nitride formation. At normal nitriding temperatures (1200–1450 °C) silicon nitride shows no noticeable plasticity, and as the overall compact volume change during nitridation of silicon powders is essentially zero, it is clear that considerable internal rearrangement of product material must occur within the pre-existing void spaces of the compact [55]

The nitridation method has proven to be flexible for the production of very different powder qualities. The raw silicon nitride formed in the nitridation process already consists of morphology such as whiskers, elongated particles, and equiaxed particles [6] as well as spherical after the milling process [56]. Additionally, with wet milling, very fine powders of up to $25\ \mathrm{m^2\,g^{-1}}$ or more with narrow particle size distributions can be produced.

Important attention is drawn to quality-determining steps of powder production, which are assumed to be responsible for the sinter-active behavior of the finest powders. A high α-phase (>95%) content is desirable in order to ensure beneficial transformation into the β-form during sintering, leading to densification and the formation of an interlocked needle structure with high strength. In silicon powder, unless the silica layer is disrupted either physically or chemically, the nitridation reaction does not start [57]. After initiation, the nitridation reaction proceeds and is controlled by factors as mean particle size and size distribution, the nature and distribution of impurities in the starting silicon powder, size and size distribution of open porosity in the silicon compacts, dimensions of the silicon compacts, and nitriding conditions.

2.2. Vapor phase reaction

By means of this method, a fine amorphous silicon nitride powder is obtained from the gas phase reaction of silicon tetrachloride, $SiCl_4$, and ammonia at temperature of 1546 °C according to the reaction:

$$3SiCl_4(g) + 4NH_3(g) \rightarrow Si_3N_4 + 12HCl(g) \qquad (2)$$