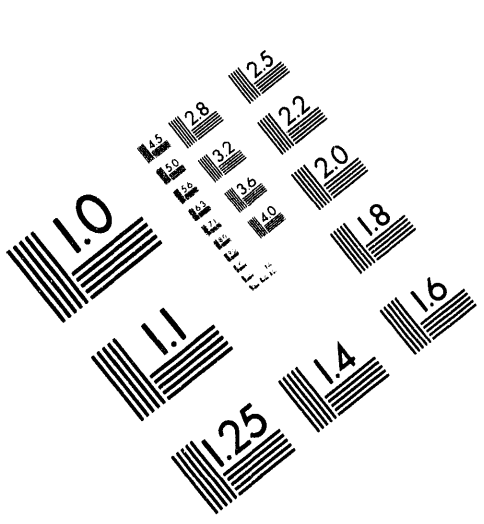

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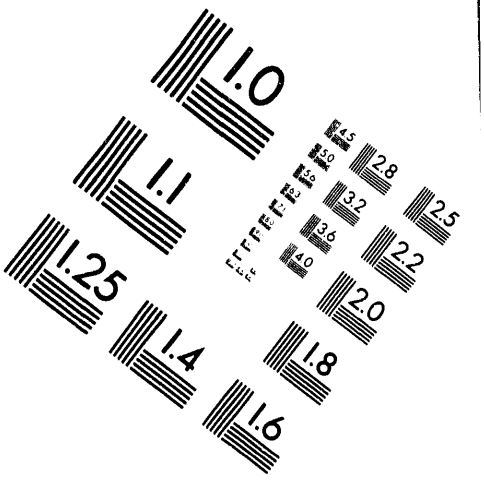

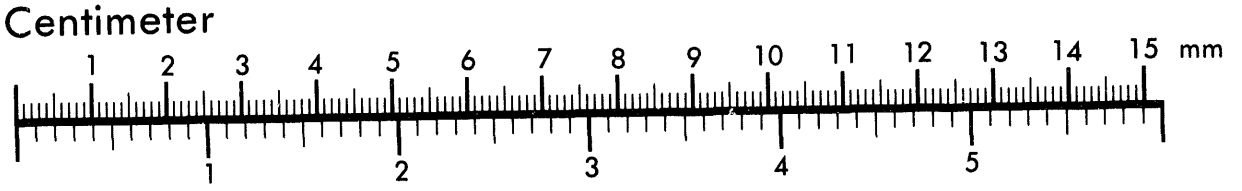

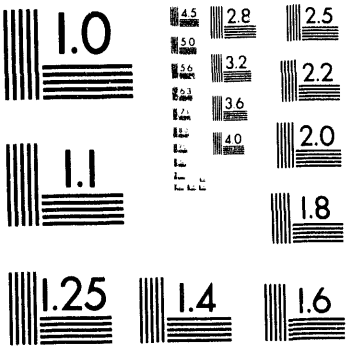

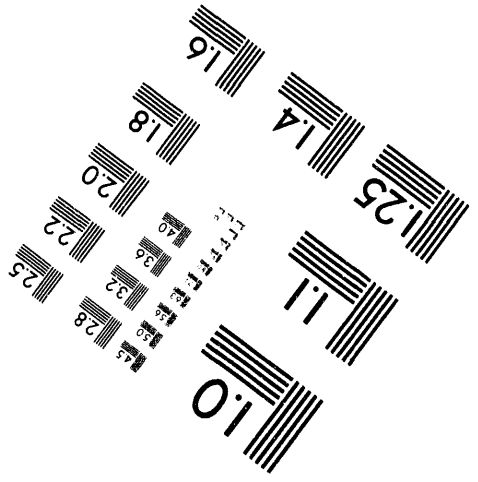

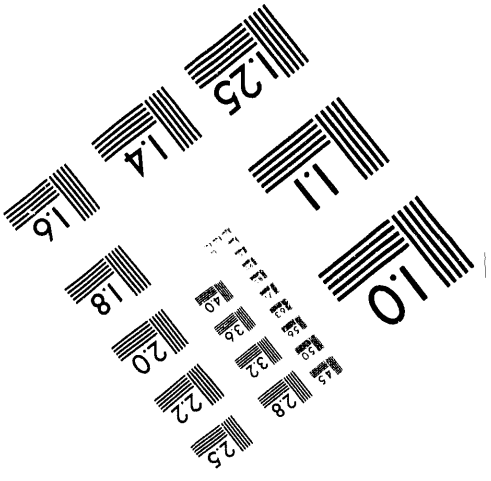

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1994 Report

DENSIFICATION OF NANO-SIZE POWDERS

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ABSTRACT

Green compacts from a nano-size silicon nitride powder were fabricated having density up to 67% of theoretical at 2.8 GPa pressure using liquid nitrogen and pentane as compaction lubricant media. Pressureless sintering of these transparent samples did not promote further densification beyond that obtained for the green state. To further increase the density of these samples, a hot-pressing device was designed. In a series of experiments, hot-pressing of these samples at 0.5 to 1.0 GPa and 800 °C, followed by pressureless sintering at 1400 °C was studied. The resulting silicon nitride ceramic had a Vickers hardness of 9.0 GPa while transparency under visible light was maintained. Without the use of hot pressing, the hardness obtained was 5.8 GPa. In addition, the effect of compaction pressure on densification was studied for nano-size Al_2O_3 to further understand factors contributing to achieving high green densities. The dense Al_2O_3 green samples were pressureless sintered to near full density at temperatures several hundred degrees lower than those needed for sintering low density green material.

INTRODUCTION

The feasibility of producing nanostructured Si_3N_4 with improved properties, and ultrafine-grained nano-phase transparent Si_3N_4 from amorphous nano-size powders without the use of sintering aids has been

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investigated in the present work. The approach uses cryogenic compaction of nano-size particles followed by pressureless sintering of the transparent green compact [1]. This new procedure potentially offers (1) improved reliability in manufacturing of ceramic parts because flaws are easily visible owing to the transparent nature of the green state, and (2) a decrease in sintering temperature from approximately 2000 to 1400 °C for fabrication of dense silicon nitrides. Early diamond anvil cell results [1] encouraged us to study the processing of silicon nitride on a larger scale. The approach does not involve the use of sintering aids and slurry processing or hot isostatic pressing (HIPing), which may have the effect of reducing the overall fabrication cost.

Cryogenic or other lubricant compaction techniques were used to produce a dense compact (67 % or higher density at 2.8 GPa) from amorphous nano-size silicon nitride powder. Following this, the dense compact was hot-pressed at pressures from 0.6 to 1 GPa at temperatures up to 800 °C in order to increase contact areas between particles. Finally, the compact was pressureless sintered at 1400 °C. This process is expected to promote a strong bonding at the contact area due to solid-state surface diffusion. The density of the new microstructure of silicon nitride ceramic with nano-scale porosity and grain size is expected to be in the range of 65 - 80 % of theoretical with enhanced optical, electrical, and mechanical properties.

The project also addresses the study of selected nano-scale oxide powders to understand the basic phenomena involved during lubricant-aided compaction of powders to high green density and further densification by sintering. These studies, aided by pore structure analysis using small angle neutron scattering (SANS) and transmission electron microscopy (TEM), were used to develop an improved understanding of limitations to achieving full densification of nano-scale powders. These data may not only help us develop a new class of materials, but also may have far reaching implications in the development of nano-powders processing technology.

OBJECTIVES

The objective of this research is to fabricate transparent Si_3N_4 from nano-size amorphous powders at much lower temperatures than the conventional sintering temperature of approximately 1800-2000 °C without using extrinsic sintering aids. Specifically, the following major steps were planned to accomplish this goal:

* Design and fabrication of computer controlled equipment for investigating the rheology of powder compaction under different lubricating conditions.
* Production of transparent green compact disks, 3 mm in diameter and 0.3-1.0 mm in thickness.
* Optimization of packing density by using cryogenic or other lubricant compaction techniques to obtain the maximum random packing density of about 67% for mono-size particles at pressures up to 2.8 GPa.
* Increase of contact area at particle interfaces by hot-pressing green compacts at 0.6 - 1.0 GPa and 800 °C.
* Pressureless sintering (at 1400 °C) to control surface solid-state diffusion along contact area interfaces.
* Characterization of dense (65-80 % theoretical) ceramic for functional and microstructural properties.

RESULTS

Equipment Design and Development

Compaction Equipment

To study the cryogenic liquid nitrogen or other lubricant compaction process in more detail and for fabricating larger volume samples, we designed and constructed a novel apparatus. This apparatus [2] is

capable of producing 3 mm disk-shaped samples under vacuum or in a variety of controlled conditions such as surrounding gaseous or liquid environments and temperatures in the range from liquid nitrogen to room, and pressures up to 3 GPa. In addition, during the compaction procedure, continuous measurements of volume of the sample, applied force, and frictional force between the sample and the die walls are performed.

The equipment is designed for two different modes of operation in the powder compaction experiments: (1) gas lubrication, and (2) liquid lubrication. In the first mode, a small amount of lubricating cover gas is introduced into the environmental chamber under controlled pressure. The introduced gas condenses on the surface of particles and the powder is compacted under dry or semi-dry conditions. An alternative design of the experimental system is to study liquid lubrication-type compaction of powders as shown in Figure 1. Due to the large amount of data accumulated during an experimental run with this system, a real-time computer control of all measurements and experimental procedures is necessary. For more details, the reader is referred to a recent publication [2].

Hot-Pressing Equipment

Experimental results using the above described equipment indicate that phase transformation and grain growth at sintering temperatures above 1400 °C will generate larger scale (about 100 nm according to TEM analysis) porosity. The transformation from amorphous to α-phase causes a volume shrinkage of the original particle which destroys the packing in the green body and produces large-scale porosity. If the size of grain and porosity are controlled in the nano-scale, the sintering temperature could be below 1500 °C.

To avoid phase transformation and grain growth, the new approach to fabricate transparent true nano-phase Si_3N_4 is to hot press the

densely-packed green compact before pressureless sintering. The contact area, ΔS divided by the total area S of a single particle, is given by

$$\frac{\Delta S}{S} = \frac{Po}{Hardness}$$

where P_0 is pressure. Therefore, the contact area of particles can be increased by elevating either the hot-pressing temperature to reduce hardness of Si_3N_4 or the hot-pressing pressure. Since the solid-state surface diffusion is much more likely to happen than the volume diffusion at low temperature, the surface diffusion along contact areas can form a very strong bond between the particles if the contact area is large enough.

To accomplish this, it was necessary to design a special apparatus to generate high temperature and high pressure. This apparatus shown in Figure 1, called the "belt apparatus," was designed and fabricated to carry out hot pressing of Si_3N_4 green compacts. The belt apparatus may be described as a cross between a piston/cylinder device and opposed Bridgman anvils. It combines massive support for the pistons with a central die for the sample. The pressure generation is through the compression of a gasket material in the apparatus.

The belt apparatus has evolved from Bridgman anvils by first incorporating a well in one of the anvils and compressing a pyrophyllite assembly. However, the pressure limit is quickly reached when the pyrophyllite expands to its limiting volume and halts further compression inside the well. A major advance in the design was made with the realization that the shape profile of the "belt system" is that of a frustum of a cone. In this design, for a given vertical compression stroke of the beveled piston, the pyrophyllite gasket material is forced to move toward the end of the cone frustum which has the smaller diameter. Thus considerable compression of the sample may be obtained before the limiting volume of the gasket is reached.

The final step was to double-end the apparatus about a horizontal axis producing a device consisting of two opposed anvils (beveled pistons) compressing a sample restricted in a central die as shown in Figure 1.

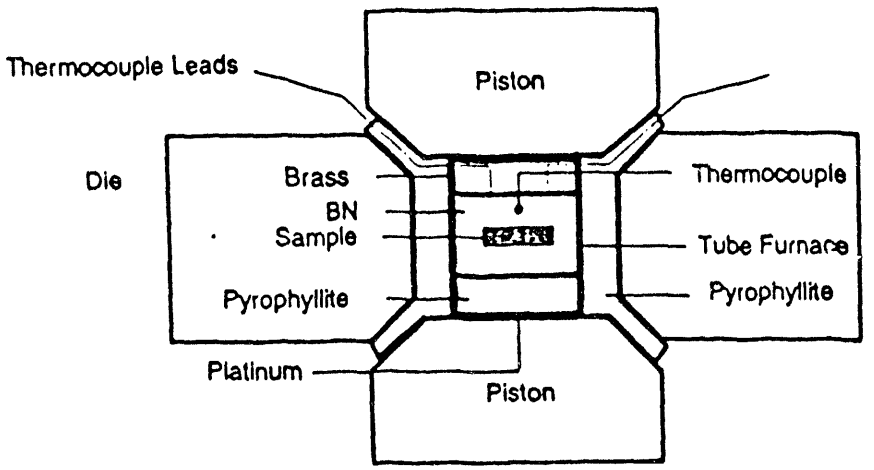

Figure 1. Configuration of a hot-pressing device, called "belt apparatus".

The piston and die are constructed from tungsten carbide. The gaskets are usually constructed separately for the upper and lower halves of the apparatus. They consist of two conical pyrophyllite gaskets sandwiching a hollow steel cone. The presence of steel which should be annealed is important since it prevents the thick pyrophyllite gaskets from breaking at low pressures and helps to lower the compressibility of the combination.

The sample is placed at the center of the internal tube furnace (made of graphite), and surrounded with boron nitride packing powder which can provide a homogeneous temperature distribution and isostatic pressure around the sample. To generate high temperature within the tube furnace, a cooling system around the die was needed to prevent heat loss to other components of the system. A power supply with 7.5 V and 200 A is necessary to provide the power needed in this

experiment. This high temperature and high pressure device was designed to generate pressures up to 1 GPa and temperatures up to 1000°C.

Experimental Data

Forming densely-packed green compacts from nano-size particles is very difficult. Strong aggregation forces, such as the Van der Waals attraction, increase dramatically as particle size decreases. For nano-size particles, the van der Waals attraction forces can prevent the particles from sliding past each other, and, thereby, promote agglomeration by diffusion across particle contact boundaries during compaction. As a result of aggregation and subsequent agglomeration of primary particles, compacts of nano-size particles usually have low densities after cold pressing. The low density is due to two factors: (1) the presence of large voids in the green-state and (2) inefficient packing of particles in the structure of the green-state. We now know that the use of suitable lubricants can improve the packing properties of the nano-size particles, but, in selecting a lubricant, one is severely limited because of the strongly reacting interface between the particles and the small size of voids in the resulting green microstructure formed by densely-packed nano-size particles.

Figure 2 shows a maximum random packing density of approximately 64% and 57% of theoretical for nano-size amorphous silicon nitride powder compacted at pressure up to 2.5 GPa under liquid nitrogen and with no lubricant, respectively. The density of green Si_3N_4 compact under pentane is about 63 % of theoretical at compaction pressure up to 2.5 GPa. These results indicate that liquid nitrogen and pentane as lubricant media are an efficient technique to reduce compaction pressure to obtain high packing density and small-scale porosity. The green bodies produced by liquid nitrogen and pentane processing exhibit transparency under visible light which is an indication of nano-scale porosity and the existence of homogeneous porosity.

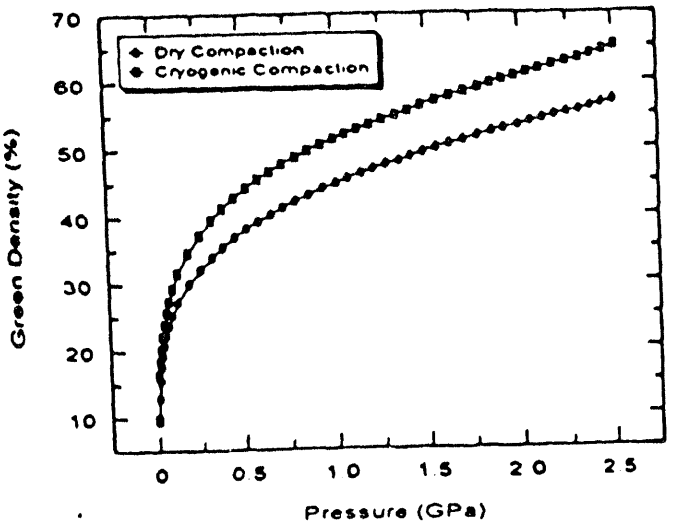

Figure 2. The variation of density of green and sintered compacts of gamma-alumina as a function of sintering temperature and compaction pressure.

The Vickers hardness of the green compacts by dry and cryogenic compaction is shown as Figure 3.

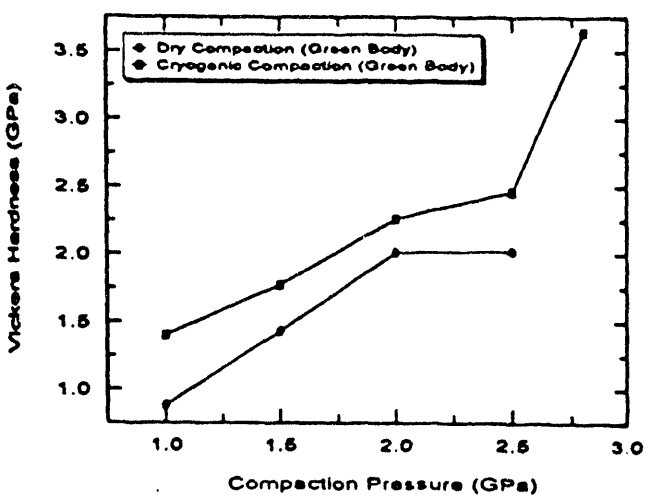

Figure 3. Green density of silicon nitride vs. compaction pressure for a nano-size silicon nitride powder.

Pressureless Sintering and HIPing

The high density green compacts were studied by pressureless sintering and HIPing to achieve additional densification. The sintering temperature was limited by phase transformation and grain growth at 1400 °C. In one series of tests, the transparent green compacts were sintered without pressure at different temperatures from 1200-1600 °C under flowing nitrogen gas. The transparency was lost at a sintering temperature of about 1500 °C as expected because the phase transformation from amorphous to α-phase is accompanied by shrinkage and grain growth. Shrinkage in atomic distances is expected to result in random shrinkage whereas, grain growth is expected to destroy the orderly porosity existing in the green body. The overall result is an increase in the scale of porosity which was estimated to be on the order of the wavelength of visible light (380nm - 780nm). The XRD, BET, and TEM measurements indicate that the phase transformation and grain growth initiate at approximately 1400 °C. Also, it should be noted that the samples were not densified at this pressureless sintering temperature. The maximum hardness of about 5.8 GPa was obtained at a (green body) compaction pressure of 2.8 GPa and 1400 °C sintering temperature.

In another series of experiments, conventional HIPing at 200 MPa using nitrogen gas as pressure transmission medium was attempted at 1200, 1300, and 1400 °C to further densify the transparent high density green compacts of nano-size Si_3N_4. The samples were embedded in BN, BN+Si_3N_4, or Si_3N_4 as packing powders. In one case, at 1300 °C with BN+Si_3N_4 as packing powders, some densification was observed. The sample was encapsulated in a glass or stainless steel envelop.

Phase transformations from amorphous to α-phase and β-phase for pressureless sintered and HIPed compacts were studied by TEM and XRD. The transformation point for both processing methods is above 1400 °C. In general, no significant densification was observed by HIPing.

In another series of experiments we used a gamma alumina nano-powder to investigate the influence of green density on sintering temperature and densification. These experiments were conducted by compacting the alumina powder at room temperature. The reason for using the alumina powder was the readily available sintering and densification data for this material. Results of these experiments, shown in Figure 4, indicate the following:

a. Low density green compacts cannot be densified at temperatures up to 1000 °C.
b. High density transparent green compacts were sintered to higher than 90% theoretical density at 1000 °C.
c. Higher compaction pressure resulted in a higher green density.

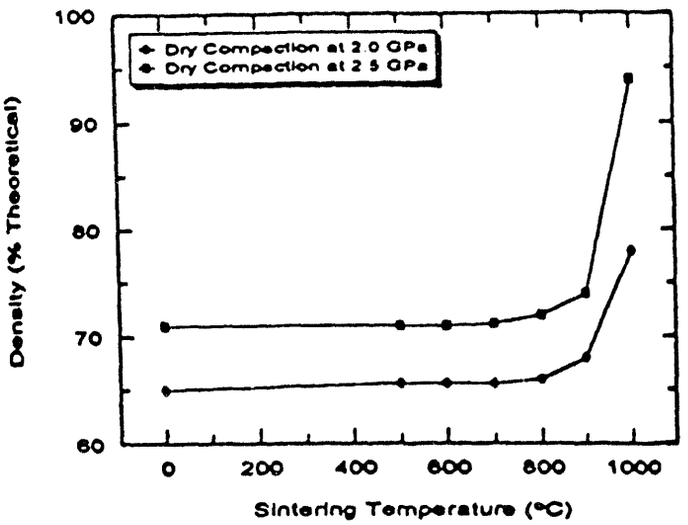

Figure 4. Vickers hardness vs. compaction pressure for green compacts using cryogenic and dry compaction techniques, respectively.

These results demonstrate that one can achieve a high degree of densification at a low sintering temperature of 1000 °C provided that sufficient high green density is achieved during compaction. Thus, the result clearly illustrates that nano-size powders must be compacted to a high density in the green state before further

densification is achieved at temperatures lower than the conventional.

Hot-Pressing of High Density Green Compacts

Experiments have been performed to study the densification behavior of silicon nitride using the newly completed hot-pressing device. The primary purpose of these experiments was to investigate the role of hot pressing to improve the mechanical properties of the resulting ceramic. The procedure consisted of the preparation of high density green compacts at 2.8 GPa followed by hot-pressing and pressureless sintering. The pressure and range of temperatures for hot-pressing were 0.6 GPa and 500-800 °C, respectively. Pressures below 0.6 GPa cannot be used because at 0.5 GPa the pressure cell gasket material leaks internal pressure fluid.

Based on results obtained from these tests, the highest Vickers hardness of 9.0 GPa was obtained using the following experimental conditions:

Pressing of powder at 2.8 GPa using a lubricant
Hot-pressing at 0.6 GPa and 800 °C
Pressureless sintering at 1400 °C for five hours

The resulting ceramic is transparent under visible light and shows the presence of a nanophase microstructure. The results are considered to be significant since the hardness has increased to 9.0 GPa from a nominal value of 5.8 GPa. This value, however, is far short of that for a commercial silicon nitride. The Vickers hardness for pressureless sintered compacts only and for hot-pressed and pressureless sintered for different compaction pressures are shown as Figure 5.

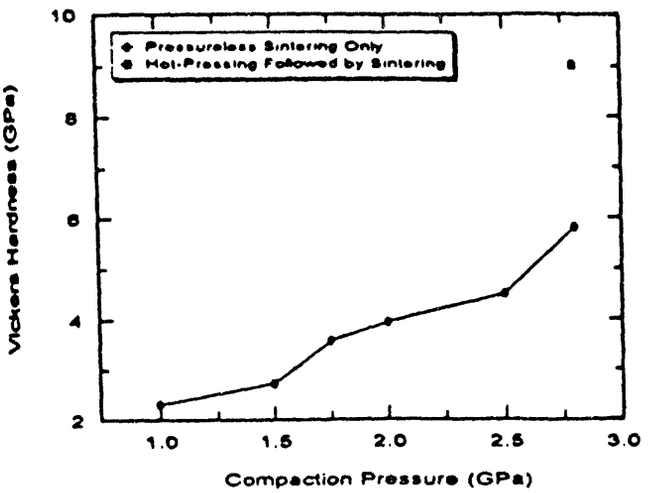

Figure 5. Vickers hardness vs. compaction pressure for hot-pressing at 0.6 GPa and 800 °C followed by pressureless sintering at 1400 °C for 5 hours, and pressureless sintering at 1400 °C for 5 hours only.

CONCLUSIONS

Lubricant-aided compaction has resulted in an improved green density for both silicon nitride and alumina powders. The green densities of these compacts are 6-8% higher than those obtained without the use of lubricants such as liquid nitrogen and pentane. Hot pressing of these green compacts followed by sintering has resulted in an increased hardness of the sintered silicon nitride to 9.0 MPa which is higher than that using low density green compacts. Studies are in progress to identify accompanying microstructural changes.

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