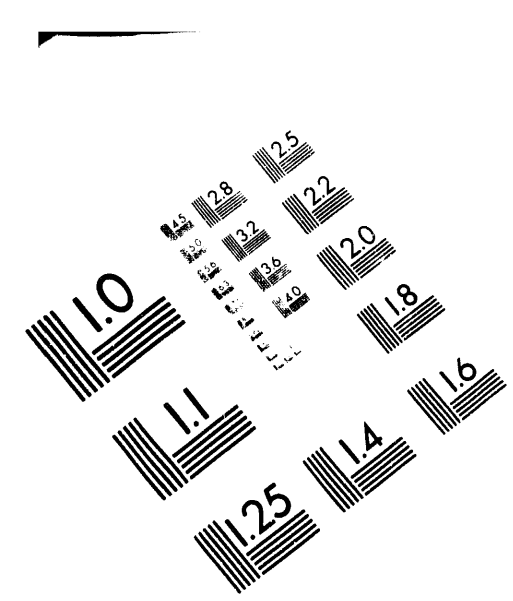

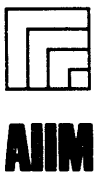

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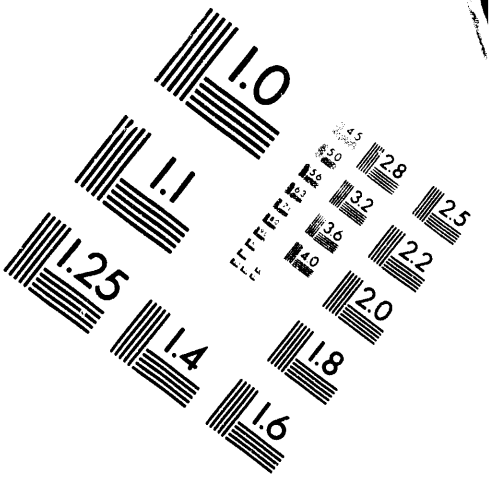

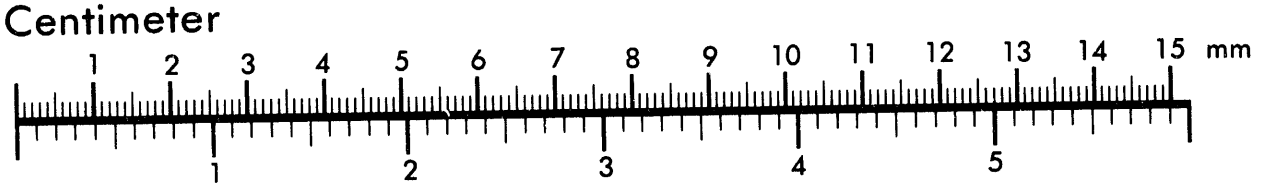

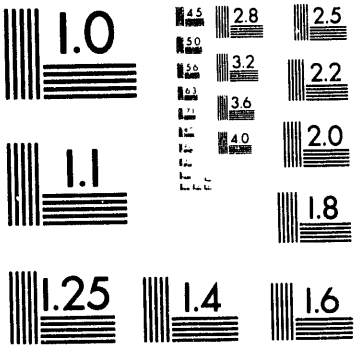

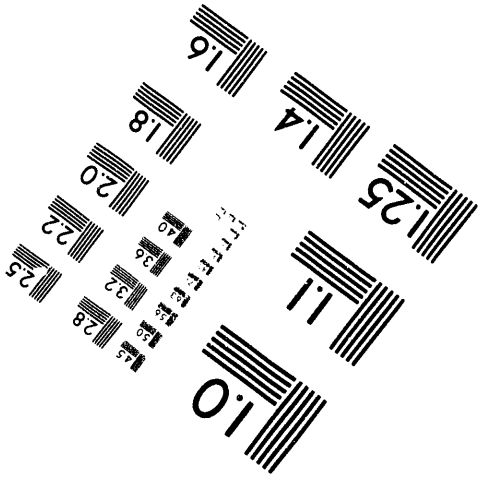

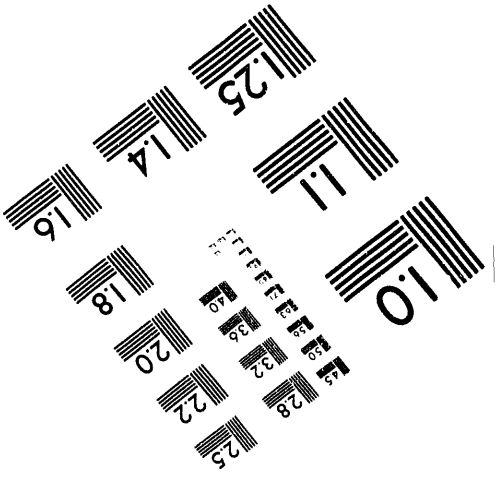

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EQUIPMENT FOR INVESTIGATION OF CRYOGENIC COMPACTION OF NANOSIZE SILICON NITRIDE POWDERS

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ABSTRACT

This paper describes a highly-specialized system for studies of time-dependent compaction of nanosize silicon nitride powders under a variety of atmospheres and at temperatures ranging from 77 to 1000 K. The system incorporates a screw-driven press (10 ton capacity) with a piston-cylinder type die and can produce cylindrical powder compacts, 3 mm in diameter and approximately 1 mm in thickness, using pressures up to 3 GPa. The system is computer-controlled and permits accurate measurements of the sample volume, and, after appropriate calibration, can determine the rate and degree of densification of the compacting powder as pressure is applied. Frictional forces between the piston and the die are measured during the compaction process.

For calibration of the system, powders with known volume-change accompanied by phase transition under pressure were studied, and good agreement with published results was demonstrated. Several Si_3N_4 samples have been compacted and sintered at 1300 to 1600°C. A maximum random packing density of 64% has been obtained using liquid nitrogen as a lubricant medium at pressures lower than 2.5 GPa. Both green samples and samples sintered at temperatures to 1500°C exhibited visual transparency under visible light.

INTRODUCTION

Recently there has been significant interest in fabricating ceramics from ultra-fine powders that consist of nanosize primary particles of 1 to 100 nm mean diameter. Theoretical predictions by Frenkel[1] and Herring[2] clearly indicate that the rate of densification varies inversely as a function of particle size. Thus, based on this

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prediction, as particle size decreases from microns to nanometers, a 9 orders of magnitude decrease in sintering time can be expected at a given temperature. Indeed, many experimental investigations support this prediction. For example, Rhodes[3] produced densely-packed compacts of nanosize zirconia particles and observed sintering of the compacts to near theoretical density at much lower temperatures than are used for sintering coarse zirconia particles. Recently, Skandan et al.[4] sintered nanosize titania at 800°C which is well below the sintering temperature for conventional titania powders.

These results suggest that nanosize particles as starting materials might offer considerable advantages for fabricating ceramics. However, forming densely-packed compacts from nanosize particles is difficult. Strong aggregation forces, such as the Van-der-Waals, increase dramatically as particle size decreases. For nanosize particles, the Van-der-Waals attraction can essentially prevent the particles from sliding and cause agglomeration by diffusion during compaction.[5] As a result of aggregation and subsequent agglomeration of primary particles, compacts of nanosize particles usually have low density after pressing. The low density is due to two factors: (1) large voids and (2) inefficient packing of particles. A proper lubricant could improve packing properties of the nanosize particles, but in selecting such lubricants one is severely limited by strongly reacting interfaces between the particles and the small size of openings in the structure formed by densely-packed nanosize particles.

To demonstrate the concept, that simple molecular liquids can provide efficient lubrication for nanosize particles, Pechenik and Piermarini[6] compacted nanosize silicon nitride particles at liquid nitrogen temperature using liquid nitrogen as a lubricant. The compaction was performed in a diamond anvil cell. This cryogenic compaction approach was successful in producing densely-packed compacts of nanosize particles that sintered close to full density at

a much lower temperature than that required for the conventional processing of silicon nitride. We decided to study the cryogenic compaction process in more detail by designing and constructing a special apparatus for fabricating larger samples than 0.2 mm diameter made in the diamond cell.

DISCUSSION OF CURRENT ACTIVITIES

Objectives of the Equipment Design

The equipment was designed to perform at least four functions. First, to produce 3 mm diameter disk-shaped samples on which accurate measurements of density, hardness, fracture toughness, optical properties, and pore-size distribution can be carried out. Second, to provide a detailed data for the measurement of compaction rheology of powders in the form of volume (or density) of compacting sample as a function of the applied pressure, the rate of pressure application, processing temperature, and atmosphere. Third, to detect and accurately measure phase transitions accompanied by volume-change. The equipment was designed to provide accurate and precise data for development of P-V curves. Fourth, to perform hot-pressing of green compacts up to 1000 K. The goal was to understand microstructural changes during hot-pressing and sintering. Hot-pressing helps to produce nanograin structures because full density can be achieved at lower temperatures than by pressureless sintering.

Equipment Configuration

A 10 ton capacity screw-driven press (INSTRON) with two large parallel platens is used to apply load. The press has a moving crosshead operated by two vertical drive screws from a servo-controlled drive system, which allows the selection of testing speeds from 0.85 to 850 micrometer per second. This is a useful feature, because the stress relaxation in a sample during powder compaction can be elucidated by changing the punch speed. To generate a 3 GPa

pressure on a 3 mm diameter sample, a 3 ton load is required.

The equipment is designed to operate under two different conditions of powder compaction; "gas lubrication," and liquid lubrication." The first mode of operation is used for "gas lubrication"-type powder compaction, where a small amount of lubricating cover gas is introduced into the environmental chamber under controlled pressure. The cover gas condenses on the surface of the particles and the powder is compacted subsequently under "dry" or "semi-dry" conditions. The basic design for these is experiments is shown in Fig. 1. The chamber is designed to control lubricant gas pressure and temperature, while the movable piston, equipped with two o-ring seals, applies force to the compacting piston.

One of the difficulties for cryogenic compaction is to calibrate the pressure in non-hydrostatic and low temperature environment. The frictional force on the wall of the die, the punches, and the sample must be taken into account for pressure calibration. Two load cells are used for pressure calibration: one to measure main load, and second one to measure frictional load.

A K-type thermocouple is placed at the center of the fixed punch as near the sample as possible to provide measurement and control of temperature. A displacement transducer is fixed on the INSTRON as shown in Figure 1 to measure the thickness of the sample versus pressure for rheological investigation.

The second approach for study of compaction, "liquid lubrication", is realized by a modified experimental system which consists of a cryogenic container that holds the die and powder, and a metal foil prevents leakage of liquid lubricant.

Hot-pressing can be performed in a WC-Co die for temperatures up to 1000 K in two steps. In the first step, the powder is compacted

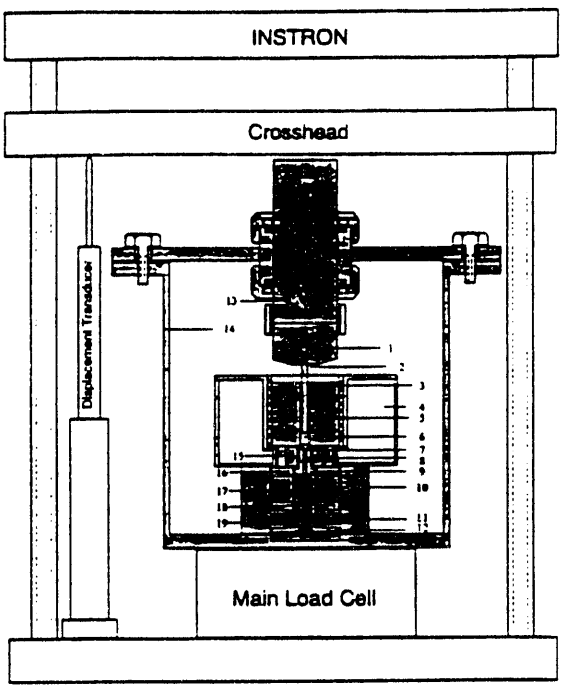

Fig. 1. Configuration of "gas lubrication"-type powder compaction assembly. (1) Bridgman anvil, (2) moving punch, (3) die, (4) cooling cylinder, (5) heater, (6) powder, (7) thermocouple, (8) fixed punch, (9) hardening disk, (10) heat insulating ring disk, (11) frictional load cell, (12) positioning and heat conducting disk, (13) pressure transmission piston, (14) environmental chamber, (15) frictional load transmission pistons, (16) hardening ring disk, (17) heat insulating disk, (18) hardening ring disk, (19) plastic positioner.

under controlled conditions. In the second step, the green compact is hot pressed by placing the assembly containing the green compact, die, and punches in a furnace with the applied load.

Computer Control and Software Development

Real-time computer control has been implemented to measure and control the temperature of the chamber, applied pressure, rate of pressure application, and displacement of the punch along with recording the data from several transducers used to measure applied

and frictional force. The computer presets temperature from remote points of a temperature control unit by means of a digital-to-analog converter card. A KEITHLEY digital multimeter combined with a scanner performs scanning of voltage measurements on the load cells, displacement transducer, and the thermocouples. IEEE-488 interface is used for communicating between the computer and digital multimeter. The computer controls the sequence of scanning measurements, presets the temperature in the environmental chamber, and conducts auto-determination of steady state temperature.

The control program uses a built-in clock as time counter for the measurement of pressure as a function of time, i.e. the rate of pressure application. The code of the program for control and monitoring the powder processing operation was written in a GFA-BASIC language for Windows on a 486 IBM-Compatible computer (Gateway 2000). Eight windows are opened to plot and provide experimental data. During an experimental run, the program estimates the range for each measurement according to the initial scanning measurements and some preset values, and replots all diagrams using an auto-scale subroutine to give an appropriate range and boundary for each quantity. The replotting is performed at a preset time interval.

Experimental Results

Both load cells were calibrated using a ring-force gauge to provide 0.5% accuracy at room temperature. After calibration, the measurement uncertainty of the displacement of the moving punch is estimated to be < 0.01 mm. To test the accuracy of the P-V curves developed by this apparatus, two well-studied materials with known pressure-volume characteristics were compacted. Since the compaction of rubidium bromide (RbBr) and potassium chloride (KCl) was thoroughly investigated by Bridgman[8,9] and Weir, et al.,[10] these materials were selected for testing of the equipment. Our results show good agreement with the critical pressures and volume changes

for these transitions published by Bridgman,[8,9] Weir et al.[10]

Following this, a series of Si_3N_4 samples were compacted at different pressures under controlled conditions. Figure 2 shows the fractional volume $V^*, [(V-V_\infty)/(V_0-V_\infty)]$, where V_0 and V_α are initial and final volumes, respectively, and green compact density versus applied pressure at two different conditions; (1) dry compaction at room temperature, (2) liquid nitrogen lubricant compaction. The volume change in Fig. 2 is measured under load while the density is measured using the dimensions and weight of samples after removing the load. Therefore, the density (% theoretical) in Fig. 2 is load-free green density versus pressure. A maximum random packing density of about 64 % is obtained at approximately 2.5 GPa by using cryogenic compaction technique as shown in Fig. 2. To get the same density as dry compaction at pressure 2.5 GPa, the applied pressure for cryogenic compaction is only about 1.5 GPa. The Vickers hardness of the green body increases with compaction pressure as shown in Figure 3. Both dry and cryogenic compacted green samples are dark brown and exhibit visual transparency under visible light.

The samples were pressureless sintered from 1300°C to 1600°C after pressing in an effort to increase their density and hardness. The Vicker hardness of samples compacted at pressure 2.5 GPa using both dry and cryogenic compaction as a function of sintering temperatures is shown in Figure 4. These results indicate that the hardness of the room temperature compacted samples did not change while the cryogenic compaction sample density increased drastically at 1500°C, though the overall density values are low.

The sintered samples are transparent with a light-brown color when the sintering temperatures are kept under 1500°C. Transparency of a sample compacted using cryogenic technique and sintered at 1400°C is demonstrated in Fig. 5.

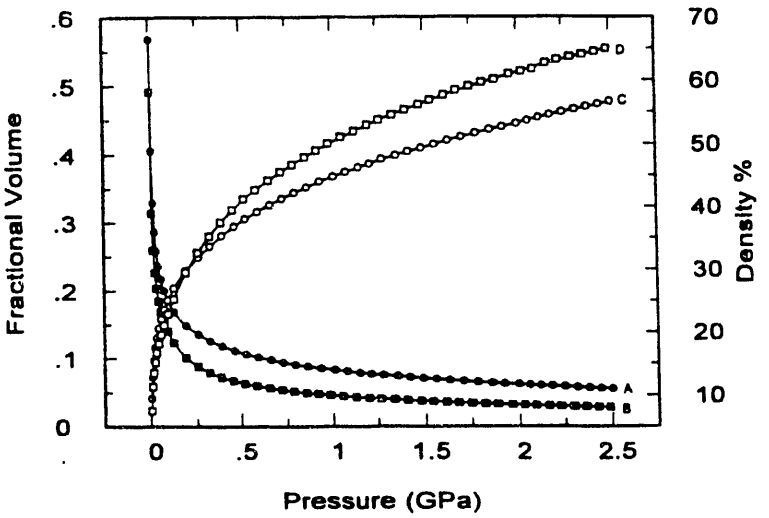

Fig. 2. Fractional volume and density versus pressure A,B - fractional volume for dry and cryogenic compaction, respectively; C,D - packing density (% theoretical) of dry and cryogenic compaction, respectively.

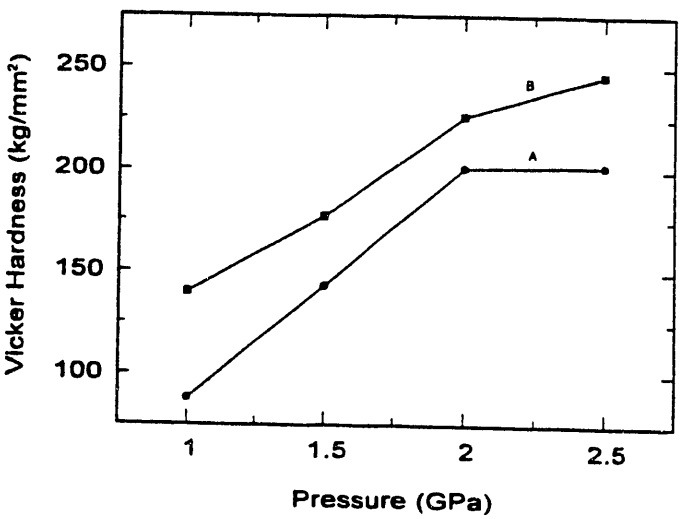

Fig. 3. The Vickers hardness of the green body versus compaction pressure for, (A) dry compaction and (B) cryogenic compaction.

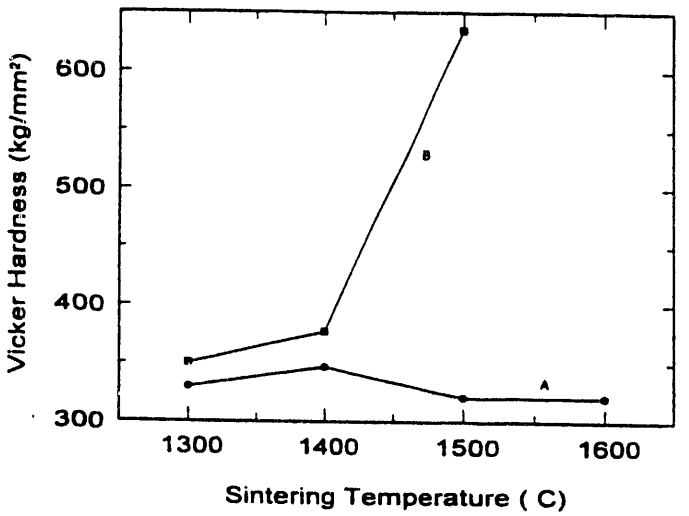

Fig. 4. The Vicker hardness versus sintering temperature for compaction pressure at 2.5 GPa; (A) dry compaction, (B) cryogenic compaction.

Fig. 5. Transparent silicon nitride; (A) green compact at 2.5 GPa; and (B) sintered at 1400°C.

Conclusions

A novel apparatus has been developed for compacting powders under pressures up to 3 GPa in a variety of atmospheres and at temperatures ranging from 77 to 1000 K. The apparatus is used for fabricating disk-shaped 3 mm diameter samples and for study of compaction rheology of powders under controlled conditions.

A maximum random packing density (64%) for Si_3N_4 was obtained using liquid nitrogen as a lubricant at 2.5 GPa. Results indicate that cryogenic compaction technique is able to compact to a high density at much lower pressures than dry compaction. The transparent properties of both green and sintered samples indicate homogeneous packing, the scale of porosity which causes a slight light scattering is much smaller than the wave length of visible light and porosity are uniformly distributed in the sample.

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