Nanocrystalline Processing and Interface Engineering of Si_3N_4-based Ceramics

Progress Report on ONR Grant No. N00014-94-1-0546
for the period July 1, 1994 - September 30, 1994

Jackie Y. Ying
Cabot Assistant Professor
Department of Chemical Engineering
Massachusetts Institute of Technology
Room 66-544, 25 Ames Street
Cambridge, MA 02139
Tel: (617) 253-2899
FAX: (617) 258-8224

During the past three months, our efforts have been devoted to synthesizing nanocrystalline Si_3N_4 and Y_2O_3. For nanocrystalline Si_3N_4, a tubular reactor design has been adopted to produce nanoclusters by inert gas condensation in a forced flux flow. This reactor involves various features that allow us to control the synthesis conditions. Evaporation of Si takes place in a crucible located near one end of the reactor. A gas flow is established through the use of a booster pump to bring the nanoclusters generated quickly out of the hot growth zone to prevent particle agglomeration. The nanometer-sized particles are deposited on a liquid-nitrogen cooled flat plate at the other end of the reactor through thermophoresis.

We have been examining the effects of this processing scheme to understand the important reaction parameters for generating nanocrystalline particles. Pure Si crystallites synthesis in helium have been used to tune the reactor conditions. We have determined the optimum reactor pressure in the isolated evaporation chamber for obtaining monodisperse nanocrystalline Si. The next step taken involved examining the gas velocity and its influence on minimizing particle growth and facilitating effective collection. It was found that high gas flow velocity prevented particle coalescence but would not allow all of the particles generated to be deposited effectively by thermophoresis on the cooled substrate. We have found parameters for a good compromise between the two objectives, allowing us to generate, stabilize, and efficiently collect nanocrystalline Si particles. We are currently investigating the effect of reactor tube length to further enhance the particle collection process. Once these parameters are determined, efforts will be devoted to the nitridation chemistry of the process. We have designed a second gas introduction feature to the reactor just beyond the evaporation source. Nitrogen introduced before that point will lead to nitridation of Si in the crucible. We will be examining the effectiveness of nitriding Si nanoclusters with N_2 or NH_3 introduced at the second gas inlet. If necessary, atomic nitrogen can be produced through microwave plasma activation of N_2 gas at that point.

We anticipate optimization of the reaction conditions to be completed in the third quarter. Currently, there has been no problem with the high evaporation rate for creating nanoclusters continuously, except that the crucible is limited in size for day-long production of nanocrystalline powder. We have designed a magnetically-coupled feeder which can add Si precursors to the crucible when the reactant supply is exhausted. We have also overcome the crucible failure problem due to the alloying between Si and the common crucible material, W. The current crucible is inert graphite, which has a higher power requirement in resistive heating. The power generator has been modified to accommodate this new specification. We

are now completing a scraper design which will provide for *in situ* powder collection for further compaction and processing without exposure to atmosphere for high-purity materials preparation.

The objective of producing ultrafine Si_3N_4 is to greatly enhance the sinterability of this material, and to examine the possibility of net-shape forming in nanostructured nitrides. We hope to achieve these goals without sintering additives, but the latter may be necessary to provide liquid phase sintering. The strategy then involves minimizing the amount of oxide additives needed such that the high-temperature strength of Si_3N_4 will not be compromised. We believe nanocrystalline oxide additives would allow us to achieve a uniform and ultrahigh dispersion as sintering aids in Si_3N_4 such that minimal amount of such additives will be needed to wet the grain boundaries of Si_3N_4. This will promote densification without creating excess oxide phases as pockets between Si_3N_4 grains which act to weaken the material drastically at high temperatures.

Nanocrystalline Y_2O_3 was developed by us during this quarter as the oxide additive for both conventional and nanocrystalline Si_3N_4 densification. This novel material was generated by chemical precipitation of yttrium chloride in a basic solution. We have examined the control of the relative rates of hydrolysis and condensation through sol composition, pH, and temperature variation to derive ultrafine well-defined colloidal particles. To preserve the advantages associated with the fine grain size, we also strived at minimizing agglomeration during processing with an understanding of powder surface chemistry. Organic washes and ultrasonication were employed to reduce inter-particle bridging from hydrogen bonding. Vacuum heat treatments were also applied to preserve the ultrafine microstructure during the annealing processes. Grain growth in nanocrystalline powder was avoided through vacuum processing which could effectively remove residual volatiles and organics at lower temperatures than conventional processing.

We have successfully synthesized pure nanocrystalline Y_2O_3 with grain size of ~10 nm and surface area of ~150 m^2/g by the chemical precipitation approach. In the next quarter, we will start investigating the sintering of Si_3N_4 with nanocrystalline Y_2O_3. Densification and phase transformation of Si_3N_4 compacts with nanocrystalline Y_2O_3 sintering aids will be followed as a function of temperature. The grain boundary structure and chemistry of Si_3N_4 associated with such nanocrystalline oxide additives will be studied with HREM and STEM.