Nanostructured Bulk Ceramics* (Part I)
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ABSTRACT
The processing and characterization of ceramic nanocomposites, which produce bulk nanostructures with attractive mechanical properties, have been emphasized and introduced at Prof. Mukherjee’s Lab at UC Davis. The following subjects will be introduced in detail in Part II, III, and IV.

In Part II, the paper will describe a three-phase alumina-based nanoceramic composite demonstrating superplasticity at a surprisingly lower temperature and higher strain rate. The next part will show that an alumina-carbon nanotube-niobium nanocomposite produced fracture toughness values that are three times higher than that of pure nanocrystalline alumina. It was possible to take advantage of both fiber-toughening and ductile-metal toughening in this investigation. In the fourth section, discussed will be a silicon-nitride/silicon-carbide nanocomposite, produced by pyrolysis of liquid polymer precursors, demonstrating one of the lowest creep rates reported so far in ceramics at the comparable temperature of 1400°C. This was first achieved by avoiding the amorphous glass phase at the intergrain boundaries. One important factor in the processing of these nanocomposites was the use of the electrical field assisted sintering method. This allowed the sintering to be completed at significantly lower temperatures and during much shorter times. These improvements in mechanical properties will be discussed in the context of the results from the microstructural investigations.

Key words: Alumina-based nanoceramic, Superplasticity, Fracture toughness, SPS

1. Nanoceramics
Nano-powders of ceramics have been available for some time. The motivation for this series is the realization that reducing the grain size of single- or multi-phase materials to nanoscale dimensions offered the potential of dramatic improvements in properties.

Typical consolidation methods such as pressureless sintering and hot-pressing lead to extreme grain growth as full density is reached by pores pin grain boundary migration. Thus, advanced processing techniques, such as High Energy Ball Milling (HEBM), Spark Plasma Sintering (SPS) and High Pressure Spark Plasma Sintering (HPSPS), are required to accelerate densification. These techniques that use nano materials like nano powders, carbon nanotubes and ceramic precursor, enabled Prof. Mukherjee’s Group at UC Davis to generate exceptional results that improved superplasticity (HSRS) and fracture toughness and lowered creep rates.

2. SPS-Accelerated Superplasticity
SPS has been demonstrated not only to be an effective sintering process to fabricate fully dense nanocrystalline ceramics and composites but also to be a new forming method to enhance ceramic ductility, as shown in Fig. 1. It is generally accepted that application of mechanical pressure is helpful in removing pores from compacts. The increasing applied pressure during deformation is expected to promote rapid densification and grain boundary sliding. Therefore, applying high pressure at a low temperature that allows the grain-boundary sliding to become kinetically favorable can enhance deformation rates. This is consistent with our findings where the strain rate increases with increasing loading rate. When a constant load instead of a constant stress is applied, the strain rates are significantly decreased. It can also be noted that the strain rates are significantly increased when a slightly higher deformation temperature is applied even though the loading rates are slightly lower, suggesting the temperature has profound effect on deformation.

In conclusion, this new SPS forming approach provides a new route for low temperature and high-strain-rate superplasticity for nanostructured materials and should impact and interest a broad range of scientists in materials research and superplastic forming technology.

3. Superplasticity and High Strain Rate Superplasticity (HSRS) in Ceramics
The advantages of improved superplasticity in metals and ceramics are near net shape formations, production of com-
plex shapes, and savings in labor-intensive machining costs such as those of clutches in automobiles, as shown in Fig. 2.

The constitutive relation for superplastic deformation (SPD) usually takes the generalized form by the Mukherjee-Bird-Dorn Equation.

$$\frac{\varepsilon}{\langle D \rangle} \cdot \frac{\lambda}{kT} \cdot \frac{D_G}{G} \cdot \frac{b}{a} \cdot \frac{d}{(c_G)^n} \cdot \frac{p}{\sigma} \cdot \frac{G}{\eta}$$

where $G$ is the elastic shear modulus, $b$ is the Burger's vector, $k$ is the Boltzmann’s constant, $T$ is absolute temperature, $d$ is grain size, $p$ is the grain-size dependence coefficient, $n$ is the stress exponent, $Q$ is activation energy, $D$ is the diffusion coefficient, and $R$ is the gas constant. The inverse of $n$ is the strain rate sensitivity, $m$. Grain boundary sliding is generally the predominant mode of deformation during the superplastic flow. Plastic deformation by grain boundary sliding is generally characterized by $n = 2$ ($m = 0.5$) and an activation energy that is either equal to the activation for lattice diffusion or to the activation energy for grain boundary diffusion.

High-strain-rate-superplasticity (HSRS) is usually referred to as the demonstration of ductility at a strain rate of $10^2 s^{-1}$ or higher. Historically, HSRS was exhibited in metallic systems as early as 1988. Typical superplastic strain rates in ceramics are in the range of $10^2$ to $10^4 s^{-1}$.

HSRS has been recently reported in ceramics 30 vol\% Al$_2$O$_3$-40 vol\% ZrO$_2$-30 vol\% MgAl$_2$O$_4$ composite by Kim et al.$^5$ at initial strain rates up to 1 s$^{-1}$ at 1650°C and ZrO$_2$-30 vol\% MgAl$_2$O$_4$ composite by Morita et al.$^6$ at initial strain rate of $3.3 \times 10^2 s^{-1}$ at 1550°C.

While scientifically significant, these results are not of practical importance due to the prohibitively high forming temperatures. Additionally, these results did not provide any phenomenological data to account for a deformation mechanism.

4. Carbon Nanotube in Ceramics

Carbon nanotubes (CNT), originally discovered as a byproduct of fullerene research, are attracting increasing interest as constituents of novel nanostructured materials for a wide range of applications. There are two main types of carbon nanotubes, single-wall carbon nanotubes (SWCN) and multi-wall carbon nanotubes (MWCN), as shown in Fig. 3(a) and (b). Both of these types can have high structural perfection, however, SWCN have a particularly desirable combination of mechanical properties. Specifically, they have an elastic stiffness comparable to that of diamond $\sim 1.5$ TPa, and they are several times as strong (yield strength 52 GPa).$^4$ The size, shape, and properties of SWCN make them prime candidates for use in the development of potentially revolutionary composite materials. Attempts have been made to develop advanced engineering materials with improved mechanical properties through the incorporation
of CNT in various matrices (polymers, metals, and ceramics) by taking advantage of the exceptional strength of the nanotubes. Most of the investigations on carbon nanotube containing composites have so far focused on polymer-based composites with improved electrical and mechanical properties. For example, their addition to a polymer matrix leads to a very low electrical percolation threshold and improved electrical conductivity. Work on carbon nanotubes in metals and ceramics has been much less focused.

The MWCN, discovered in 1991, is concentric tubes of increasing diameter bonded together by van der Waals forces. SWCN, discovered in 1993 is typically 0.7 to 2.0 nm in diameter (averaging ~1 nm) with aspect ratios in the 100s and 1000s.

The characteristics of SWCN are known as below,

- **The Strongest Fiber Known** (E~1.5 TPa and TS~ 52 GPa)
- **Electrical Conductivity of Metals** (like the copper used in wires, where electrons can move freely) or **Semiconductors** (like the silicon in computer chips, where electrons have restricted motion)
- **Thermal Conductivity of Diamond**
- **The Chemistry of Carbon**
- **The Size and Perfection of DNA**

SWCN offer revolutionary electrical, thermal, and mechanical properties on the nanometer scale, as shown in Fig. 4.

Fig. 5. (a) and (b). Single-wall carbon nanotube (indicated by arrows) morphology in the fully dense 5.7 vol\% SWCN/Al₂O₃ nanocomposite.

5. Polymer Precursor Derived Nanoceramics

Search for new ways to make creep-resistant silicon nitride system ceramics has been made to establish the creep mechanism in covalent nanocomposites.

Amorphous Si-N-C powder and Si-N-C-B powder, derived from pyrolysis of a liquid polymer precursor from a commercial vendor (CerasetTM SN, Kion International, Columbus,
OH) were introduced to obtain a high creep resistance at specified temperature and compressive stress.

For consolidation without sintering aids as shown in Fig. 6, in-situ consolidation/pyrolysis from polymer precursors was to form amorphous Si-N-C-(B), as shown in Fig. 7. Crystallization of bulk amorphous Si-C-N-(B) into Si$_3$N$_4$/SiC/(B) nanocomposites was made by Electric Field Assisted Sintering (EFAS) from the polymer-derived Si-N-C-(B).

Polymer-pyrolysis produces amorphous Si-N-C-(B) powders with molecular-level homogeneity and performed fast low-temperature sintering by EFAS.

In summary of previous reported achievements,

- High density bulk amorphous Si-N-C and Si$_3$N$_4$/SiC nano-composites were obtained without additive by in-situ pyrolysis/solidification
- Creep tests generated the first observation of stable creep stage for amorphous Si-N-C
- EFAS of Si-C-N produced nanocomposites with superior creep resistance to conventional silicon nitride with same level of additive amount, leading to transition of microstructure from micro-nano to nano-nano, creep property approaching the level of HIP/hot-isostatic pressing and GPS (gas-pressure sintering)-processed materials with less additive
- Si$_3$N$_4$/SiC nano-nano composites with oxide additives were produced, which have a strong potential for enhanced superplastic formability

6. Concluding Remarks

Advances in synthesis and processing of ceramic nano-composites have opened up new vistas for practical utilization of such materials.

The following subjects, based on Prof. Mukherjee’s plenary talk at the last Korean Ceramics Society Fall Meeting, will be continued in series Part II, III and IV; Superplasticity and High Strain Rate Superplasticity (HSRS) in Ceramics, Carbon Nanotube Ceramics and Polymer Precursor Derived Nanoceramics, which were successfully done at Prof. Mukherjee’s Lab in the University of California, Davis, USA.

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