

STUDIES IN CREEP, SUPERPLASTICITY, AND FRACTURE TOUGHNESS IN NANOCERAMIC COMPOSITES

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Introduction

Nanoceramic composites have received much interest in the last two decades due to their potential of achieving interesting properties and versatility in tailoring microstructure. There have been significant efforts in the authors' group in exploring nanoceramic composites with improved mechanical properties [2, 4, 3, 1]. Here we report three kinds of nanocomposites including Si_3N_4 -SiC, Al_2O_3 -single wall carbon nanotube and Al_2O_3 - ZrO_2 - MgAl_2O_4 that exhibit superior creep resistance, fracture toughness, and superplasticity, respectively.

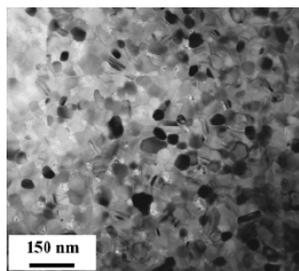


Fig. 1
 Si_3N_4 -SiC
nanocomposite.

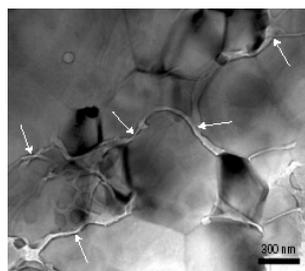


Fig. 2
 $\text{SWCN-Al}_2\text{O}_3$
nanocomposite.
The arrows indicate
the SWCN phase.

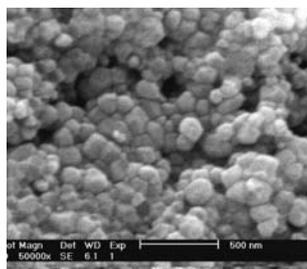


Fig. 3
Nanocomposite
 Al_2O_3 - ZrO_2 -
 MgAl_2O_4 .

Si_3N_4 -SiC nano-nano composite: This type of composite was made by using polyureasilazane precursor in liquid form as a precursor. After polymerization at around 200°C and pyrolysis in nitrogen at 1450°C , an amorphous Si-C-N solid was obtained. The Si-C-N powder was then mixed with 0–8 wt% Y_2O_3 by ball milling. Sintering was conducted using spark plasma sintering system in vacuum. The grain size of the sintered composites decreases monotonically with decreasing additive amount. A nano-nano type composite was obtained when Y_2O_3 content is less than 3 wt%. The grain size reduced to about 27 nm for the composite without additive (Fig. 1). The composite contains a prominent population of grain boundaries that do not have an apparent amorphous layer. Creep test at 1400°C shows the steady-state creep rate of the nanocomposite is as low as $6.3 \times 10^{-11} \text{ s}^{-1}$ at 50 MPa stress. To the best of the authors' knowledge, this shows the highest creep resistance ever in ceramics. The apparent activation energy for the 1 wt% Y_2O_3 nanocomposite was determined to be about 205 kJ/mol, significantly lower than that of microcrystalline silicon nitride. Considering that N is the slower diffusing species in Si_3N_4 , and that the activation energy for grain boundary diffusion is lower than that for lattice diffusion, N diffusion through (oxygen enriched) grain boundaries is considered to be the controlling mechanism in the creep of the composite. Due to the relatively shorter sintering time and large amount of grain boundary in the nano-nano composite, the oxygen content at each individual grain boundary is diluted to the extent that in some of the grain boundaries no effective glassy grain boundary layer can be formed, thus, diffusion-based mechanisms other than solution-precipitation become the dominant mechanism.

Carbon Nanotube Reinforced Al_2O_3 -based Nanocomposite: Purified single-wall carbon nanotubes and gas condensation synthesized γ - Al_2O_3 with average particle sizes of 15 nm were used as starting materials. The γ - Al_2O_3 was subjected to high energy ball milling (HEBM) before wet ball milling with carbon nanotubes. A typical bright-field TEM

image of SWCN–Al₂O₃ nanocomposite is shown in Fig. 2. The entangled ropes of SWCN appear to envelop the alumina grains like a net. High resolution TEM reveals a clean and intimate contact between nanotubes and alumina, which is an indication of effective toughening. Raman spectra were recorded to study the effect of sintering temperature on the carbon nanotube. The specimen sintered at 1150°C retains the single wall nanotube structure. The characteristic single-wall carbon nanotube shoulder besides the 1580cm⁻¹ peak disappears at higher temperatures, indicating the loss of nanotube structure. The decreased intensity of peak for D-band relative to G-band with increasing temperature means the increase in graphite content. The 1580cm⁻¹ peak shift of the composite as compared to the pure single-walled carbon nanotube indicates a thermal residual stress has developed after cooling down from high sintering temperature. The residual stress in the Al₂O₃-SWCNT composite sintered at 1150°C is calculated as $\sigma_{Al_2O_3} = -2.0$ GPa, $\sigma_{SWCNT} = 18$ GPa. The high residual stress in the single-walled carbon nanotubes indicates efficiency of load transfer. The specimen sintered at 1150°C exhibits a best combination of hardness (1610 kg/mm²) and toughness (9.7 MPa m^{1/2}). The hardness drastically decreases with increasing sintering temperature above 1150°C. The toughness steadily decreases with increasing the temperature, yet it remains at least two times higher than that of monolithic alumina. The decrease in hardness and toughness can be readily explained by the conversion of carbon nanotube to graphite confirmed by Raman spectra. The excellent toughness of the present composites can be attributed to crack bridging by carbon nanotube, crack deflection, and fiber pull-out. The high residual compressive stress in the matrix alumina grains calculated above is another important factor increasing the crack resistance.

Al₂O₃-ZrO₂-MgAl₂O₄ Nanocomposite: The starting materials were commercially available nano-sized powders: γ -Al₂O₃ (Nanotechnologies, Austin, Texas) with 15-20 nm particle size; MgO (Nanopowder Enterprises Inc., Piscataway, New Jersey), with 40 nm particle size; tetragonal ZrO₂ stabilized with 3 mol. % Y₂O₃ (Tosoh, Tokyo, Japan), with 24 nm particle size. Sintering by SPS was conducted at 1150°C for 3min. Fig. 3 shows the nanocrystalline structure of the composite. A fully dense disk was compressed in the SPS equipment at 1150°C and successfully formed into a part with complicated shape. A deformation rate of approximately 10⁻² s⁻¹ was calculated according to the displacement curve recorded during SPS forming. To the best of our knowledge, this is the first time a dense ceramic blank was formed into such a complex shape at a commercially attractive temperature and strain rate.

By combining sintering and forming in one step, other complex shapes (Fig. 4) have been successfully achieved in a timely fashion. Strain rate jump tests reveal a strain rate sensitivity ($m = 0.55$) and activation energy of the deformation process ($Q = 620$ kJ/mol) for the composite. The inverse of 0.55 that is very close to an n-value of 2 strongly indicates that grain boundary sliding is likely the mechanism for elevated temperature plasticity in this nanocomposite.

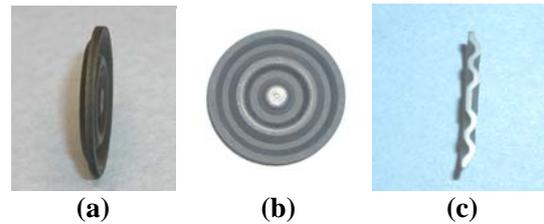


Fig. 4 Different view of a fully dense part (with a diameter of 20 mm): (a) side view; (b) top view; (c) cross-section view.

Acknowledgements

This work is funded by the U.S. Office of Naval Research (Grant No. N00014-00-1-0186 and N00014-03-1-0148) with Dr L. Kabacoff as Program Manager and the U.S. Army Research Office (Grant No. G-DAAD 19-00-0-0185) with Dr. William Mullins as the Program Manager.

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