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13. ABSTRACT *(Maximum 200 words)*

Exploitation of ceramic superplasticity requires development of superplastic ceramics which have stable fine grains of high cohesive strength but low flow stress. Systematic development of a methodology with the above intent has been practiced for the first time for alumina ceramics with considerable success. Low temperature sintering achievable via advanced colloidal processing and additives allows the attainment of very fine grain sizes, c.a. 0.5 μm. Stability of grains against deformation can be improved by adding a small amount of zirconia dispersoids. Flow stress was found to be sufficiently low, and cohesive strength sufficiently high. for the above ceramics to be superplastically deformed, in biaxial tension, to very large strains ($\geq$ 100%).

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CRYSTAL CHEMISTRY AND MICROSTRUCTURAL DESIGN FOR CERAMIC SUPERPLASTICITY

FINAL REPORT

I-WEI CHEN

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U.S. ARMY RESEARCH OFFICE

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I. STATEMENT OF THE PROBLEM

Ceramic superplasticity is a relatively recent phenomenon first discovered in tetragonal zirconia polycrystal stabilized by yttria (3Y-TZP) in 1986. It is believed that the very fine grain size of this material, c.a 0.3 μm, facilitates superplasticity. Subsequent research by Chen and his coworkers at the University of Michigan on the zirconia system has further identified the following as the main attributes of Y-TZP pertaining to its excellent superplastic characteristics:

(a) a stable grain size resistant to coarsening in sintering and in deformation due to aliovalent solute segregation to the grain boundary;

(b) a thin glass layer on the grain boundary which facilitates deformation;

(c) a relatively low grain boundary energy due to solute segregation and crystallography which imparts considerable strength against cavitation.

The intent of the current research is to develop a methodology to similarly explore other ceramic systems for significant superplasticity. Although three material systems, alumina, spinel, and silicon carbide, have been identified for the exercise, intended for a three-year grant, an inadvertant funding shortfall on the part of ARO resulted in the premature termination of the program after the first year. The present report summarizes our research during the first year. The work focussed on the alumina system only—major accomplishments are described below.

II. SUMMARY OF ACCOMPLISHMENTS

2.1 Deformation and Ceramic Growth of Low-temperature Sintered, High Purity Alumina

Through close control over green state powder processing, pure alumina ceramics of 0.5 μm grain size were obtained by sintering at 1250°C. The static grain growth of this material was modest at temperatures below 1300°C. However, dynamic grain growth occurred rapidly during superplastic deformation. Therefore, although the ultrafine-grained alumina exhibited rather low initial flow stress at relatively low deformation temperatures, dynamic grain growth-induced strain-hardening gave rise to high flow stress causing cavitation and cracking. As a result, superplastic deformation could not be achieved for the ultrafine-grained pure alumina.

2.2 Superplastic Alumina Ceramics with Grain Growth Inhibitor

Superplastic deformation of alumina ceramics was studied at 1400-1450°C at strain rate of $4x10^{-5}$ to $5x10^{-4}$ s^{-1}. MgO and ZrO_2 were introduced to suppress dynamic grain growth. The latter was especially effective; grain growth was minimum in 10 vol% ZrO_2-containing material. Both materials were superplastically stretched under biaxial tension to 100% engineering strain with good surface finishing, demonstrating the feasibility of superplastic forming for alumina ceramics.

2.3 Low Temperature Sintering of Alumina with Liquid Forming Additives

Simultaneous application of colloidal processing and liquid-forming additives to alumina resulted in a sintered density of >99% in 1 hour at a temperature as low as 1070°C for a commercial high purity alumina powder at a total dopant level of 2 mole%. The additives were 0.9% CuO + 0.9% TiO_2 + 0.1% B_2O_3 + 0.1% MgO. At higher temperatures or after prolonged sintering, the doped alumina ceramic developed a duplex microstructure containing large elongated grains and exhibited a relatively high fracture toughness of ~3.8 MPa $m^{1/2}$ as compared to a value of ~2.6 MPa $m^{1/2}$ for the undoped alumina.

2.4 Transformation of γ-Al_2O_3 to α-Al_2O_3

Liquid forming additives enhance the γ to α transformation of alumina. ZnF_2 was found to be the strongest enhancing agent. On the other hand, ZrO_2 proved to be most effective in retarding the transformation. Additive effects on sintering/shrinkage were similar except for the added effect of reaction sintering and a faster transformation kinetics due to the better contact between powders in a compact.

2.5 Methodology of Alloy Development of Superplastic Ceramics

Superplastic structural ceramics, Y-TZP, Al_2O_3, Si_3N_4 and their composites, that can withstand biaxial stretching to large strains, have been developed recently. Microstructural design of these ceramics first calls for an untrafine grain size that is stable against coarsening during sintering and deformation. A low sintering temperature is a necessary, but not sufficient, condition

for achieving the above. In many cases, the selection of an appropriate phase, such as tetragonal phase in zirconia or α phase in silicon nitride which is resistant to grain growth, is crucial. The use of sintering aids and grain growth inhibitors, particularly those that segregate to the grain boundaries, can be beneficial. Second phase particles are especially effective in suppressing static and dynamic grain growth. Another major concern is to maintain an adequate grain boundary cohesive strength, relative to the flow stress, to mitigate cavitation or grain boundary cracking during large strain deformation. Existing evidence suggests that a lower grain boundary energy is instrumental in achieving this objective. The selection of an appropriate phase and the tailoring of the grain boundary or liquid phase composition can sometimes drastically alter the cavitation resistance. Related observations on forming methods, forming characteristics, and sheet formability are also reviewed. It is found that the basic deformation characteristics are akin to diffusional creep and dominated by grain boundary diffusion. However, they are frequently altered by interface reactions, second-phase hardening/softening, and dynamic grain growth induced strain hardening. Ductility and formability, on the other hand, are controlled by the flow stress and flaw distribution, not by deformation instability as in superplastic metals. Analytical models and empirical correlations are presented to describe various constitutive relations in the above areas.

III. LIST OF PUBLICATIONS AND TECHNICAL REPORTS

1. L.A. Xue and I-W. Chen, "Development of Superplastic Structural Ceramics," *Journal of American Ceramic Society*, **73** [9] 2585-2609 (1990).

2. L.A. Xue and I-W. Chen, "Deformation and Grain Growth of Low Temperature Sintered High Purity Alumina," *Journal of American Ceramic Society*, **73** [11] 3518-21 (1990).

3. I-W. Chen, "Superplastic Ceramics," in Ceramic Powder III, Ceramic Transactions, V. 12, Proceedings of 3rd Internationl Symposium on the Science of Processing, Eds. E. Messing, S-I. Hirano, American Ceramic Society, p. 607-17 (1990).

4. L.A. Xue, X. Wu and I-W. Chen, "Superplastic Alumina Ceramics with Grain Growth Inhibitor," *Journal of American Ceramic Society*, **74** [4] 842-45 (1991).

5. I-W. Chen, "Superplastic Forming of Ceramic Composites," to be published in Composites, Eds. M. Sacks, *Proceedings of Second Ceramic Congress* (1991).

6. L.A. Xue and I-W. Chen, "On the Transition of α-Al_2O_3 to γ-Al_2O_3," accepted for publication in *Journal of Materials Science Letters* (1991).

7. L.A. Xue and I-W. Chen, "Low Temperature Sintering of Alumina with Liquid Forming Additives," accepted for publication in *Journal of American Ceramic Society* (1991).

IV. LIST OF INVITED TALKS

1. "Superplastic Forming of Fine-Grained Ceramics," at Department of Materials Science & Engineering, University of Washington, Seattle, WA, January, 1990.

2. "Superplastic Forming of Fine-Grained Ceramics," at the Third International Conference on Ceramic Powder Processing Science, San Diego, CA, February, 1990.

3. "Superplastic Ceramics," at Albrecht-Rabenau Symposium on Contemporary Issues in Ceramic Science, Tegernsee, Germany, July 1990.

4. "Superplastic Forming of Ceramic Composites," at Symposium on Composites, Orlando, FL, November, 1990.

V. LIST OF PARTICIPATING SCIENTIFIC PERSONNEL

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VI. REPORT OF INVENTION

None