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13. ABSTRACT (Maximum 200 words)

At the time of initiation of this research, the materials community was just becoming aware of the pioneering work on nanophase materials by Prof. Gleiter, in Germany, and the forecasts of new materials with highly desirable properties were being offerred. For ceramic materials, the potential for low temperature sintering and superplastic deformation were very exciting possibilities, while the effect of nanoscale grain structures on other properties were also of interest. This research, therefore, was initiated to evaluate the properties of monolithic, nanophase ceramic materials.

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# NANOPHASE CERAMICS

FINAL REPORT ROBERT S. AVERBACK

MAY 21, 1992

U.S. ARMY RESEARCH OFFICE

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UNIVERSITY OF ILLINOIS URBANA-CHAMPAIGN

# FINAL REPORT

## Statement of Problem:

At the time of initiation of this research, the materials community was just becoming aware of the pioneering work on nanophase materials by Prof. Gleiter, in Germany, and the forecasts of new materials with highly desirable properties were being offerred. For ceramic materials, the potential for low temperature sintering and superplastic deformation were very exciting possibilities, while the effect of nanoscale grain structures on other properties were also of interest. This research, therefore, was initiated to evaluate the properties of monolithic, nanophase ceramic materials.

## Summary of the Most Significant Results:

1. Superplastic deformation in nanophase $TiO_2$

One of the primary motivations for having studied nanophase ceramics derives from their potential for superplastic defomation. Fig.1, which illustrates the ductility of $TiO_2$ in compression, demonstrates that large deformations are, indeed, possible in nanophase ceramics, and at relatively low temperatures, approximately one-half the melting temperature, $T_m$. This study also began to develop constitutive relations for the deformation. For the generalized equation,

$$\dot{\varepsilon} = \frac{A\sigma^n}{d^q} \exp\{-\Delta H/kT\}$$

we have found that $n \approx 3$ and $q \approx 1.5$. The activation enthalpy has not yet been obtained. This work remains the only creep study on a dense nanophase ceramic material. It is noteworthy that the Gleiter group has published that nanophase $TiO_2$ can be plastically deformed at room temperature, i.e., $T < 0.2T_m$; however, from our investigations we can infer that this was possible only because the density of the samples employed for those experiments were less than 80% dense. Nevertheless, our investigations clearly demonstrates that nanophase ceramics are very conducive to superplastic deformation at $T \approx 0.5\ T_m$, which is still quite extraordinary.

Fig.1 Photograph of a nanophase $TiO_2$ sample before and after deformation at 800 °C. The cylinder was compacted using sinter-forging; its initial density was > 98% and its grain size was ≈ 40nm.

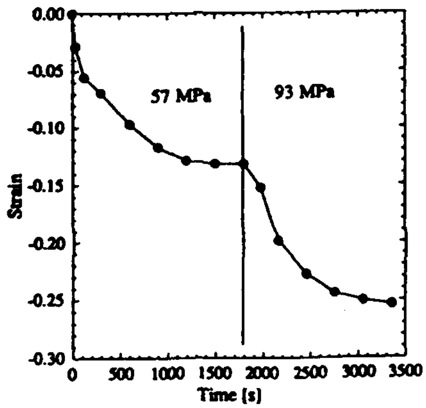


Fig. 2 Change in length of nanophase $TiO_2$ under uniaxial stress at 650 °C.

An important problem that limits the superplastic response of nanophase ceramics is their propensity for grain growth. We were able to fabricate specimens whose grain sizes in the green body, which was ≈ 78% dense, were less than ≈ 10nm, but the grains grew to ≈ 40-50 nm during densification, and then to ≈ 400 nm during the deformation process that led to the deformed specimen illustrated in Fig. 1. It is clear that methods for controlling the grain size will be required, if these materials are to be used for structural applications where high densities are important.

## 2. Sinter-forging

One of the methods for enhancing the densification rate during sintering is to apply an external stress. The application of a hydrostatic stress during sintering, i.e., hipping, has long been used for this purpose. The application of a uniaxial stress, however, can also be beneficial. For example, the specimen illustrated in Fig.1 was densified at 600 °C to nearly full density, while the grain size increased from 10 nm to 40 nm. Sintering of similar specimens without an applied stress revealed that complete densification could not be achieved below ≈ 950 °C, and at that temperature, the grain size had increases to ≈ 0.5 µm. In addition to providing a convenient and efficient means to enhance sintering, sintering-forging provides fundamental information about the deformation mechanisms in the material.

$$F \cdot dx = \Delta\gamma \cdot dA$$
$$\Delta\gamma = \gamma_s - \gamma_{gb}$$

$$\sigma \cdot b \cdot l \cdot \cos(\theta)\, dx = \{2\Delta\gamma \cdot bl/d\}\, dx$$

$$\sigma_{th} = 2\Delta\gamma/d \cdot \cos(\theta)$$
$$\Delta\gamma = 1 J/m^2$$
$$d = 20 \text{ nm}$$

$$\sigma_{th} = 100 \text{ MPa}$$

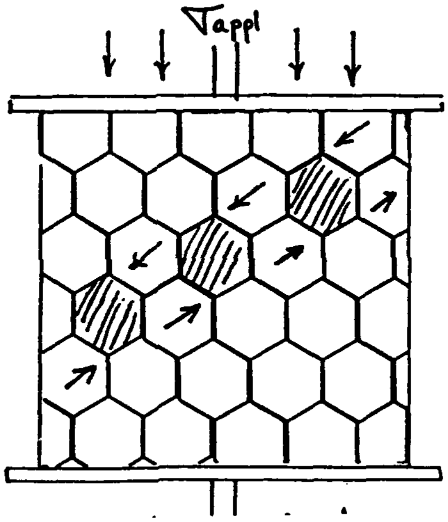

Fig.3 Model of grain boundary sliding during sinter-forging

Fig. 2 illustrates the densification of nanophase $TiO_2$ during sinter-forging; it shows the change inlength of a nanophase $TiO_2$ cylinder as a function of time. It should be noticed that the densification takes place at 650 °C, which is < 0.5 $T_m$; similar results were obtained at 600 °C , as well. The data in Fig. 2 also show that the densification does not go to completion at the applied stress of 57 MPa, but rather a "metastable" density is obtained. The metastable density was found to be a function of applied stress and temperature. The existence of a threshold stress observed in these sinter-forging experiments appears to be unique to nanophase materials. Although we are still in the process of developing a model to describe this phenomenon, we feel the threshold stress is a consequence of grain boundary sliding as illustrated in Fig.3. In this simplified picture of sinter-forging, it is shown that as grain boundary sliding occurs in the vicinity of a pore, the surface area of the pore increases while grain boundary area decreases, with a net increase in energy. This increase in energy is provided by the work performed by the applied stress. Densification is activated during this process by (i) improving packing of the grains as grains slide past

The fracture toughness of nanophase $TiO_2$ is plotted in Fig. 7 as a function of grain size. These data were obtained by indentation methods. Clearly shown is that the fracture toughness of the sample is independent of grain size.

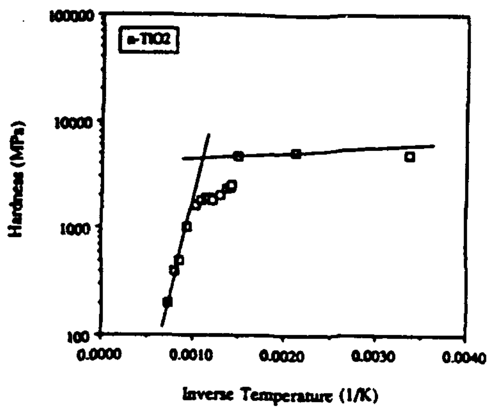


Fig.6 Vickers microhardness as a function of inverse temperature

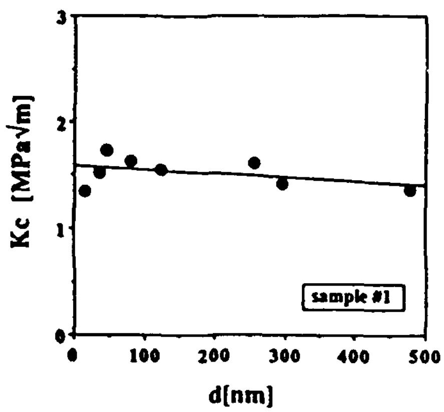


Fig.7 Fracture toughness $K_{1c}$ as a function of grain size

<u>Sintering of Nanophase $TiO_2$ and $ZrO_2$</u>

A thorough investigation of the sintering of nanophase $TiO_2$ and $ZrO_2$ was carried out, and it was found that sintering temperatures are reduced by several hundred K relative to μm-sized materials. Below ≈ 900 °C, both nanophase oxide materials densified with increasing sintering temperature and without significant grain growth. But above this temperature, when the density became greater than ≈ 90%, the samples underwent rapid grain growth. For $TiO_2$, this led to grain sizes of ≈ 1μm before full density could be achieved. The $ZrO_2$ samples,which had a monoclinic structure, became fully dense at similar sintering temperatures, but the grain size remained below ≈ 0.1μm. Data for the $ZrO_2$ sample are shown in Fig.8. Preliminary studies on the effect of impurity doping on grain growth during sintering of $TiO_2$ were performed, and it was observed that the grain size could be maintained below ≈ 0.1μm during densification.

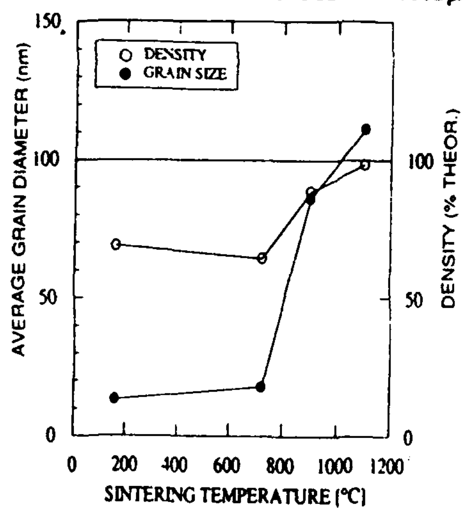


Fig. 9 Grain size and density of nanophase $ZrO_2$ as a function of sintering temperature

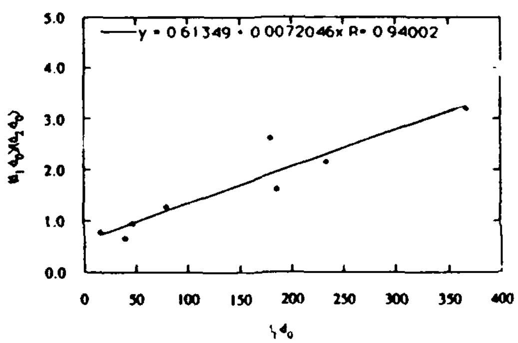


Fig. 10 The ratio of grain sizes in pure and Y-doped nanophase $TiO_2$ as a function of grain of pure nanophase $TiO_2$ during isothermal annealing.

each other, (ii) hipping, since the hydrostatic component of the uniaxial stress is 1/3 $\sigma_{appl}$, and (iii) destabilizing the equilibrium shape of the pore and reinitiating sintering. In this simple model, the threshold stress is given by,

$$\sigma_{thresh} = g \frac{\Delta\gamma}{d}$$

where $\Delta\gamma$ is the difference in the surface and grain boundary energies, g is a geometry factor of order unity, and d is the grain size. Because of the small grain size, d ≈ 10 -20 nm, the threshold stress is on the order of 50 - 100 MPa.

Fig. 4 shows the dependence of strain rate on applied stress, and it is seen that the the stress exponent ("n" in eq. (1), above) is approximately three. In larger grain ceramic materials, the stress exponent is usually one, again showing the difference between nanocrystalline and microcrystalline materials

Mechanical properties of $TiO_2$

As part of a survey of the mechanical properties of nanophase ceramic materials, we examined the hardness and fracture toughness of $TiO_2$ as a function of grain size; the results are illustrated in Figs. 5, 6 and 7. The hardness data reveal two regimes. At larger grain sizes, the Vickers microhardness follows normal Hall-Petch behavior, i.e., the hardness increases as the inverse square root of grain size. However, below a critical size, ≈ 40 nm, the hardness becomes much less sensitive to the grain size, although still increasing slightly with decreasing grain size. In regards to the absolute value of the hardness, the Vickers microhardness of nanophase samples, when fully dense, is somewhat higher, ≈ 25%, than bulk samples. The temperature dependence of the hardness is illustrated in in Fig. 6, where it is shown that significant softening begins at temperatures greater than ≈ 400 °C.

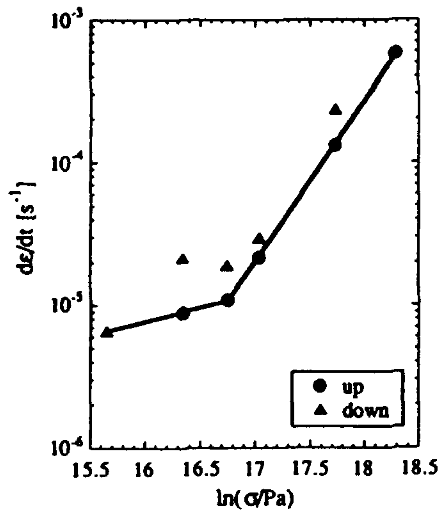


Fig.4 Dependence of strain rate on stress in nanophase $TiO_2$ during sinter-forging.

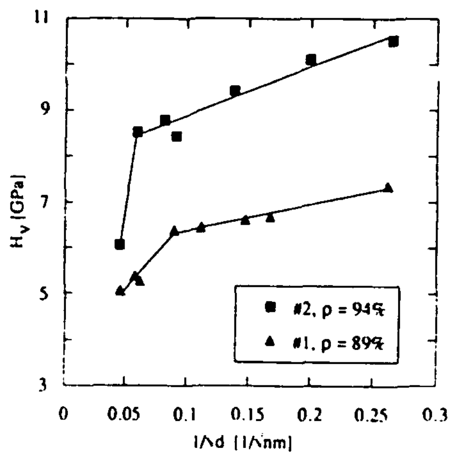


Fig.5 Vickers microhardness as a function of inverse square-root of grain size

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Mat. Res. Soc. Symp. Vol. 132 (1989).

2. Kinetic and Thermodynamic Properties of Nanophase Materials,
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3. The Production of Nanocrystalline Powders by Magnetron Sputtering
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4. Low Temperature Sintering and Deformation of Nanocrystalline $TiO_2$
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5. Grain Growth in Nanocrystalline $TiO_2$ and Its Relation to Vickers Hardness and Fracture Toughness
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J. Am. Cer. Soc. 74, (1991) 2672.

8. Processing and Properties of Nanophase Materials
R.S. Averback and H.J. Höfler
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9. Sintering and Deformation of Nanocrystalline Ceramics
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11. High Temperature Mechanical Properties of Nanostructured Materials
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Nanostructured Materials, 1 (1992) 95.

12. Sintering Characteristics of Nanophase Ceramics
R.S Averback, H.J Höfler, H. Hahn and J.C. Logas
Nanostructured Materials, 1 (1992) 173.

Developments in Processing Nanophase Ceramics:

During the course of this investigation, some efforts were focused on developing the processing capabilities of nanophase ceramics. A major improvement was the development of a magnetron sputtering system for the production of refractory type materials. The $ZrO_2$ samples, for example, were produced by first preparing nanophase Zr powder by magnetron sputtering and subsequently oxidizing it. This method is particularly useful when alloy materials are desired since the composition can be well controlled.

A "flow" system for processing nanophase powder was also developed. Unlike the original Gleiter method, which employs thermophoresis for the collection of powder, this system utilizes force flow and collection of the powder in a filter. The system has the advantages that it is conducive to scale up and is cheaper to build.

Papers in progress and initiated under ARO funding:

1. Sinter-forging of Nanophase $TiO_2$
   H.J. Höfler and R.S. Averback

2. Properties of Nanophase $ZrO_2$
   M. Pollack and R.S. Averback

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| 7. | Rong Tao | Laboratory Assistant - currently working on Ph.D. |