CONF-890426--32

PROCESSING AND PROPERTIES OF NANOPHASE OXIDES*

J. A. Eastman, Y. X. Liao**, A. Narayanasamy† and R. W. Siegel
Materials Science Division
Argonne National Laboratory
Argonne, IL 60439-4838

CONF-890426--32

DE90 003826

August 1989

Invited Paper presented at Materials Research Society Spring Meeting, Symposium L: "Processing Science of Advanced Ceramics:, Volume 55 of the MRS Symposium Proceedings Series, edited by I. A. Aksay, G. L. McVay and D. R. Ulrich, April 27-28, 1989, San Diego, CA.

*Work supported by the U. S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-Eng-38.
**Permanent address: Measure and Testing Center, Sichuan University, Chengdu, People's Republic of China.
†Permanent address: Department of Nuclear Physics, University of Madras, Madras, India.

PROCESSING AND PROPERTIES OF NANOPHASE OXIDES*

J. A. EASTMAN, Y. X. LIAO†, A. NARAYANASAMY‡ and R. W. SIEGEL
Materials Science Division, Argonne National Laboratory, Argonne, IL 60439-4838.

ABSTRACT

Nanophase oxides (Al_2O_3, MgO, ZnO and TiO_2), with typical grain sizes in the range 2-20 nm, have been synthesized by the condensation of ultrafine particles in a convective inert gas followed by their collection and in-situ consolidation in vacuum at ambient temperature. These new materials, owing to the reduced scale of their grains along with the enhanced cleanliness of their grain boundaries, are found to have significantly improved properties relative to those of their coarser-grained, conventionally-prepared counterparts. Nanophase rutile (TiO_2) with an initial mean grain diameter of 12 nm, for example, has been found to sinter at 400 to 600°C lower temperatures than conventional rutile powders, without the need for compacting or sintering aids, while retaining a small grain size. Additionally, the importance of the extremely clean surfaces obtained with the gas condensation method has been demonstrated by comparing the sintering behavior of powders with and without air exposure prior to consolidation. The research completed on the processing and properties of nanophase ceramics is reviewed, and the potential for engineering advanced ceramics using the nanophase processing method is discussed.

INTRODUCTION

Nanophase materials (ultrafine-grained bulk materials, typically with grain sizes of 2-20 nm) produced by the gas-condensation process [1, 2] have recently been found to possess a variety of interesting and novel properties which are often superior to those of their coarser-grained counterparts. A number of review articles on this subject have recently appeared (e.g., [3-6]). Ultrafine-grained ceramics and ceramic-based composites are of particular interest because of the wide variety of potential applications which exist, where nanophase processing may impart particular advantages. For example, indications that the inherent brittleness of conventional

---

* Work supported by the U. S. Department of Energy, BES-DMS, under Contract W-31-109-Eng-38.

† Permanent address: Measure and Testing Center, Sichuan University, Chengdu, People's Republic of China.

‡ Permanent address: Department of Nuclear Physics, University of Madras, Madras, India.

ceramics may be overcome in ultrafine-grained TiO_2 and CaF_2 have been seen [7]. Also, it has been shown that nanophase TiO_2 powder sinters at 400-600°C lower temperatures than conventional powders, without the need for compacting or sintering aids [8], and that ultrafine grain size is maintained in the process.

While many ultrafine ceramic powders have previously been produced by the gas-condensation method (e.g., [9, 10]), it is only in the past few years that researchers have attempted to consolidate such powders in situ to produce ultrafine-grained bulk materials, as first suggested for the synthesis of nanocrystalline metals by Gleiter [11]. In the present paper, the conditions required to produce several nanophase oxides by the gas-condensation technique are described, the advantages of the gas-condensation process over other small particle-producing techniques are demonstrated, and the potential for producing materials with specially tailored properties by means of nanophase processing is discussed.

PROCESSING OF NANOPHASE CERAMICS

The nanophase ceramics produced in this study were synthesized in an ultrahigh-vacuum (UHV) system fitted with resistively-heated evaporation sources, a collection device and scraper assembly, and in situ compaction devices for consolidating the powders produced and collected in the chamber. Such an apparatus is depicted schematically in Figure 1. Ultrafine powder is produced by evaporating material in the chamber after pumping the system to a vacuum of better than 10^{-5} Pa and then backfilling with a controlled high-purity gas atmosphere [1,2,12]. The gas atmosphere is typically a few hundred Pa of an inert gas such as He. Reactive gas mixtures containing inert gases plus partial pressures of reactive gases such as oxygen can also be used if desired. Because the atoms or molecules being evaporated collide with the gas atoms in the chamber, lose their energy, and condense, small gas-borne particles are formed rather than continuous films, which would be produced by evaporating materials onto a substrate under vacuum conditions. Collection of the powders formed in close proximity to the evaporation source is carried out by establishing convective currents inside the chamber by means of a liquid nitrogen cold finger. In the apparatus presently being used, the cold finger is the powder collection device as well, and is in the form of a hollow tube which is filled with liquid nitrogen from outside the vacuum chamber. After completing the evaporation process, the powders that have been collected are removed from the tube using a Teflon annular ring, which is moved downward along the length of the cold finger. The tube is in a vertical orientation so that gravity can be used in order to transfer the powder to the in situ compaction devices located below the base of the main vacuum chamber.

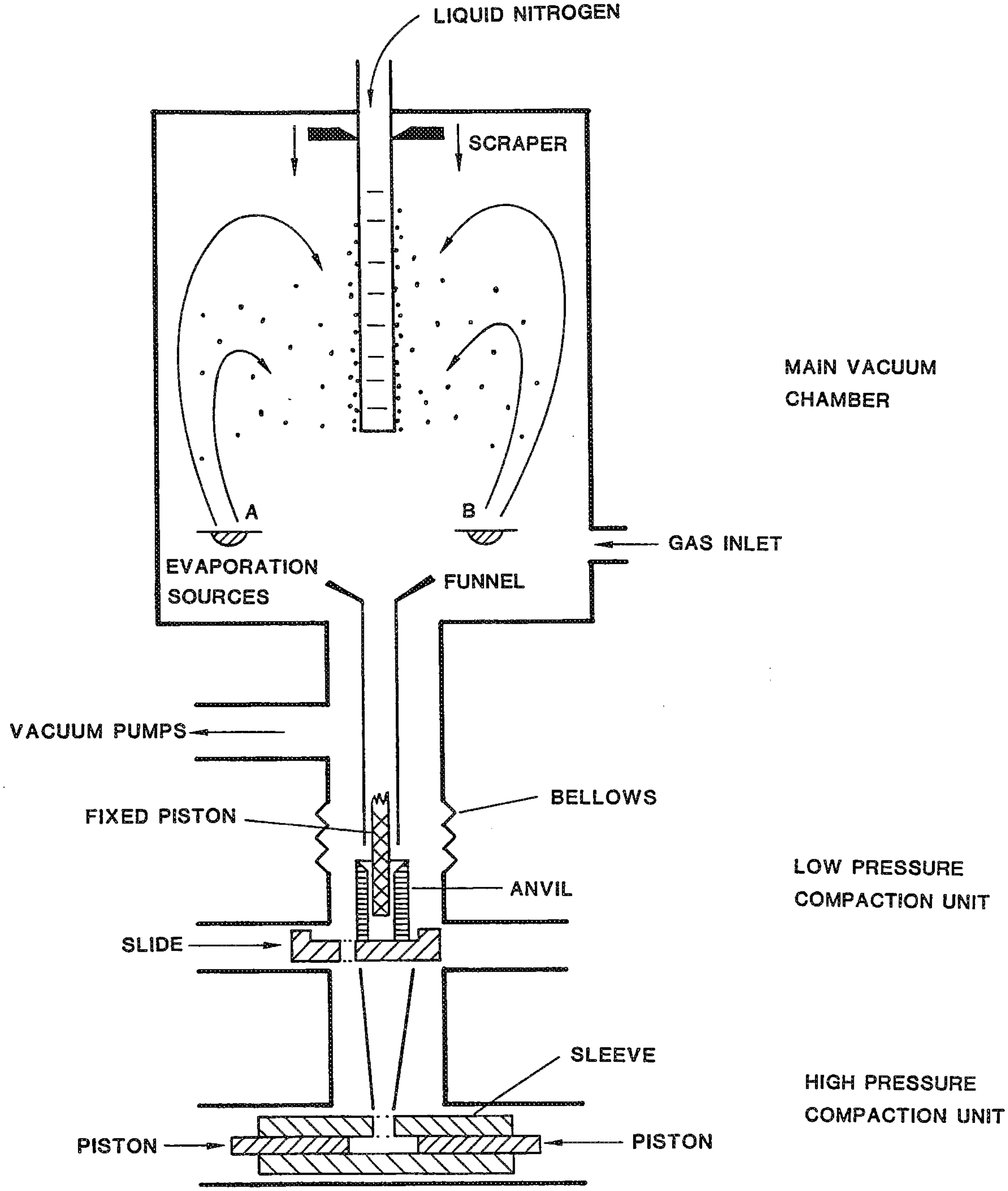

Figure 1. Schematic drawing of a gas-condensation chamber for the synthesis of nanophase materials. The material evaporated from sources A and/or B condenses in the gas and is transported via convection to the liquid-N_2 filled cold finger. The powders are subsequently scraped from the cold finger, collected via the funnel, and consolidated first in the low-pressure compaction device and then in the high-pressure compaction device, all in vacuum. From [4].

The consolidation of the powders to form a bulk ceramic is presently accomplished using a two-stage compaction unit. The upper stage consists of a simple piston and anvil arrangement which operates using very low consolidation pressures in order to form a loosely-compacted pellet. This pellet is transferred under vacuum to a second unit, in which the pellet is consolidated at ambient temperature under high pressures (typically 1.4 GPa) between two tungsten-carbide pistons. The scraping and consolidation are performed under UHV conditions after removal of the inert or reactive gases from the chamber, in order to maximize the cleanliness of the particle surfaces and the interfaces that are subsequently formed in the material. Surprisingly high densities of the as-compacted samples have been measured. Typical values are 50 to 80% of bulk density measured for TiO_2 and MgO, respectively, by weighing the samples in air and comparing with their volume; higher values of 75-90% are obtained by Archimedes method measurements [13]. (It is not certain at present whether the differences in results from these two types of measurements are due simply to a lack of precision owing to small sample size or to partial pore filling via capillarity in the application of the Archimedes method.) The resulting samples are disk-shaped and are typically 9 mm in diameter and 0.1 to 0.5 mm in thickness. While these dimensions are rather small by normal industrial standards, the need at present is only to produce samples large enough to facilitate characterization of their structure and properties. If design modifications were to be made, there are believed to be no impediments which preclude scaling the process up to produce larger commercial-sized samples.

Four nanophase oxides have been produced to date in this ongoing study: TiO_2, Al_2O_3, MgO and ZnO. Different procedures are required to produce the different materials. TiO_2, the properties of which have been studied in the most detail so far [8], is produced by first evaporating Ti (99.99% purity) to form small Ti metal particles, and then subsequently introducing oxygen rapidly into the chamber. During this second process, the Ti particles collected on the cold finger, which is warmed to room temperature, are spontaneously converted to TiO_2 (predominantly the rutile phase). A rapid rate of oxygen introduction to the chamber has been found to be important; bleeding oxygen in slowly results in the formation of a mixture of rutile and other oxide phases. Following oxidation, the chamber is evacuated again; the oxide powder is then collected and consolidated under vacuum conditions. The resulting material has a log-normal grain-size distribution with a typical mean grain size of approximately 12 nm. Post-oxidation at room temperature of metal particles to form oxides has not been found to be a viable process for any materials tested yet other than Ti, however. For materials such as Al or Mg, which are also extremely reactive with oxygen, a thin protective amorphous coating is believed to form, which prevents the complete oxidation of the metal. Because of this, it has been necessary to search for different techniques to produce other oxides. In order to produce Al_2O_3, ultrafine Al powders are first produced and then annealed in air at 1000°C, which results in transformation of the powder to the thermodynamically stable α-phase of Al_2O_3. Little increase in particle size occurs during the annealing process; the final average particle size obtained is about 18 nm using these conditions.

Most oxides have very high melting points and, because of this, are not good candidates for evaporation by resistive heating. MgO and ZnO are special, however, in that they have high vapor pressures at temperatures well below their melting points. This makes it possible to produce ultrafine powders of these materials by directly subliming the oxide. Ultrafine grain sized MgO has been produced by directly heating MgO in tungsten boats to 1600°C (MgO melts at 2852°C) in 200 Pa of He. The material which sublimes is oxygen deficient, but is fully converted to stoichiometric MgO by subsequent exposure to oxygen introduced into the vacuum chamber. The MgO that has been produced to date has a mean grain size of only 5 nm, but it has been determined to be not pure, single-phase MgO because of difficulties encountered in finding suitable evaporation sources that do not react. For instance, it has been found that if the MgO is sublimed from tungsten boats, the resulting material is a mixture of ultrafine-grained MgO and WO_x phases. While a composite such as this may have very interesting and desirable properties not found in other larger-scale composites, this points out a potential, troublesome limitation of vaporizing materials using Joule-heating techniques. To overcome problems such as these, alternative heating methods must be employed. An electron-beam evaporation system is currently being developed at Argonne to avoid such problems and to allow the synthesis of a wider range of nanophase materials under controlled conditions.

Production of nanophase ZnO has required considerable engineering in order to find a successful production scheme. ZnO resembles MgO in that it has a high vapor pressure at temperatures considerably below its melting point, thus making it possible to sublime ZnO by Joule heating. Ultrafine-grained ZnO powder with a mean size of 6-15 nm has been produced by subliming coarse-grained ZnO from graphite boats at 1400°C (T_m = 1972°C). X-ray diffraction has revealed that as-produced, consolidated samples contain not only ZnO, but also significant quantities of Zn metal. This is observed even if the powder has been exposed to oxygen prior to consolidation. In some cases, only Zn is observed in x-ray θ–2θ scans, as shown in Figure 2(a). An amorphous oxide phase must also be present in these samples, however, since chemical analysis has shown that the material contains typically 40 at.% oxygen. Annealing the material in air at 300°C for 3 hours has been found to successfully fully convert the Zn to ZnO, as shown in Figure 2(b), while maintaining a grain size under 20 nm. The degree of consolidation of the material prior to this anneal has been found to be important in determining the amount of time (and, thus, the final grain size) at a

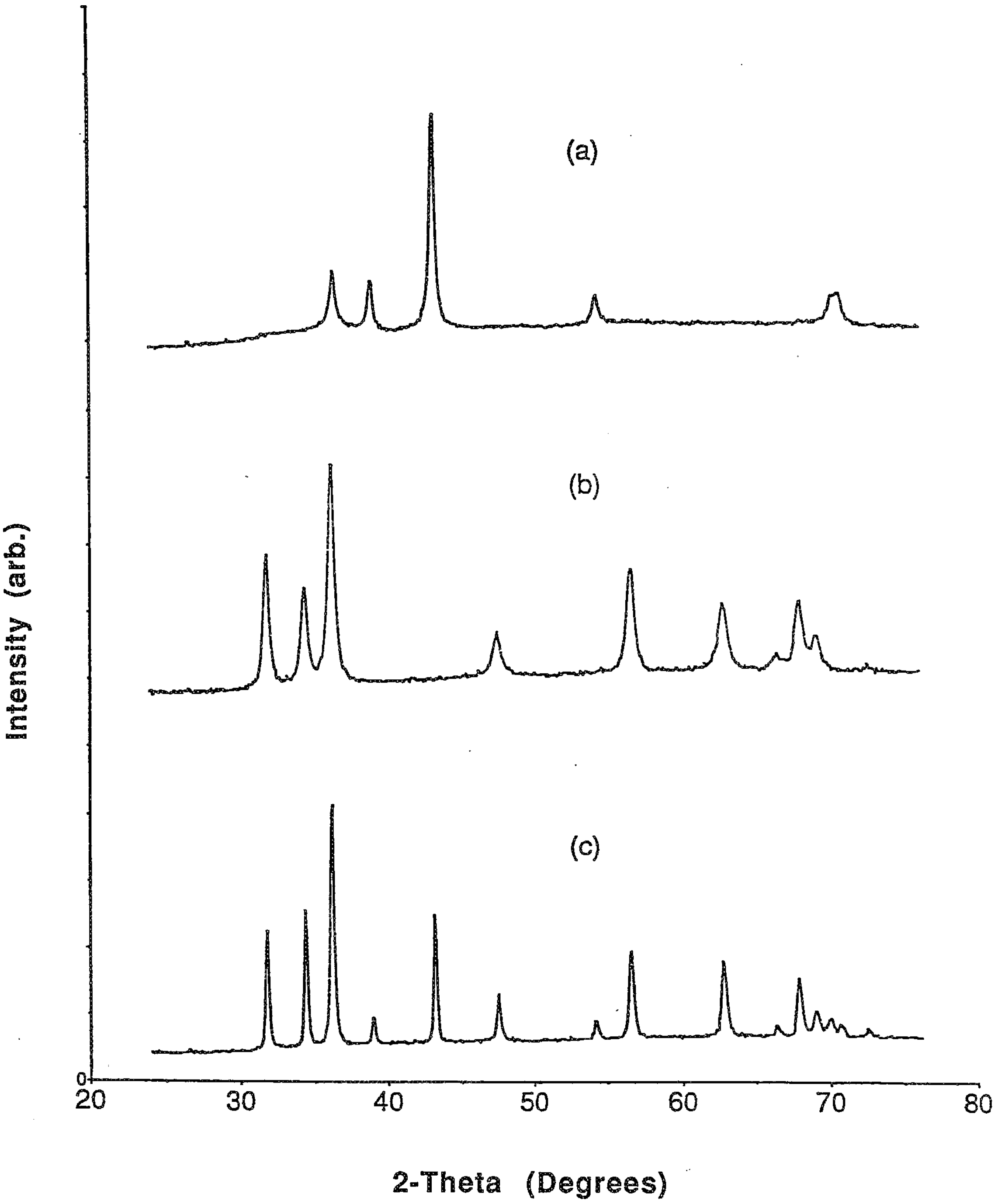

Figure 2. X-ray θ–2θ scans from nanophase ZnO. (a) is a scan from a sample which was compacted using only the low-pressure compaction unit. Only Zn is observed; no ZnO is present in this sample. (b) shows the effect of annealing the sample in (a) for three hours at 300°C in air. Complete conversion to ZnO occurred with little accompanying grain growth. (c) shows the importance of annealing samples in an oxygen atmosphere prior to high-pressure compaction. The sample in (c) was compacted at 1.4 GPa prior to annealing and still contains both Zn and ZnO phases, even after 6 hours at 600°C. Grain growth has occurred, as seen by the sharpening of the diffraction peaks.

given temperature required for complete oxidation. Material that is only lightly compacted prior to annealing transforms more easily than highly compacted material, as shown in Figure 2. Material that has been consolidated at 1.4 GPa remains partially Zn metal even after 6 hours at 600°C (180°C above the melting point of Zn). Whether this phenomenon is due to a greater accessibility of the Zn grains to oxygen in the more lightly compacted material or to a strain-induced suppression of the phase change is not yet understood. Nanophase processing can apparently stabilize unexpected phases, as shown by the observation of new phases of erbium oxides [14] and titanium-based oxides [15] in nanophase samples.

PROPERTIES

As already mentioned, the properties of nanophase ceramics that have been measured appear to be rather different and often considerably improved in comparison with those of conventional, coarser-grained ceramics. For a more complete discussion of these properties, the reader is referred to several review articles which have recently appeared [3-5]. In the present report, only a few recent results will be emphasized. It was earlier shown [8] that 12 nm grain size nanophase TiO_2 sinters at 400-600°C lower temperatures than conventional rutile powders, and does so without the usual need for compacting or sintering aids. The rutile thus produced has hardness and fracture toughness values similar to those for coarse-grained rutile, and a reduced sintering temperature (by 200°C) for transgranular fracture [16]. While the ultrafine grain sizes and narrow grain-size distributions available in the gas-condensation method are obvious advantages to sinterability, another attribute of this synthesis method, which has recently been demonstrated, is the importance of clean powder surfaces to the sintering behavior of nanophase TiO_2.

Figure 3 shows a comparison of the sintering behavior of ultrafine TiO_2 powder with and without exposure to air prior to initial powder consolidation, as evidenced by the effect on Vickers microhardness measurements. It can be clearly seen in this figure that not only does the vacuum-consolidated material [8] begin sintering at lower temperatures than the air-consolidated material, but also the ultimate hardness obtained is limited severely in the air-consolidated material. Presumably, this is due to the detrimental effect of surface adsorbates, primarily water vapor, resulting from the air exposure. This points out one major advantage of the gas-condensation process over chemical techniques, such as sol-gel processing, for the production of ultrafine powders. Chemical techniques, while able to produce large quantities of powders rapidly, lack the inherent control of surface chemistry available with the gas-condensation process.

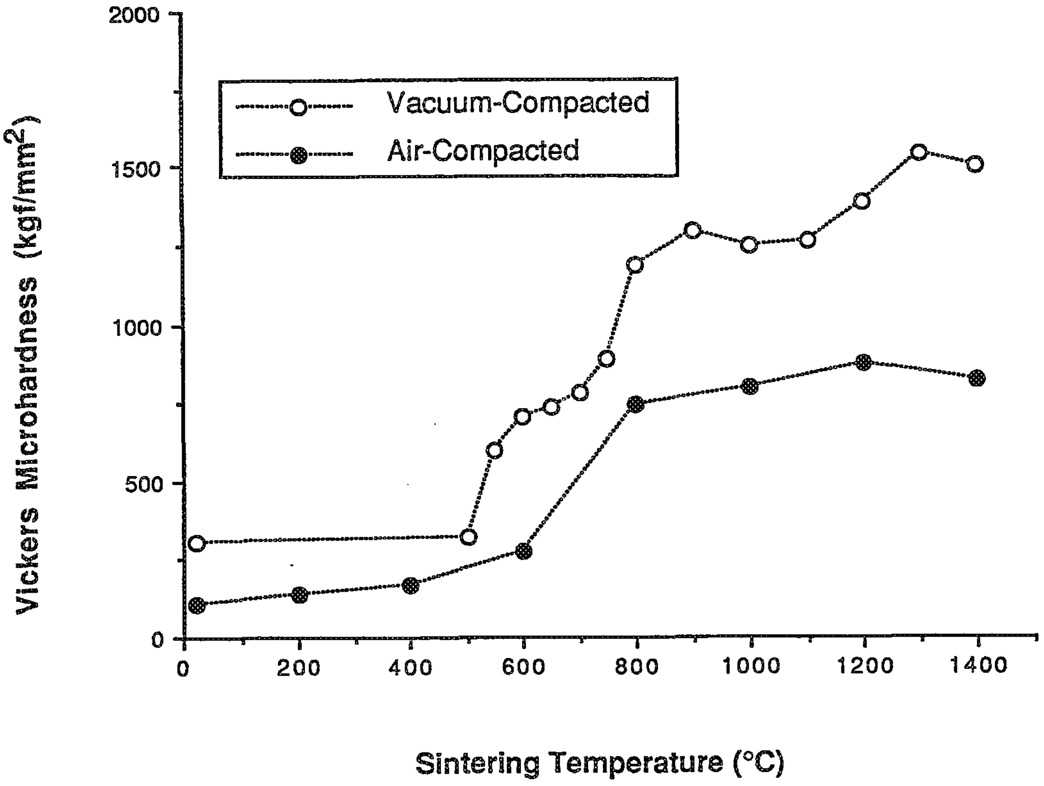

Figure 3. Vickers microhardness of 12 nm average grain-sized TiO_2 (rutile) samples measured at room temperature as a function of one-half hour sintering at successively higher temperatures in air. Results for a sample compacted in air are compared with those for a sample prepared via the normal nanophase processing route [8], which was compacted under vacuum conditions with no exposure to air. The superior sintering behavior of the in situ vacuum-consolidated sample is clearly demonstrated.

One concern with the use of nanophase ceramics in commercial applications is whether the stability of the small grain sizes is sufficient to allow use of these materials at temperatures above ambient. Characterization of mean grain size as a function of temperature has been carried out for TiO_2, MgO (containing WO_x) and ZnO, and the results are shown in Figure 4. It is clear from this figure that these consolidated ceramics all withstand heating to at least a few hundred degrees without significant grain growth. The temperature regime in which rapid grain growth begins to take place is a function of both the melting point of the material and the diffusion behavior. However, it appears to be the general behavior of nanophase ceramics that their ultrafine grain sizes are rather deeply metastable to ca. 40-50% of their melting points. Stabilization of the grain size to even higher temperatures may be possible by suitable doping of nanophase ceramics, which is made easier by the exceptionally high atomic mobility in these materials [4, 13].

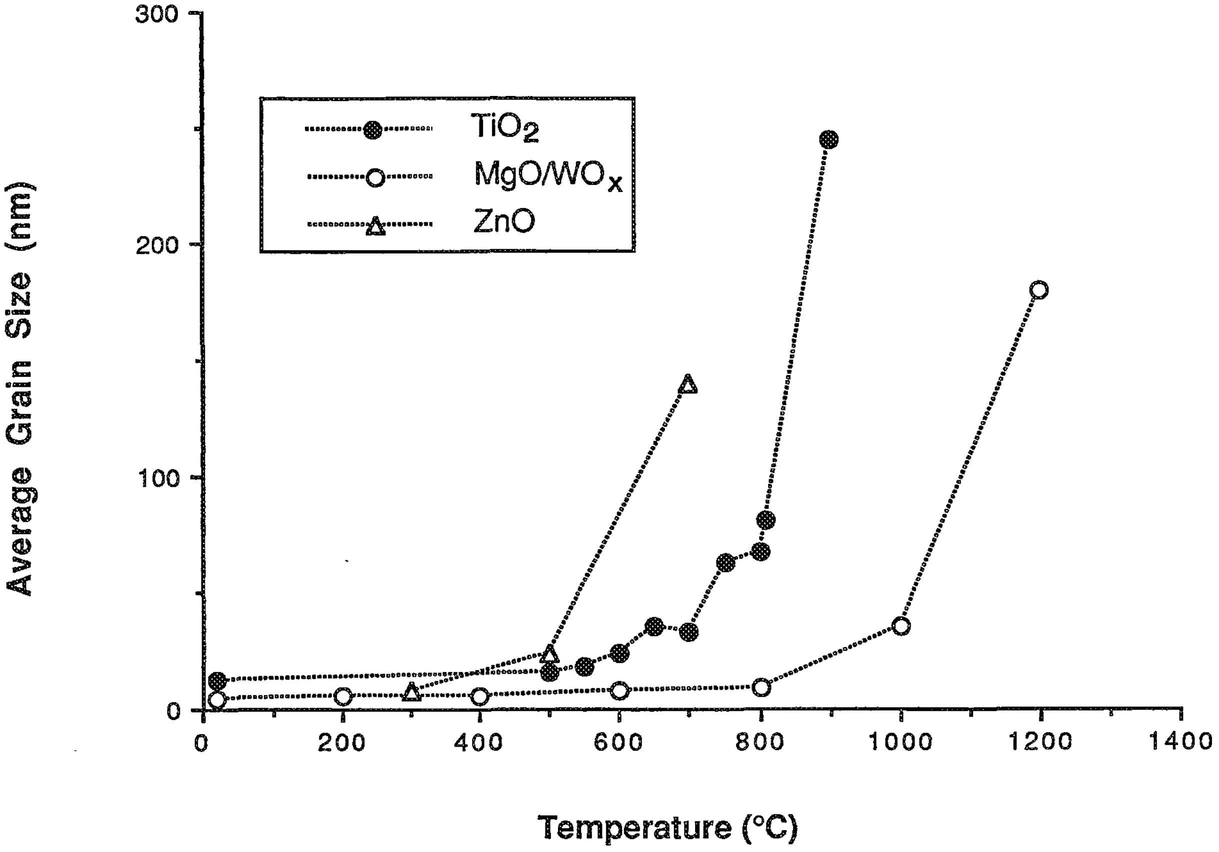

Figure 4. Variation of average grain size with sintering temperature for nanophase TiO_2, MgO/WO_x and ZnO. The samples were annealed for one-half hour in air at each temperature.

The relatively deep metastability of the ultrafine grain sizes in nanophase ceramics, coupled with their enhanced sinterability, allows for the synthesis of fully-dense ceramics with rather uniform ultrafine grain size. Figure 5 shows the 'window' between rapid sintering, as indicated by increased microhardness, and rapid grain growth for nanophase TiO_2, that demonstrates this capability of nanophase processing. Indeed, corresponding 'windows' have been measured for nanophase MgO/WO_x and ZnO. Recent density and grain size measurements [13] as a function of sintering temperature on similar TiO_2 samples to those studied previously [8] have also confirmed this possibility, and have shown that this 'window' can be opened further by sintering of the nanophase compact at elevated pressures or by appropriate doping. This is an important aspect of the processing of nanophase ceramics, since it appears that it will be generally possible to process fully-dense nanophase ceramics while retaining their ultrafine grain sizes and the unique properties associated with such grain sizes. Subsequently, the grain size can be adjusted by annealing to conform to a prescribed set of properties.

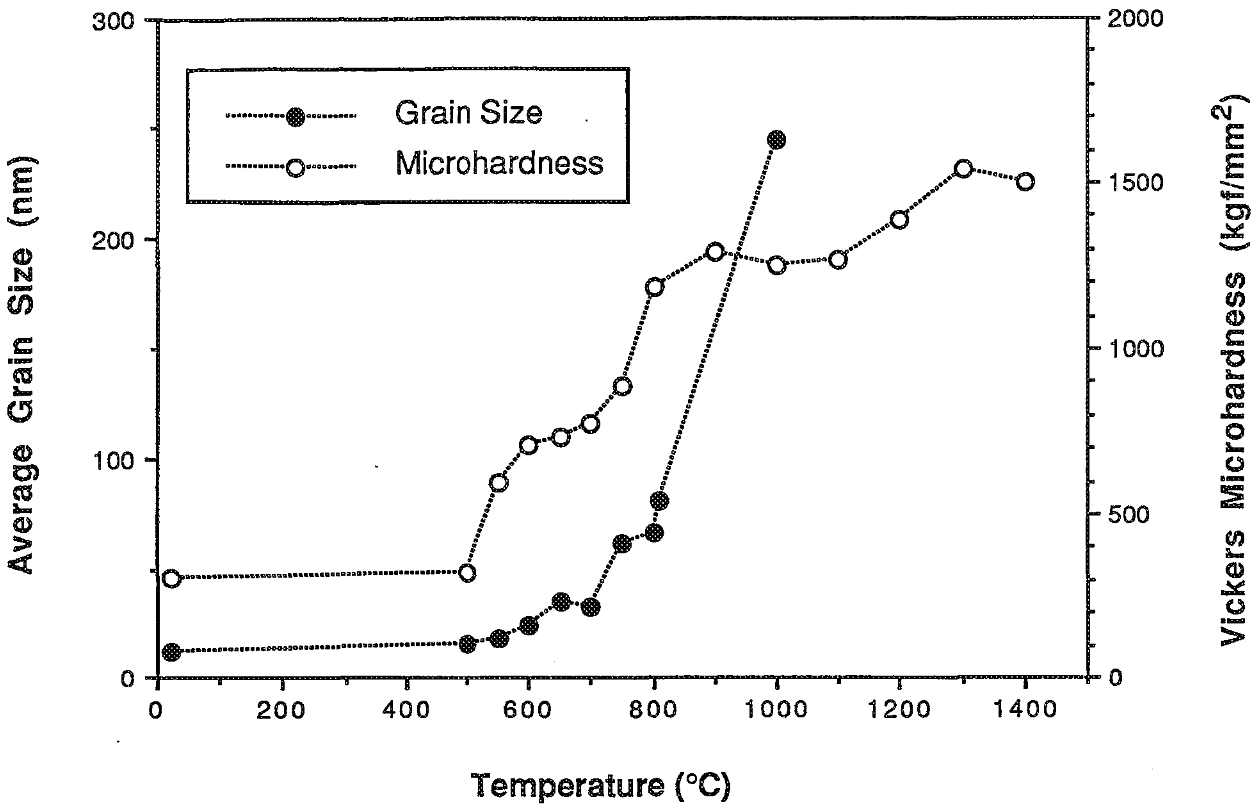

Figure 5. Nanophase TiO_2 Vickers microhardness versus temperature from Figure 3 compared with average grain size versus temperature for the same material from Figure 4. Sintering of the material is seen to occur prior to significant grain growth. From [8].

It should be pointed out that the metastability of the ultrafine grain sizes in nanophase ceramics appears to be an intrinsic result of their rather narrow grain size distributions, giving the analog to a closed-cell foam-like microstructure, and not simply caused by grain-boundary stabilization via porosity. While the latter extrinsic stabilization is observed in many cases for conventional ceramics [17-19], the ability to decrease the temperature for full densification of nanophase TiO_2 by sintering at elevated pressures while concomitantly increasing the temperature at which rapid grain growth occurs [13], clearly demonstrates that such extrinsic void stabilization does not underlie the grain-size metastability in nanophase ceramics. Furthermore, for the ultrafine grain sizes extant in nanophase ceramics, the driving forces for grain growth would likely overwhelm the drag forces due to the presence of grain-boundary porosity in any event.

The possibilities to process nanophase ceramics at considerably lower temperatures than their conventional coarse-grained counterparts are made even more interesting because of the inherent ease of their formability [7, 8] and the indications from recent strain-rate sensitivity measurements [20] of significant ductility in nanophase TiO_2.

CONCLUSIONS

It is clear that the future of nanophase ceramics is extremely bright but still largely uncharted. Several interesting and technologically important nanophase oxides have already been produced and some of their properties are now being elucidated. A brief review has been presented here. However, much more research needs to be done on these new materials, as well as on the wide range of additional ceramic compounds that can be synthesized by the gas-condensation method. This research will need to focus on a variety of aspects regarding both processing and properties, and the relationships between these and the structure of nanophase ceramics.

In the processing area, it is clear that in addition to the very small and narrow size distributions of grains, clean particle surfaces (and hence uncontaminated grain boundaries) are important attributes of the synthesis of nanophase ceramics. Just how much further improvement of the sinterability can be achieved by reducing gas-condensed particle sizes still further must be studied. The importance of the width of the grain size distribution to the sinterability and subsequent properties of nanophase ceramics also needs to be considered further. It is possible to produce very narrow (even monosized) size distributions of atomic clusters by means of more sophisticated gas-condensation techniques than used to date for the synthesis of nanophase materials [5], but yields must be vastly increased in order to impact significantly on most materials applications. Nevertheless, it is quite apparent that with the inherent simplicity of the gas-condensation process for synthesizing nanophase materials, 'scale up' will not be a major problem as long as sufficiently new and/or improved properties are available with these materials.

The question of the properties of nanophase ceramics needs much further attention. While their mechanical properties have already received some scrutiny, largely directed toward an initial assessment of their durability, formability, and suitability for application, the electrical and optical properties of these ultrafine-grained ceramics have only begun to be investigated. These may well be the properties that find the greatest technological application in the future. The capability to easily dope nanophase ceramics with impurities at relatively low temperatures via their dense grain-boundary networks, with only few atomic jumps separating their grain interiors from grain boundaries, for example, should allow for efficient introduction of impurity levels into the band gaps of oxides and the control over electrical and optical properties that this would yield. Many other possibilities for engineering advanced ceramics with useful properties by means of the nanophase processing method will undoubtedly occur to the reader.

REFERENCES

1. K. Kimoto, Y. Kamiya, M. Nonoyama, and R. Uyeda, Jpn. J. Appl. Phys. 2, 702 (1963).
2. C. G. Granqvist and R. A. Buhrman, J. Appl. Phys. 47, 2200 (1976).
3. R. Birringer and H. Gleiter, in **Encyclopedia of Materials Science and Engineering**, Suppl. Vol. 1, R. W. Cahn, ed. (Pergamon Press, Oxford, 1988) p. 339.
4. R. W. Siegel and J. A. Eastman, Mater. Res. Soc. Symp. Proc. 132, 3 (1989).
5. R. P. Andres, R. S. Averback, W. L. Brown, L. E. Brus, W. A. Goddard, III, A. Kaldor, S. G. Louie, M. Moscovits, P. S. Peercy, S. J. Riley, R. W. Siegel, F. Spaepen, and Y. Wang, J. Mater. Res. 4, 704 (1989).
6. F. H. Froes and C. Suryanarayana, J. Metals 41 (6), 12 (1989).
7. J. Karch, R. Birringer, and H. Gleiter, Nature 330, 556 (1987).
8. R. W. Siegel, S. Ramasamy, H. Hahn, Z. Li, T. Lu, and R. Gronsky, J. Mater. Res. 3, 1367 (1988).
9. K. Yamauchi, S. Yatsuya, and K. Mihama, J. Cryst. Growth 46, 615 (1979).
10. M. Shiojiri and C. Kaito, J. Cryst. Growth 52, 173 (1981).
11. H. Gleiter, in **Deformation of Polycrystals: Mechanisms and Microstructures**, N. Hansen et al., eds. (Risø National Laboratory, Roskilde, 1981) p. 15.
12. H. Hahn, J. A. Eastman, and R. W. Siegel, Ceramic Transactions B 1, 1115 (1988).
13. R. S. Averback, H. Hahn, H. J. Höfler, J. L. Logas, and T. C. Shen, Mater. Res. Soc. Symp. Proc. 153, 3 (1989).
14. Z. Li, H. Hahn, and R. W. Siegel, Mater. Letters 6, 342 (1988).
15. J. A. Eastman, Mater. Res. Soc. Symp. Proc. 132, 27 (1989).
16. Z. Li, S. Ramasamy, H. Hahn, and R. W. Siegel, Mater. Letters 6, 195 (1988).
17. W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, **Introduction to Ceramics**, Second Edition (John Wiley & Sons, New York, 1976).
18. E. A. Barringer, Ph. D. Thesis, Massachusetts Institute of Technology (1983).
19. L. H. Edelson, M. S. Thesis, Lawrence Berkeley Laboratory, University of California at Berkeley (1986).
20. M. J. Mayo, R. W. Siegel, A. Narayanasamy, and W. D. Nix, to be published.