HIGH TEMPERATURE MATERIALS CHEMISTRY IX

Editor
Karl E. Spear

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Editor

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PREFACE

This book contains the proceedings of the 9th International Conference on High Temperature Materials Chemistry (HTMC IX) held at Penn State, University Park, PA on May 19-23, 1997. HTMC IX was part of a series of IUPAC-sponsored international conferences on this topic that are held every three years. The international character of this particular conference was extensive. Out of 115 papers presented, 64 were from 22 countries other than the USA. The professional expertise and activities of attendees were quite mixed, and there was a good distribution among academic, national laboratory, and industrial personnel.

The overall focus of HTMC IX was on the exchange of interdisciplinary information related to both the science and technology of high temperature materials, which include ceramics, metals, alloys, and composites. While seeking to fulfill this goal, the hope was that this meeting would help to inspire the development of new materials and processes which will overcome the limitations that currently hold back advances in technology. These advances include more efficient and cleaner energy sources and storage systems; smaller and more reliable electronic, magnetic, optical, and mechanical devices; lightweight, corrosion-resistant structural materials for use at elevated temperatures in extreme environments; and economic methods for recycling and safely disposing of our waste materials.

History of High Temperature Materials Chemistry Conferences

The conferences in this series have been formally sponsored by the Inorganic Chemistry Division, Commission II.3, "High Temperature Materials and Solid State Chemistry", of the International Union of Pure and Applied Chemistry (IUPAC). Below is a listing of some previous conference locations/years (the names of earlier conferences varied slightly from HTMC). Commission II.3 of IUPAC has settled on a period of three years between conferences, with a subcommittee chosen from past HTMC chairs and Commission members to make recommendations to Commission II.3 as to future conference locations and chairs.

HTMC III	1981	Harwell, UK
HTMC IV	1984	Sante Fe, NM USA
HTMC V	1987	Rome, Italy
HTMC VI	1989	Gaithersburg, MD USA
HTMC VII	1991	Orleans, France (not IUPAC sponsored)
HTMC VIII	1994	Vienna, Austria
HTMC IX	1997	State College, PA USA
HTMC X	2000	Juelich, Germany

Technical Program of HTMC IX

The interdisciplinary technical program for HTMC IX included presentations on measuring and predicting the chemistry related to processing, fabrication, behavior, properties and disposal of high temperature materials systems in both reactive and non-reactive environments. The program content ranged from experimental observations to predicting behavior, from scientific principles to engineering design, from atomic-scale models to performance while in use. The discussed materials ranged from metals to ceramics to polymer precursors to composites, and from high melting solids to liquids to gaseous molecules and ions. The common thread of interest that bonded this diverse mix of

participants was the desire to measure, predict, and understand the chemistry of materials at high temperatures in order to advance both materials science and materials technology.

The session topics for the HTMC IX conference program have also been used as the format for organizing this proceedings volume, and are listed below:

- Thermodynamics/Phase Equilibria/Chemical Bonding/Structure
- Waste Disposal and Environmental Issues
- Precursor Design for Ceramic Synthesis and Properties
- Interface Chemistry, Structure, Transport and Properties
- Special Synthesis Methods/Materials/Models
- Gas-Solid Reactions and Vapor Deposition Synthesis
- Gas Phase Chemistry/Clusters/Vaporization/Mass Spectrometry
- Leaching/Etching/Corrosion/Oxidation

The communication of the technical content was by oral communications, poster papers, and computer demonstrations. Nine plenary lectures provided detailed coverage of primary topic areas. Shorter invited contributions provided more detail on a particularly relevant body of research. Contributed oral papers were chosen to collectively provide a broad coverage of a specific session topic subject. Poster papers relevant to a specific session topic area were designated as such, and were clustered in the poster room to facilitate the communication of current knowledge. Posters were on display during the entire conference.

Because of the increasing chemical complexity of advanced materials, the extreme thermal and chemical environments to which they are being subjected, and the stringent specifications to which they must be fabricated, a focused portion of HTMC IX was devoted to computer modeling of the type that a typical experimentalist can use to more efficiently design laboratory research or pilot plant testing. ChemSage, FACT, MTData, Thermo-Calc and MALT2 thermochemical computer software were demonstrated, and conference participants had an opportunity to use the software and discuss its applications with experts. The hope was that these demonstrations and hands on use of thermochemical modeling software by participants would: (i) provide experimentalists with insight into how they could better use modeling techniques, and (ii) encourage more interaction and cooperation among experimental and modeling efforts around the world. Reliable models for predicting a material's behavior and lifetime at high temperatures are needed for both safety and economic reasons.

The plenary lectures given at HTMC IX are listed below:

- "Precursor Derived Ceramics," F. Aldinger, Max-Planck-Inst. Metallf., Germany
- "Thermodynamic Modeling of Solution and Ordered Phases - Application to Phase Diagram Calculations," I. Ansara, LTPCM-ENSEEG, France
- "High Temperature Chemical Aspects of Waste Disposal and Environmental Clean-up," B.R. Bowsher, AEA Technology, UK
- "Wide Temperature Range Observations on Reactions of Metal Atoms and Small Radicals," A. Fontijn, Rennsaeleer Polytechnique Institute, Troy, USA
- "Simulation of Surface Reactions," M. Frenklach, Univ. of California-Berkeley, USA
- "Thermal Plasma Synthesis of Diamond," S.L. Girshick, University of Minnesota, USA

- "High Temperature Oxidation of Ceramic Matrix Composites: SiC Matrices with BN Coated Fibers," N. Jacobson, NASA Lewis Research Center, USA
- "Interfacial Microchemistry," F.J.J. van Loo, Technical University-Eindhoven, The Netherlands
- "Enhancing Materials Design Capability through Understanding Multicomponent Phase Relationships," D.-S. Yan, Shanghai Inst. Ceramics, Chinese Academy Sci., China

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A NOVEL ROUTE FOR THE PREPARATION OF ULTRAFINE YTTRIA-DOPED ZIRCONIA POWDERS

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Ultrafine zirconia powders, doped with various amounts of yttrium oxide, have been prepared from inverse microemulsions consisting of cyclohexane as the oil phase, mixed poly(oxyethylene)$_5$ nonyl phenol ether (NP5) and poly(oxyethylene)$_9$ nonyl phenol ether (NP9) as the non-ionic surfactant, and aqueous solution containing zirconium (yttrium) salts as the water phase. The precipitation reaction between zirconium (yttrium) oxynitrate and ammonia solution was made to take place in the nanosized microemulsion domains. Subsequent calcination of the hydroxide precursors at 600 ^{o}C led to the formation of ultrafine zirconia powders. This paper also presents a comparison between the microemulsion-derived zirconia powders and that commercially available for particle size, size distribution and densification at various sintering temperatures.

INTRODUCTION

Yttria stabilized tetragonal zirconia is considered to be one of the most promising candidate materials for structural applications due to its excellent mechanical properties such as high fracture toughness and fracture strength. It has been extensively studied in recent years (1). Its performance is largely dependent on parameters such as the amount of yttria doped, grain size and size distribution, sintered density, and the type and amount of grain boundary phase present at grain boundaries and grain junctions in sintered ceramic.

Many novel techniques have been employed for the preparation of ultrafine zirconia powders, including aerosol reactions (2), spray pyrolysis (3), coprecipitation in emulsions (4) and the electrostatic atomization of liquid droplets into air (5). In recent years, several important ceramic powders have also been successfully prepared from water-in-oil microemulsions (6). It has been shown that the microemulsion-derived ceramic powders are finer in particle size, narrower in particle size distribution, higher in sinterability, and more homogeneous in composition than those prepared conventionally. An inverse microemulsion, which consists of an oil phase, a surfactant and an aqueous phase, is a thermodynamically stable isotropic dispersion of the aqueous phase in the continuous oil phase (7). The size of the aqueous droplets is in the range of 5 to 20 nm, rendering the microemulsion systems optically transparent. Chemical reactions, such as coprecipitation, will take place when droplets containing the desirable reactants collide with each other. Each of these aqueous droplets in the two microemulsion systems will thus be acting as a nanosized reactor for forming nanosized precursor particles.

The aim of the present work is to prepare and characterize an ultrafine yttria-doped zirconia powder via microemulsion processing route.

EXPERIMENTAL PROCEDURES

The starting materials used in the present work included: a high purity zirconyl nitrate solution (MEL Chemical Co., UK) in which the concentration of ZrO_2 was 207.7 mg/ml as analysed using atomic emission technique; yttrium (III) nitrate hexahydrate (> 99.9%, Acros Company, Belgium); a high purity cyclohexane (Analyzed Grade, J. T. Baker Inc., USA) and an ammonia solution (concentration: 28.0 - 30.0 wt%, AJAX Chemicals Co., Australia). A commercially available yttria-doped zirconia powder (TZ3Y), which was doped with 3 mol.% Y_2O_3, was characterised for comparison purpose.

The procedure of establishing a partial phase diagram at room temperature for the ternary system consisting of cyclohexane, NP5+NP9 and an aqueous solution has been detailed elsewhere (6). To locate the demarcation between the microemulsion and non-microemulsion regions, the aqueous phase was titrated into a mixture of given cyclohexane

to surfactant ratio. Thorough mixing of the three components was achieved using a Vortex mixer. Microemulsion compositions appear optically transparent when the size of aqueous droplets is in the range of 5 to 20 nm, due to the fact that the nanosized aqueous droplets do not cause a substantial degree of light scattering. A series of such demarcation points were obtained by varying the cyclohexane to surfactant ratio. Two types of aqueous phase was studied: 2.85 M $NH_3 \cdot H_2O$ and 0.570 M $ZrO(NO_3)_2$ containing 0.029 M and 0.036 M $Y(NO_3)_3$, respectively.

Two microemulsion compositions were prepared. They both consisted of 56.0 wt% cyclohexane, 24.0 wt% NP5/NP9 (2:1, wt%) and 20.0 wt% aqueous phase. The aqueous phase was either 0.570 M $ZrO(NO_3)_2$ + x M $Y(NO_3)_3$ (x = 0.029 or 0.036) or 2.85 M $NH_3 \cdot H_2O$. Precursors were prepared by mixing the two microemulsion systems together via vigorously stirring for 1 hour at room temperature. To retrieve the precipitates formed in microemulsions, the oil and surfactant phases were washed off using distilled ethanol, and the precursors were recovered by centrifugation, followed by vacuum-drying at room temperature for 48 hours. Oxides were then acquired by calcining the hydroxide precursors at 600 °C in a furnace for 3 hours using a heating/cooling rate of 5 °C/min. The resulting zirconia powders are referred to as Z2.5Y and Z3Y, corresponding to 0.570 M $ZrO(NO_3)_2$ + 0.029 M $Y(NO_3)_3$ and 0.570 M $ZrO(NO_3)_2$ + 0.036 M $Y(NO_3)_3$ in the aqueous phase, respectively.

The two as-dried precursors from the above processing route and the resulting zirconia powders were analyzed using X-ray diffraction (CuKα, Philips PW1729, 30 kv and 20 mA) for phases present. Crystallite sizes were estimated on the basis of line broadening at half maximum of the (111) peak. The calcined zirconia powders were characterised for particle/agglomerate size distribution using laser light scattering technique (Horiba LA-910). BET surface analyser (Nova 2000, Quantachrome) and scanning electron microscope (JEOL, JSM-35CF) were also employed to analyse the specific surface area, and particle/agglomerate morphology of the zirconia powders, respectively. The microemulsion-derived zirconia powders, together with the commercial one (TZ3Y), were then compacted into pellets of 10 mm in diameter at a pressure of 250 MPa, following by sintering at various temperatures ranging from 800 to 1500 °C at a heating/cooling rate of 10 °C/min. The sintered pellets were measured for sintered density (Ultrapycnometer 1000).

RESULTS AND DISCUSSION

Figures 1(a,b) show the partial phase diagrams established at room temperature for the ternary systems consisting of cyclohexane, NP5+NP9 and aqueous solution containing 2.85 M ammonia and 0.570 M $ZrO(NO_3)_2$ + 0.029M $Y(NO_3)_3$ respectively. In both systems, the microemulsion region increases with increasing surfactant to cyclohexane ratio. It is apparent that the composition of 56.0 wt% cyclohexane, 24.0 wt% NP5/NP9 (2:1, wt%) and 20.0 wt% aqueous phase is within the microemulsion region in both ternary

systems.

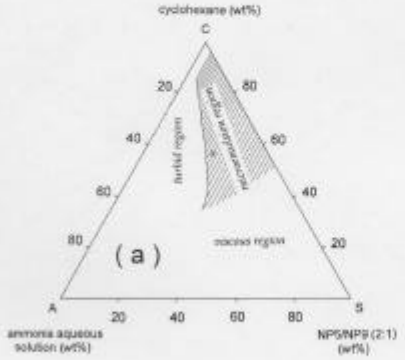
The as-dried zirconia precursors exhibit a broadened XRD trace, indicating that they were amorphous. Calcination at 600 °C for 3 hours resulted in the occurrence of crystallization in these precursors. Figure 2 shows that tetragonal is the only phase detectable in both Z2.5Y and Z3Y. This is different from the phases present in TZ3Y, in which there exists ~20 wt% monoclinic phase. The absence of monoclinic phase in the microemulsion-derived zirconia powders may be accounted by the much more refined crystallite sizes when compared with that of TZ3Y, although many other parameters may affect the phases present in a zirconia powder (8). As shown in Figure 2, the two microemulsion-derived zirconia powders exhibit a more apparent broadening of $(111)_T$ peak than that of TZ3Y. Using Scherrer equation (9), an average crystallite size of 7 nm was estimated for the former two, in contrast to ~22.5 nm for the latter.

The particle/agglomerate size and size distributions of the three powders are shown in Figure 3. The two microemulsion-refined powders are similar in particle/agglomerate size distribution (in the range of 0.1 to 1.5 μm), although Z2.5Y is slightly smaller in average particle size than that of Z3Y. Both are finer than TZ3Y, which covers the size range from 0.20 to 2.6 μm. This is supported by the specific surface areas of the three powders. For example, Z2.5Y and Z3Y exhibit a specific surface area of 89.6 and 106.9 m^2/g, respectively, in contrast to 11.6 m^2/g for TZ3Y. Therefore, the microemulsion-derived zirconia powders (11.1 and 9.3 nm for Z2.5Y and Z3Y, respectively) are much finer in discrete particle size than that of the commercially available one (85.6 nm).

Table I Characterization of Z2.5Y, Z3Y and TZ3Y

Powders	Z2.5Y	Z3Y	TZ3Y
mean particle size (nm) from light scattering	294	335	512
specific surface area (m^2/g) from BET	89.6	106.9	11.6
average particle diameter (nm) from BET (nm)	11.1	9.3	85.6
average crystallite size (nm) from XRD	7.0	6.9	22.5

Figures 4(a,b,c) are SEM micrographs showing the microstructure of the three zirconia powders. The two microemulsion-derived zirconia powders are similar in appearance. They both consist of small particle agglomerates (in the range of 100 nm), which are rounded in morphology, although small particle agglomerates can be seen. They are considerably different from TZ3Y, which is much larger in particle/agglomerate size and much more irregular in particle/agglomerate morpgology. These SEM observations are



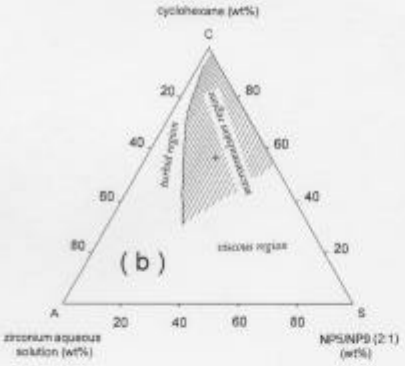


Fig. 1: Partial phase diagrams established at room temperature for the ternary system consisting of cycloheane, NP5+NP9, and aqueous solution containing (a) 2.85 M ammonia solution; (b) 0.570 M $ZrO(NO_3)_2$ and 0.029 M $Y(NO_3)_3$ solution.

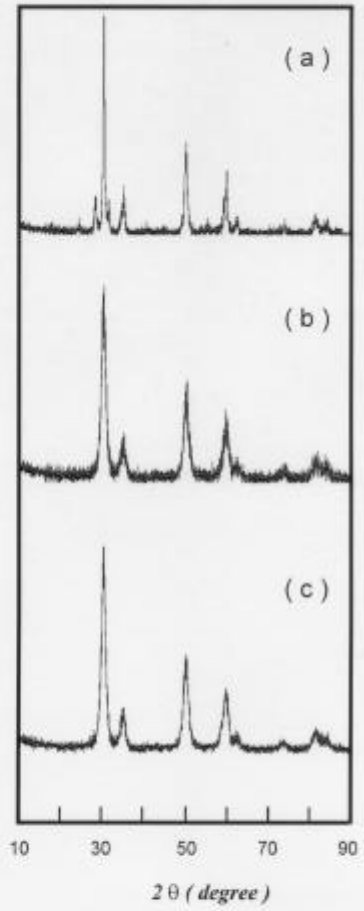


Fig. 2: XRD traces of the powders (a) TZ3Y; (b) Z2.5Y; and (c) Z3Y.

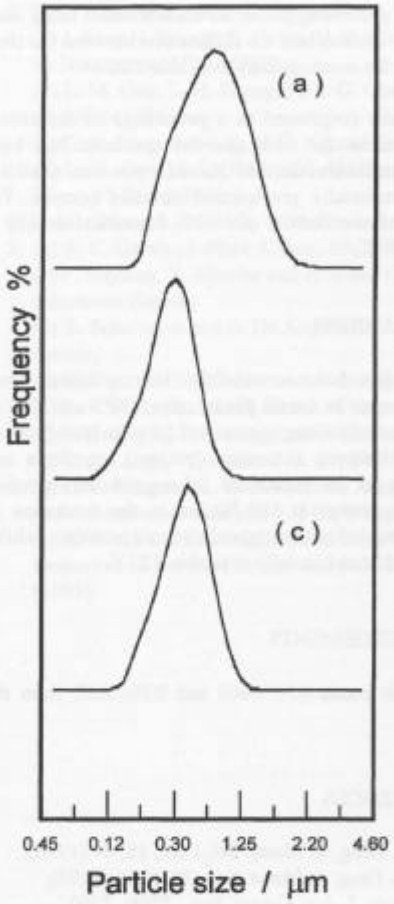


Fig. 3: The particle/agglomerate size distribution of powders.
(a) TZ3Y; (b) Z2.5Y calcined at 600 °C for 3 hours; (c) Z3Y calcined at 600 °C for 3 hours.

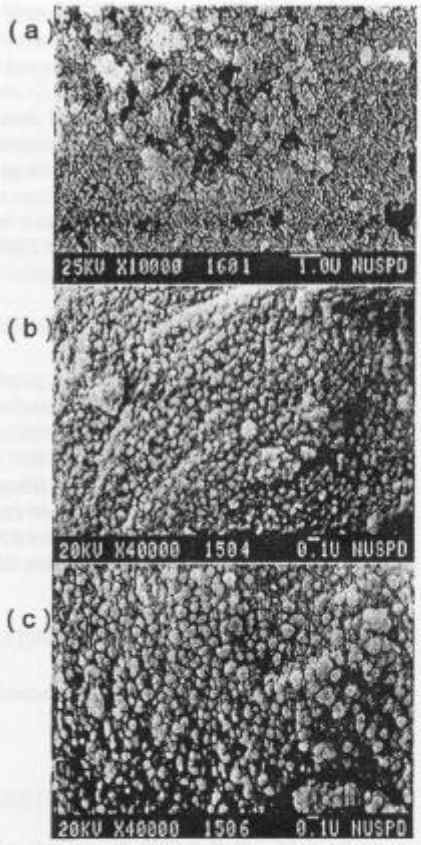


Fig. 4: SEM micrographs showing the yttria-doped zirconia powders.
(a) TZ3Y; (b) Z2.5Y; (c) Z3Y

in agreement with the experimental results of particle/agglomerate measurement using laser scattering technique discussed above. Table I summarizes the differences between the two-microemulsion-derived zirconia powders and the commercially available TZ3Y.

A preliminary study of sintered density (expressed as a percentage of theoretical density) as a function of sintering temperature for each sintered specimen has been performed. It has shown that the two microemulsion-derived zirconia powders exhibit a higher sinterability than that of the conventionally precipitated zirconia powder. For example, the former two were sintered to a relative density of > 90% theoretical density at 1200 °C and > 95% theoretical density at 1300 °C.

CONCLUSIONS

Ultrafine yttria-doped zirconia powders have successfully been prepared from inverse microemulsions consisting of cyclohexane as the oil phase, mixed NP5 and NP9 as the non-ionic surfactant, and aqueous solution containing zirconium (yttrium) oxnitrate as the water phase. The precipitation reaction between zirconium (yttrium) oxynitrate and ammonia solution was made to take place in the nanosized microemulsion domains. Subsequent calcination of the hydroxide precursors at 600 °C led to the formation of ultrafine zirconia powders. The microemulsion-derived tetragonal zirconia powders exhibit a much finer particle/agglomerate size than the commercially available TZ3Y.

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REFERENCES

1. (a) W. Z. Zhu, T. C. Lei, Y. Zhou and Z. S. Ding, J. Mater. Sci. Lett., **15**, 69 (1996);
   (b) W. Z. Zhu, T. C. Lei, Y. Zhou and Z. S. Ding, J. Mater. Sci., **30**, 6235 (1995);
   (c) S. D. Ramamurthi, Z. Xu and D. A. Payne, J. Am. Ceram. Soc., **73(9)**, 2760 (1990);
   (d) F. Wakai, S. Sakaguchi and Y. Matsuno, Advanced Ceramic Materials, **1(3)**, 259 (1986).
2. B. J. Ingebrethsen, E. Matijevic and R. E. Partch, J. Colloid Interface Sci., **95**, 228 (1981).
3. C. B. Martin, R. P. Kurosky, G. D. Maupin, C. Han, J. Javadpour and I. A. Aksay, Ceram. Trans., **12**, 99 (1990).
4. W. T. Minehan and G. L. Messing, J. Non-Cryst. Solids, **121**, 375 (1990).

5. E. B. Slamovich and F. F. Lange, Mater. Res. Soc. Symp. Proc., **121**, 257 (1988).
6. (a) J. Fang, J. Wang, S.-C. Ng, C.-P. Chew and L.-M. Gan, accepted for publication by Nanostruct. Mater. (1996);
(b) L. M. Gan, L. H. Zhang, H. S. O. Chan, C. H. Chew and B. H. Loo, J. Mater. Sci., **31**, 1071 (1996);
(c) G. K. Lim, J. Wang, S. C. Ng and L. M. Gan, Mater. Lett., **28**, 431 (1996);
(d) L. M. Gan, H. S. O. Chan, L. H. Zhang, C. H. Chew and B. H. Loo, Mater. Chem. Phys., **37**, 263 (1994).
7. T. H. Chieng, L. M. Gan, C. H. Chew and S. C. Ng, Polymer, **36**, 1941 (1995).
8. (a) R. C. Garvie, J. Phys. Chem., **69**, 1238 (1965) and references therein;
(b)Y. Suyama, T. Mizobe and A. Kato, Ceramurgia Int., **3(4)**, 141 (1977) and references therein;
(c) R. Srinivasan and R. De Angelis, J. Mater. Sci., **1(4)**, 583 (1986) and references therein;
(d) E. Tani, M. Yoshimura and S. Somiya, J. Am. Ceram. Soc., **66(1)**, 11 (1983);
(e) E. P. Butler and A. H. Heuer, J. Am. Ceram. Soc., **65(12)**, C-206 (1982);
(f) T. K. Gupta, F. F. Lange and J. H. Bechtold, J. Mater. Sci., **13** , 1464 (1978);
(g) F. F. Lange, J. Mater. Sci., **17**, 240 (1982).
9. (a) H. P. Klug and L. E. Alexander, X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials, p. 512, Wiley, New York, (1954);
(b) A. Wold and K. Dwight, Solid State Chemistry, Synthesis, Structure, and Properties of Selected Oxides and Sulfids, p. 20, Chapman & Hall, Inc., New York, (1993).