Pergamon

NanoStructured Materials, Vol. 8, No. 4, pp. 499-505, 1997
Elsevier Science Ltd

0965-9773/97 $17.00 + .00

PII S0965-9773(97)00179-7

ULTRAFINE ZIRCONIA POWDERS VIA MICROEMULSION PROCESSING ROUTE

Jiye Fang[1], John Wang[1]*, Ser-Choon Ng[2], Chwee-Har Chew[3] and Leong-Ming Gan[3]

[1]Department of Materials Science,
[2]Departments of Materials Science and Physics, and
[3]Departments of Materials Science and Chemistry
Faculty of Science, National University of Singapore, Singapore 119260

(Accepted April 9, 1997)

Abstract *— Nanosized zirconia powders have been prepared via inverse microemulsion processing routes, in which cyclohexane was used 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 an aqueous solution containing zirconium oxynitrate solution as the water phase. The precipitation reaction between zirconium oxynitrate and oxalic acid to form zirconium oxalate was made to take place in the nanosized microemulsion domains. Subsequent calcination of the oxalate precursors at 600°C led to the formation of ultrafine zirconia powders. Two synthesis routes, namely, a single-microemulsion processing route and a double-microemulsion processing route, were studied and compared. © 1997 Acta Metallurgica Inc.*

INTRODUCTION

Zirconia-based and zirconia-containing ceramics are a class of advanced structural materials due to their much more improved mechanical properties, such as fracture toughness and fracture strength, over those of many other ceramic materials in association with the stress-induced transformation toughening (1-5). Preparing a fine and agglomerate/aggregate-free zirconia powder is the first and perhaps the most important step in obtaining a sintered zirconia ceramic of desirable microstructure and therefore mechanical properties (6). Various chemistry-based novel approaches have been taken for the preparation of nanosized zirconia powders, including co-precipitation, sol-gel, hydrolysis, thermal decomposition, and hydrothermal processing (7-12). The degree of success of these processing techniques varies considerably from one to another.

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 (13,14). It has been successfully used to prepare several ceramic powder systems of nanosize (15-18). Many of the processing parameters, such as the concentration of inorganic salts in the aqueous phase and weight percentage of the aqueous phase in the microemulsion, affect the characteristics,

including the particle size, particle size distribution, agglomerate size and phases of the resulting ceramic powders. The objective of the present work is to investigate the feasibility of preparing ultrafine zirconia powders from inverse microemulsions, via both a single microemulsion and a double microemulsion processing route, respectively.

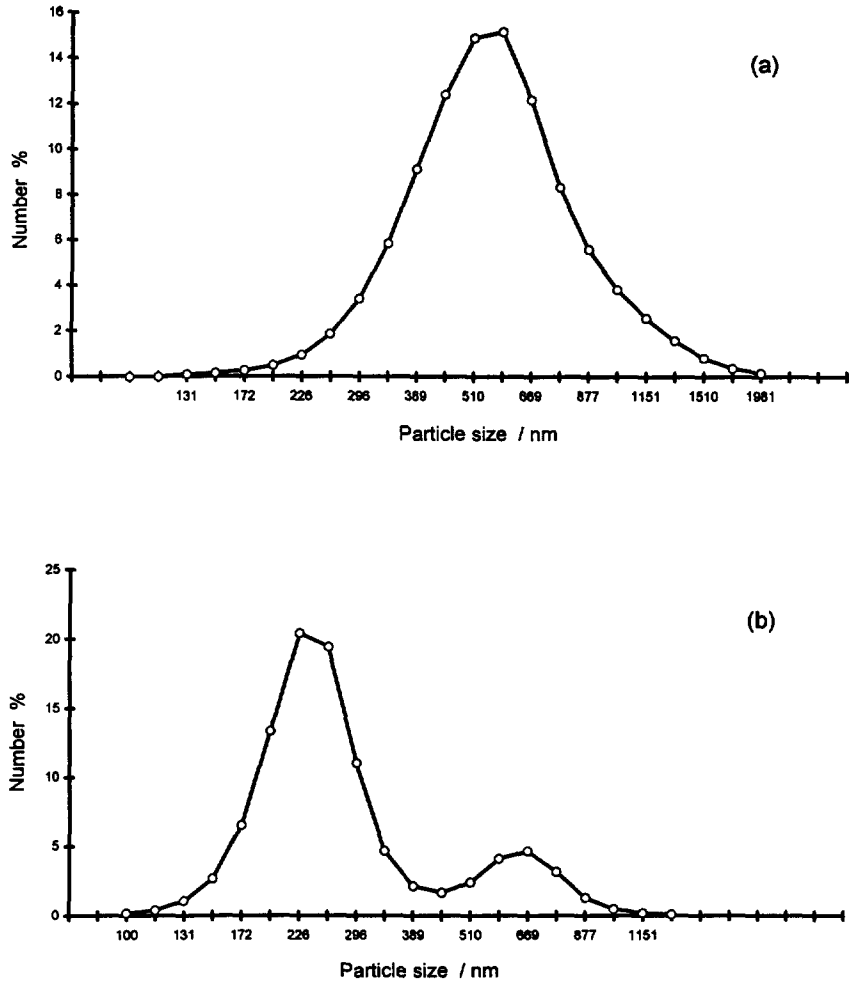
EXPERIMENTAL PROCEDURES

The starting materials used in the present work included a high purity zirconium oxynitrate solution (MEL, Manchester, UK), a high purity cyclohexane, an oxalic acid (both from J.T. Baker, USA), and mixed poly (oxyethylene)$_5$ nonyl phenol ether (NP5) and poly (oxyethylene)$_9$ nonyl phenol ether (NP9) (weight ratio: 2:1, Albright and Wilson Asia Pte Ltd, Singapore). Three microemulsion compositions were prepared: (i) 61.2 wt.% cyclohexane + 26.3 wt.% NP5/NP9 + 12.5 wt.% 0.28 M $ZrO(NO_3)_2$; (ii) 65.6 wt.% cyclohexane + 21.9 wt.% NP5/NP9 + 12.5 wt.% 0.28 M $ZrO(NO_3)_2$; and (iii) 65.6 wt.% cyclohexane + 21.9 wt.% NP5/NP9 + 12.5 wt.% 0.67 M $H_2C_2O_4$.

Two synthesis routes, namely single-microemulsion and double-microemulsion processing routes, were used to prepare the zirconium oxalate precursors. In the single-microemulsion route, 0.67 M oxalic acid was titrated drop by drop into the microemulsion consisting of 61.2 wt.% cyclohexane, 26.3 wt.% NP5/NP9 and 12.5 wt.% aqueous phase containing 0.28 M $ZrO(NO_3)_2$. In the double-microemulsion processing route, the precipitation reaction was brought about by mixing the microemulsion containing 12.5 wt.% of 0.28 M $ZrO(NO_3)_2$ into the one containing 12.5 wt.% of 0.67 M $H_2C_2O_4$. Thorough mixing was achieved by vigorously stirring the mixture for more than 15 minutes. To retrieve the oxalate particles, ethanol was used to destabilize the microemulsion systems, followed by centrifugation recovery. The precursors were then dried in an oven at 90°C, before they were calcined at 600°C for 4 hours to form zirconia powders. Particle size and particle size distribution of the calcined zirconia powders were analyzed using laser scattering techniques (Horiba LA-910). Nova-2000 BET analyzer was used to measure the specific surface area and Philips PW179 X-ray diffractometer (CuKα) was used to analyze phases present in the calcined zirconia powders. The particle/agglomerate morphology of the microemulsion-derived zirconia powders was characterized using a scanning electron microscope (SEM, Jeol-JSM 35-CF).

RESULTS AND DISCUSSION

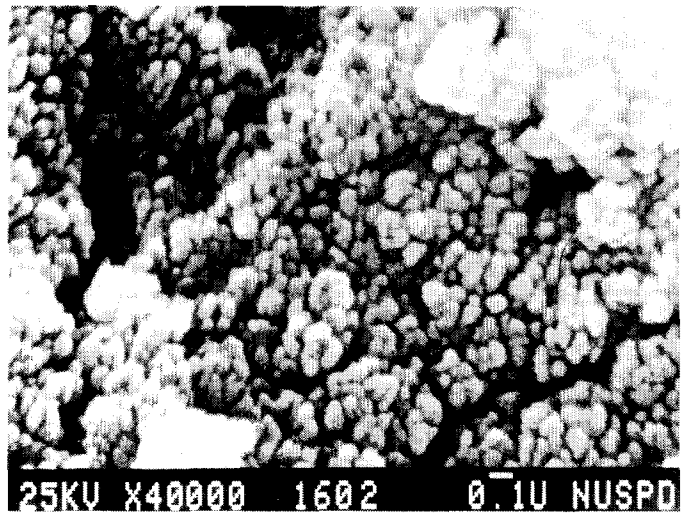
The microemulsion composition of 61.2 wt.% cyclohexane, 26.3 wt.% NP5/NP9 and 12.5 wt.% aqueous phase containing 0.28 M $ZrO(NO_3)_2$ remained transparent when the required amount (calculated on the basis of stoichiometry) of 0.67 M oxalic acid was added. In the double-microemulsion processing route, the mixture was also transparent when compositions (ii) and (iii) were mixed together. Therefore, the precipitation reaction between zirconium oxynitrate and oxalic acid was expected to take place in the nanosized aqueous domains for both processing routes. The reacted compositions became slightly milky when they were left undisturbed for more than 24 hours. This is believed to be due to the coalescence of nanosized oxalate particles in the microemulsions.



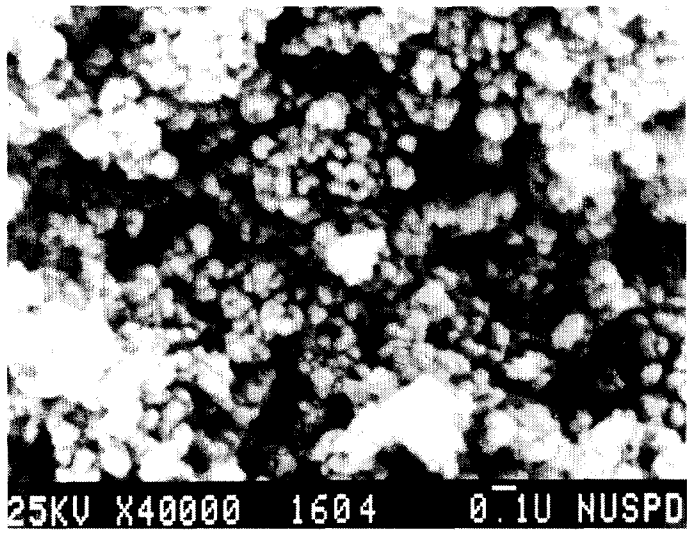
Figures 1(a,b): The particle size distribution of calcined zirconia powders, prepared by combining 0.28 M $ZrO(NO_3)_2$ and 0.67 M $H_2C_2O_4$ via the single-microemulsion and double-microemulsion processing routes, respectively.

Figures 1(a,b) show the particle size distribution of the calcined zirconia powders at 600°C for 4 hours, prepared via the single-microemulsion and double-microemulsion processing routes, respectively. The average particle size of the single-microemulsion derived zirconia (559 nm) is almost twice that of the double-microemulsion derived zirconia powder (295 nm). Specifically, the particle size distribution of the former covers a wide size range from 100 nm up to 2.0 μm. In contrast, more than 80% of the double-microemulsion derived zirconia particles are smaller than 400 nm. BET surface analysis showed that the two powders exhibited similar specific surface areas, 52.2 and 49.8 m^2/g for the single-microemulsion and double-microemulsion derived zirconias, respectively. These specific surface area values indicate that the discrete particle sizes

(a)



(b)



Figures 2(a,b): Two SEM micrographs showing the microstructure of the calcined zirconia powders at 600°C for 4 hours, prepared via the single-microemulsion and double-microemulsion processing routes, respectively.

(19 to 20 nm) are very similar in the two zirconia powders. It may also be concluded that the particle size distribution curves shown in Figures 1(a,b) represent the agglomerate size distributions in the two powders, respectively. As shown in Figures 2(a,b), particle agglomeration occurs in both the zirconia powders. However, the double-microemulsion derived zirconia powder exhibits a lower degree of particle agglomeration than that of the single-microemulsion derived zirconia powder.

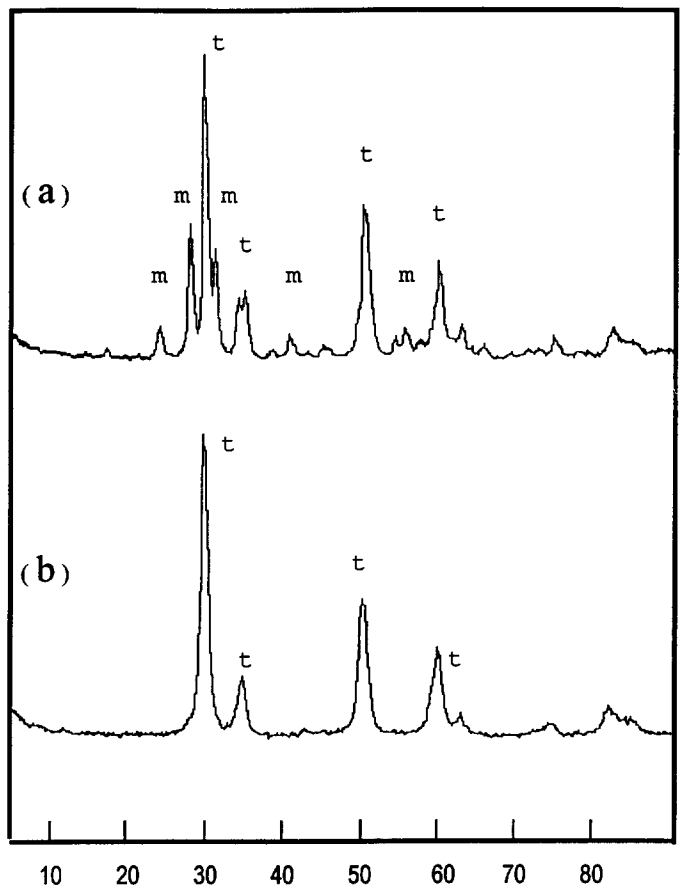


Figure 3: XRD traces for the zirconia powders prepared via the single-microemulsion (a) and double-microemulsion (b) processing routes, respectively. "m": monoclinic; "t": tetragonal.

The phases present in the single-microemulsion derived zirconia powder are also different from those in the double-microemulsion derived zirconia powder when they are calcined at 600°C for 4 hours. As shown in Figure 3, the latter consists of 100% tetragonal zirconia and the former consists of a mixture of tetragonal and monoclinic phases. It was estimated using the equation of Garvie and Nicholson (19) that the single-microemulsion derived zirconia powder contained >40% monoclinic phase. The difference in phases present in these two zirconia powders may be accounted for by the difference in processing conditions, although there exist strong arguments with respect to how and why the metastable tetragonal and/or cubic phases are retained in many chemistry-derived zirconia powders (7, 20-23). In the single-microemulsion processing route, titrating 0.67 M oxalic acid into the microemulsion containing 12.5 wt.% 0.28 M $ZrO(NO_3)_2$, led to an apparent increase in the overall content of aqueous phase in the microemulsion and, therefore,

an increase in the overall size of aqueous droplets (13,14). In the double-microemulsion processing route however, combining the two microemulsions containing the same amount of aqueous phases (12.5 wt.% of 0.28 M $ZrO(NO_3)_2$ and 0.67 M $H_2C_2O_4$, respectively) did not result in an increase in the overall content of aqueous phase in the mixed microemulsion. It may, therefore, be believed that the oxalate precursor was formed in smaller aqueous domains in the double-microemulsion processing route than those in the single-microemulsion processing route. A decrease in the domain size of aqueous droplets, due to a decrease in aqueous content in the microemulsion, will lead to an apparent decrease in the size of oxalate particles. This may, in turn, result in smaller crystallite sizes in the double-microemulsion derived zirconia powder than those in the single-microemulsion derived zirconia powder, when calcined at 600°C. As has been established, small enough crystallites will occur in tetragonal form as a result of high surface area (24). As shown in Figure 3, a noticeably higher degree of peak broadening is observed in the XRD trace for the double-microemulsion derived zirconia powder than that for the single-microemulsion derived zirconia powder. It was estimated, using Scherrer equation (25), that the former exhibited a crystallite size of 7.8 nm , compared to 11.5 nm for the latter.

CONCLUSIONS

Nanosized zirconia powders have been prepared from microemulsions via both a single-microemulsion and a double-microemulsion processing route, using $ZrO(NO_3)_2$ solution and oxalic acid as the starting materials. The precipitation reaction between zirconium oxynitrate and oxalic acid was made to take place in the nanosized aqueous domains of the inverse microemulsions, which contained cyclohexane as the oil phase and mixed poly (oxyethylene)$_5$ nonyl phenol ether (NP5) and poly (oxyethylene)$_9$ nonyl phenol ether (NP9) as the nonionic surfactant. Subsequent calcination of the microemulsion-derived precipitates at 600°C led to the formation of ultrafine zirconia powder particles. The double-microemulsion derived zirconia powder is monoclinic-free and finer in particle size than the single-microemulsion derived zirconia powder.

ACKNOWLEDGMENTS

The authors wish to thank Madam Phua Swee Wah of the Department of Physics at the National University of Singapore for her help in using scanning electron microscope. This work was supported by research grants RP950613 and RP950605 from the National University of Singapore.

REFERENCES

1. Lange, F.F., *Journal of Materials Science*, 1982, 17, 225.
2. Wang, J., and Stevens, R., *Journal of Materials Science*, 1989, 24, 3421.
3. Wang, J., and Stevens, R., *Journal of Materials Science*, 1988, 23, 804.
4. Wang, J., Zheng, X., and Stevens, R., *Journal of Materials Science*, 1992, 27, 4348.
5. Wang, J., Wadsworth, I., Rainforth, W.M., and Stevens, R., *Journal of the European Ceramic Society*, 1992, 10, 21.
6. Lange, F.F., *Journal of the American Ceramic Society*, 1989, 72, 3.

7. Djuricic, B., Pickering, S., McGarry, D., Glaude, P., Tambuyser, P., and Schuster, K., *Ceramics International*, 1995, 21, 195.
8. Bourell, D.L., and Kaysser, W., *Journal of the American Ceramic Society*, 1993, 76, 705.
9. Debsikdar, J.C., *Journal of Non-Crystalline Solids*, 1986, 86, 231.
10. Ward, D.A., and Ko, E., *Chemistry of Materials*, 1993, 5, 956.
11. Li, C., Yamai, I., Murase, Y., and Kato, E., *Journal of the American Ceramic Society*, 1989, 72, 1479.
12. Huang, Y., and Guo, C., *Powder Technology*, 1992, 72, 101.
13. Rosano, H.L., and Claussen, M., *Microemulsion Systems*, Marcel Dekker Inc, New York, 1987.
14. Martellucci, S., and Chester, A.N., ed., *Progess in Microemulsions*, Plenum Press, New York, 1989.
15. Gan, L.M., Chan, H.S.O., Zhang, L.H., Chew, C.H., and Loo, B.H., *Material Chemical Physics*, 1994, 37, 263.
16. Gan, L.M., Zhang, L.S., Chan, H.S.O., Chew, C.H., and Loo, B.H., *Journal of Materials Science*, 1996, 31, 1071.
17. Wang, J., Lee, S.E.., Ng, S.C.and Gan, L.M., *Materials Letters*, 1997, 30, 119.
18. Lim, G.K., Wang, J., Ng, S.C., and Gan, L.M., *Materials Letters*, 1996, 28, 431.
19. Garvie, R.C., and Nicholson, P.S., *Journal of the American Ceramic Society*, 1972, 55, 303.
20. Benedetti, A., Fagherazzi, G., Pinna, F., and Polizzi, S., *Journal of Materials Science*, 1990, 25, 1473.
21. Srinivasan, R., Simpson, S., Harris, J.M., and Davis, B.H., *Journal of Materials Science Letters*, 1991, 10, 352.
22. Mamott, G.T., Barnes, P., Tarling, S.E., Jones, S.L., and Norman, C.J., *Journal of Materials Science*, 1991, 26, 4054.
23. Wu, F.C., and Yu, S.C., *Journal of Materials Science*, 1990, 25, 970.
24. Garvie, R.C., *Journal of Physical Chemistry*, 1965, 69, 1238.
25. Klug, H.P., and Alexander, L.E., *X-ray Diffraction Procedures*, Wiley, New York, 1954.