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Synthesis of nanocrystalline ZrO_2 powders by mechanochemical reaction of $ZrCl_4$ with LiOH

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Abstract

Mechanochemical reaction of anhydrous $ZrCl_4$ with LiOH has been used to synthesize nanocrystalline powders of ZrO_2. The mechanism of chemical reaction was found to depend on the presence of LiCl diluent in the initial reactant mixture. In the absence of LiCl diluent, reaction of the precursors occurred in a combustive manner and resulted in the formation of agglomerated nanoparticles of tetragonal ZrO_2 embedded within a matrix of LiCl and $LiCl{\cdot}H_2O$. Continued milling after the combustion event resulted in a progressive loss of specific surface area and transformation of the tetragonal ZrO_2 to the equilibrium monoclinic structure. Dilution of the initial reactant mixture with 4LiCl suppressed combustive reaction. Reaction of the precursors occurred gradually and resulted in the formation of an amorphous ZrO_2 gel that crystallized with the tetragonal structure on calcination at 500 °C for 1 h.

Keywords: Mechanochemical processing; Phase evolution; Powders-chemical preparation; ZrO_2

1. Introduction

The kinetics of solid-state chemical reactions are ordinarily limited by the rate at which the reactant species are able to diffuse across phase boundaries and through intervening product layers.[1] As a result, conventional solid-state processing techniques generally require the use of high temperatures to ensure that diffusion rates are maintained at sufficiently high level. However, recent studies have shown that the necessity for high processing temperatures can be avoided through the use of mechanochemical processing.[2]

Mechanochemical processing uses high-energy mechanical processing to induce structural and chemical changes in a solid-state powder charge. In this process, collisions between the grinding media cause repeated welding and fracture of the powder charge, thus developing and dynamically maintaining a large interfacial contact area between the reactant phases. As a consequence, solid-state reactions that would otherwise be inhibited by kinetic constraints can readily be promoted without need of applied heating.[2]

Mechanically activated exchange reactions have recently been examined for the synthesis of ultrafine powders. In this process chemical precursors undergo reaction, either during milling or during subsequent low temperature heat treatment, to form a nanocrystalline composite consisting of ultrafine particles embedded within a salt matrix. The ultrafine powder is then recovered by removing the salt through a simple washing procedure.[3–11] This technique has successfully been used to synthesize a wide variety of materials including transition metals,[3] magnetic intermetallics,[4] sulfide semiconductors,[5] and oxide ceramics.[6–11]

This paper presents the results of an investigation into the synthesis of nanocrystalline ZrO_2 powders by mechanochemical reaction of anhydrous $ZrCl_4$ with LiOH. The effect of milling time and diluent additions on the reaction mechanism, average particle size, and phase content is reported and discussed.

2. Experimental techniques

Reactant mixtures were milled within a hardened steel vial using a Spex 8000 mixer/mill. All millings used a 10 g powder charge with 20 9.5 mm stainless steel balls as the grinding media. Milling times ranged from 1 min

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up to 24 h. To ensure an inert atmosphere during milling, the grinding media and reactants were loaded into the vial whilst within a high-purity argon filled glovebox. In order to detect combustion of the reactant powder charge during milling, the temperature of the vial was continuously measured by a thermocouple attached to the outer surface.

To remove the LiCl by-product phases, the reacted powders were washed several times with deionised water and methanol in an ultrasonic bath. Following each wash, the ZrO_2 powder was recovered from the solvent by means of centrifugation and decantation. Washed powders were subsequently dried for several h in air at approximately 80 °C.

The chemical evolution of the reactant mixtures during processing was followed by X-ray diffraction (XRD) using a Siemens D5000 diffractometer. The average crystallite size of the washed powders was estimated from the peak breadth using the Scherrer equation.[12] The tetragonal volume fraction of the washed powders was derived from the integral peak intensities using the equations given by Toraya et al.[13]

Simultaneous thermogravimetric–differential thermal analysis (TG–DTA) was performed using a Rigaku Thermoflex system. Due to the hygroscopic nature of the chemicals involved, the sample crucibles were loaded within the argon filled glovebox and the measurements were performed under a flowing argon atmosphere. A heating rate of 20 °C/min was used for all measurements.

Specific surface area of the washed powders was measured by five-point BET gas adsorption using a Micromeretics Gemini 2360 instrument. All powders were vacuum degassed at 200 °C for 1 h prior to analysis. The measured values of specific surface area were used to derive estimates of the average particle diameter through the relation given by $D=6/S\rho$, where D is the average particle diameter, S is the specific surface area, and ρ is particle density.

Particle morphology of the washed powders was examined by transmission electron microscopy (TEM) using a Philips 430 microscope with a beam energy of 300 keV. Samples were prepared by ultrasonically dispersing the washed powder in ethanol and then evaporating a drop of the dispersion on a carbon coated specimen grid.

3. Experimental results

3.1. Undiluted reaction

Fig. 1 shows the vial temperature as a function of time during milling of $ZrCl_4+4LiOH$. The temperature gradually increased for the first min of milling as a result of heat generated by collisions of the grinding media. This was followed by a sharp temperature spike, which is characteristic of the sudden heat release associated with mechanically activated combustion reactions. Following the combustion event, the vial temperature leveled off to a constant steady-state value.

Immediately following the temperature spike, the powder charge was partially fused onto the grinding media and the interior of the vial. This suggests that the heat liberated by the combustion reaction was sufficient to cause at least partial melting of the reaction products. Further milling dislodged the fused powder from the grinding surfaces, thus allowing further mechanochemical processing of the powder after the combustion event.

Fig. 2 shows the XRD pattern of the $ZrCl_4+4LiOH$ reactant mixture following (a) the combustion event and (b) subsequent washing. The pattern of the combusted powder consists of diffraction peaks corresponding to $LiCl{\cdot}H_2O$, LiCl, and tetragonal ZrO_2. No peaks corresponding to either reactant phase are evident, which suggests that complete reaction of the precursors occurred during the combustion event. Following washing, only those peaks corresponding to tetragonal ZrO_2 remained, indicating the successful removal of the LiCl by-product phases.

Continued milling of the powder charge after the combustion event was found to result in a progressive transformation of the tetragonal ZrO_2 reaction product to the equilibrium monoclinic structure. This behavior is illustrated in Fig. 3, which shows XRD patterns of washed ZrO_2 powders that were synthesized from $ZrCl_4+4LiOH$ using milling times ranging from 1 min up to 24 h. The pattern of the powder that was prepared using a milling time of 1 min contains only the (111) tetragonal diffraction peak. Milling for 2 h resulted in the appearance of monoclinic diffraction peaks. The intensity of these peaks increased with further milling at the expense of the tetragonal peak.

Fig. 4 shows the phase content of the washed ZrO_2 powder as a function of milling time. The monoclinic volume fraction rapidly increased with milling time up to a steady-state value of approximately 86%. Also shown in Fig. 4 is the variation in the BET particle size and XRD crystallite size. The particle size estimated from BET measurements shows a near linear increase with milling time from approximately 9 to 13 nm. In contrast, the XRD crystallite sizes of the tetragonal and monoclinic phases remained roughly constant with milling time.

Fig. 5 shows bright field TEM images of washed ZrO_2 powders synthesized from $ZrCl_4+4LiOH$ using milling times of (a) 1 min and (b) 24 h. The powder prepared using the shorter milling time consists predominantly of highly agglomerated particles. Milling for 24 h evidently resulted in compaction of these agglomerates, which accounts for the increase in BET particle size with continued milling after the combustion event.

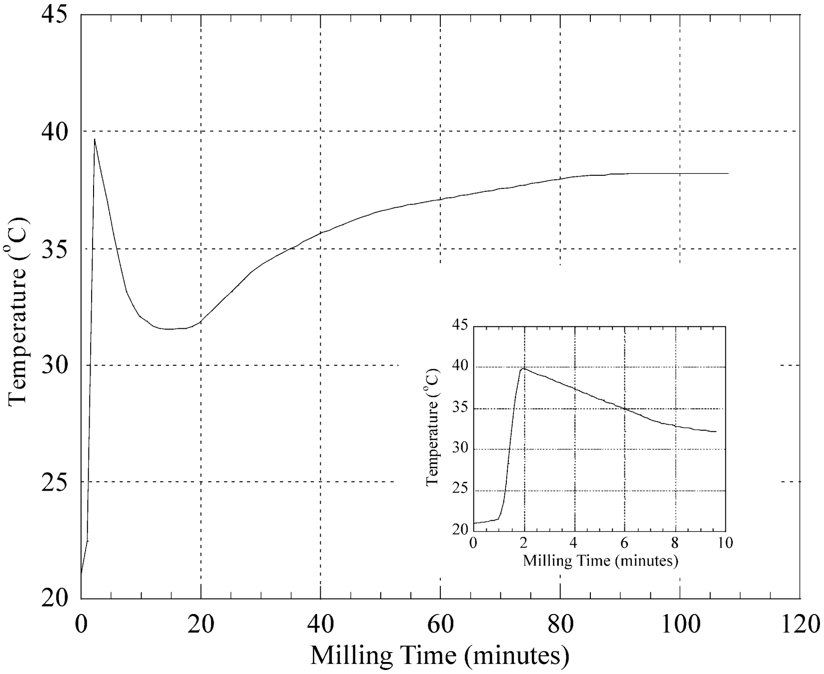

Fig. 1. Vial temperature as a function of time during milling of $ZrCl_4 + 4LiOH$.

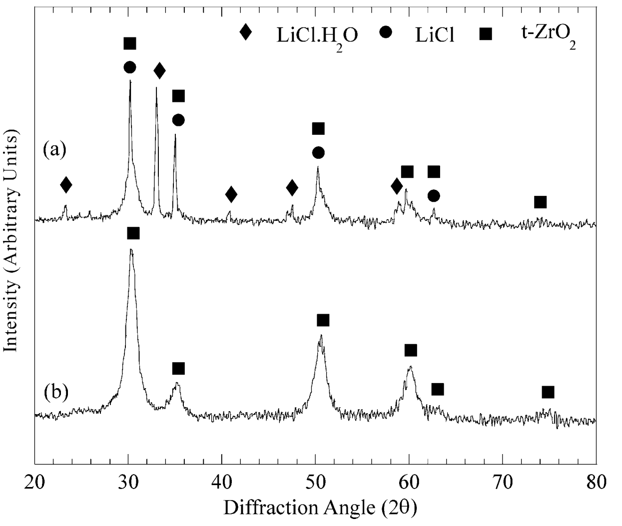

Fig. 2. XRD pattern of $ZrCl_4 + 4LiOH$ following (a) milling for 1 min and (b) washing.

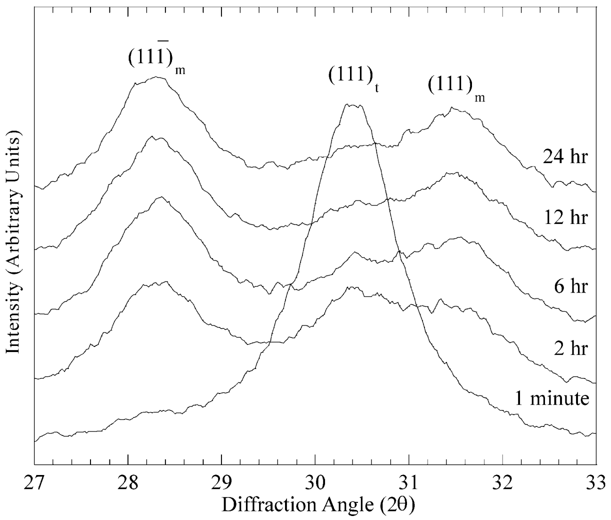

Fig. 3. XRD pattern of washed ZrO_2 synthesized from $ZrCl_4 + 4LiOH$ using milling times ranging from 1 min to 24 h.

3.2. Diluted reaction

Dilution of the $ZrCl_4 + 4LiOH$ with 4 mol of LiCl was found to suppress combustive reaction of the precursors. Measurement of the vial temperature during milling $ZrCl_4 + 4LiOH + 4LiCl$ revealed only a gradual increase up to a steady-state value, as would be expected for a gradual reaction mechanism. The reaction was essentially complete following 6 h of milling and yielded a hydrated ZrO_2 product with an amorphous structure.

Fig. 6 shows the XRD pattern of $ZrCl_4 + 4LiOH + 4LiCl$ following (a) milling for 6 h, (b) washing, and (c) calcination at 600 °C for 1 h. The pattern of the as-milled powder contains diffraction peaks corresponding to LiCl and $LiCl{\cdot}H_2O$. No other peaks are evident, which suggests that the reaction was complete and that the ZrO_2 reaction product was amorphous. Consistent with this assertion, the pattern of the washed powder contains no readily discernible diffraction peaks. Calcination of the washed powder resulted in the appearance of tetragonal ZrO_2 diffraction peaks.

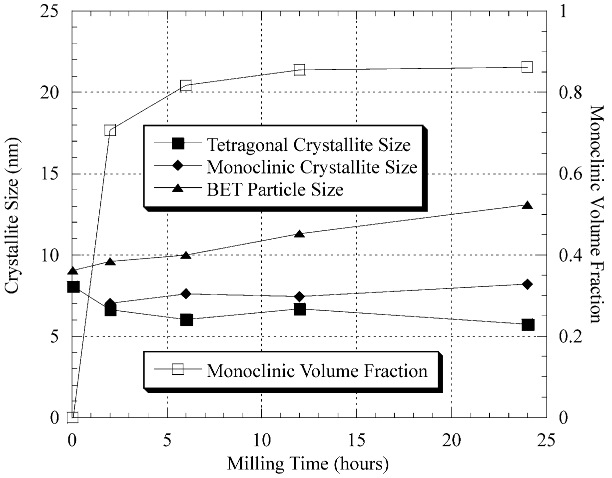

Fig. 4. Crystallite size and phase content as functions of milling time for ZrO_2 synthesized from $ZrCl_4+4LiOH$.

Fig. 7 shows TG–DTA traces of $ZrCl_4+4LiOH+4LiCl$ that was milled for 6 h. Mass loss due to the evolution of water vapor occurred in two stages. The first stage was comparatively rapid and appears to be associated with the two endothermic events located at approximately 86 and 130 °C. This was followed by a second stage of gradual mass loss that continued until approximately 520 °C. The exothermic peak at approximately 480 °C corresponds to crystallization of the tetragonal ZrO_2 phase. The large endothermic peak at high temperature was due to melting of the LiCl phase.

The first stage of mass loss and the accompanying endothermic events can be attributed to evaporation of free water and decomposition of the $LiCl·H_2O$ phase: the free water either being produced by mechanochemical reaction during milling or acquired during transfer and handling of the hygroscopic powder outside of the argon filled glovebox. The second stage of mass loss appears to be due to calcination of the amorphous ZrO_2 phase. The theoretical mass% of water produced by reaction of $ZrCl_4+4LiOH+4LiCl$ is approximately 7.23%, which is slightly less than the total mass loss observed by thermal analysis of the as-milled powder. This suggests that the powder did indeed acquire some additional water from the atmosphere.

The gradual reaction mechanism of the diluted system suggests that nanocrystalline ZrO_2 powders could be synthesized by milling the precursors for a short duration and then driving the reaction to completion by a subsequent low temperature heat-treatment. This possibility was confirmed by milling $ZrCl_4+4LiOH+4LiCl$ reactant mixtures for times ranging from 10 min up to 6 h and then heat-treating at 450 °C for 30 min. Fig. 8 shows the XRD patterns of the washed ZrO_2 powders. Short milling times yielded powders composed of both monoclinic and tetragonal polymorph. The volume fraction of the monoclinic polymorph decreased with milling time. The peak broadening initially increased with milling time before decreasing to a steady state value.

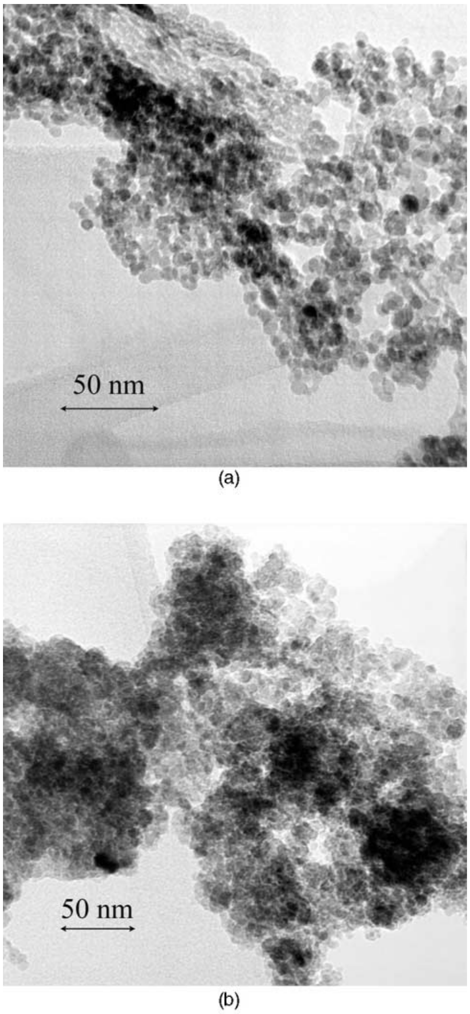

Fig. 5. Bright field TEM images of washed ZrO_2 synthesized from $ZrCl_4+4LiOH$ using milling times of (a) 1 min and (b) 24 h.

Fig. 9 shows the crystallite size and phase content of the washed ZrO_2 powder as functions of milling time. Both the XRD and BET crystallite sizes show a similar variation. The crystallite size initially decreased before reaching a minimum and then rising to a steady-state value. The tetragonal volume fraction increased from approximately 50% after 10 min of milling to 100% following 3 h.

Fig. 10 shows bright TEM images of washed ZrO_2 synthesized from $ZrCl_4+4LiOH+4LiCl$ reactant mixtures using milling times of (a) 10 min, (b) 30 min, and (c) 3 h. Powder synthesized using a milling time of 10 min consists of distinct crystallites. A milling time of 30 min yielded a powder consisting of aggregates of smaller crystallites. Following 3 h of milling the powder consists of large particles that are composed of aggregated crystallites.

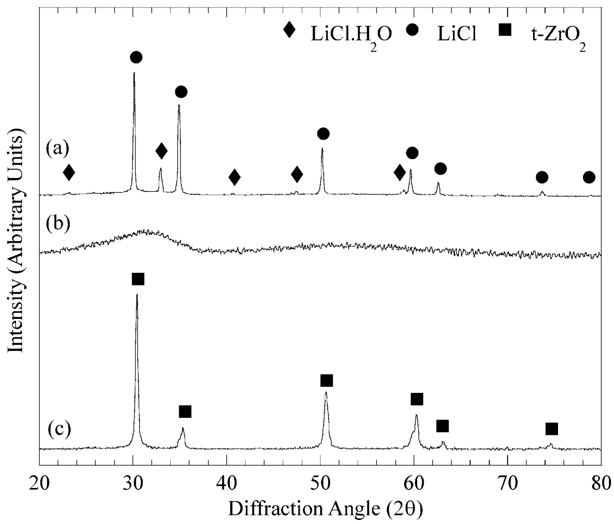

Fig. 6. XRD pattern of $ZrCl_4 + 4LiOH + 4LiCl$ following (a) milling for 6 h, (b) washing, and (c) calcination at 600 °C for 1 h.

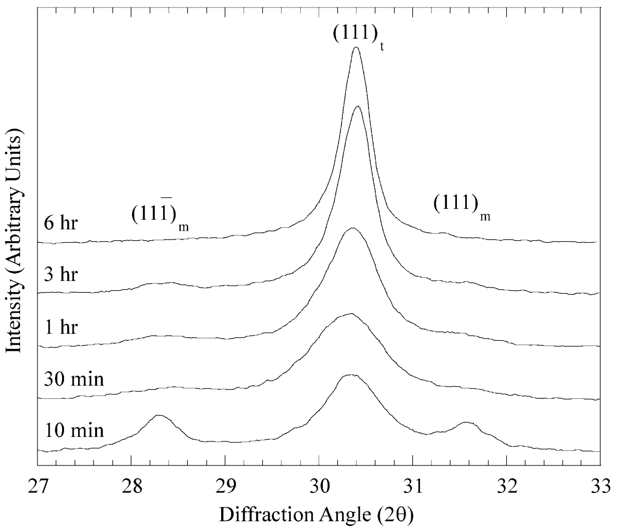

Fig. 8. XRD patterns of washed ZrO_2 powders synthesized from $ZrCl_4 + 4LiOH + 4LiCl$ using milling times ranging from 10 min to 6 h.

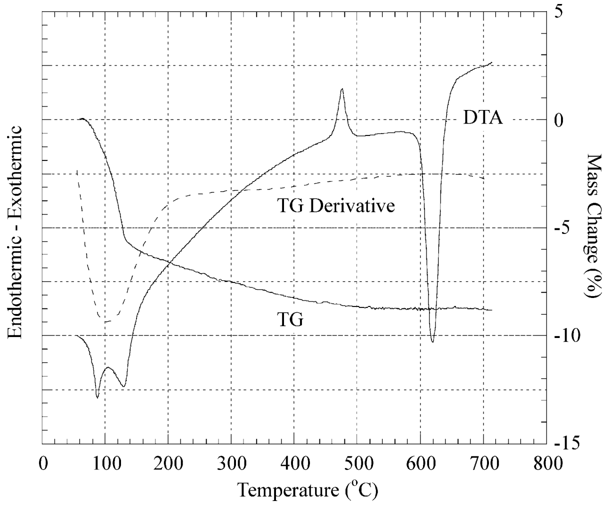

Fig. 7. TG–DTA traces of $ZrCl_4 + 4LiOH + 4LiCl$ that was milled for 6 h.

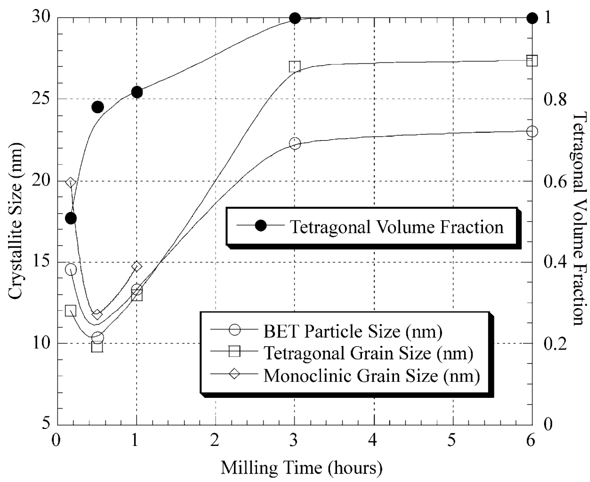

Fig. 9. Crystallite size and phase content as functions of milling time for washed ZrO_2 synthesized from $ZrCl_4 + 4LiOH + 4LiCl$.

4. Discussion

4.1. Reaction mechanism

Chemical reaction during milling either occurred gradually or combustively depending on the presence of LiCl diluent in the initial reactant mixture. This behavior is consistent with previous studies of mechanochemical reaction systems, which have shown that inert diluents inhibit combustive reaction by absorbing heat, reducing the interfacial contact area between the reactant phases, and slowing the overall rate of heat transfer.[8]

An earlier study of ZrO_2 synthesis by mechanically activated reaction of $ZrCl_4 + 2Li_2O$ found that the precursors only underwent chemical reaction during post-milling heat-treatment. Milling merely resulted in amorphisation of the $ZrCl_4$ phase and overall microstructural refinement.[7] Such behaviour is in distinct contrast to that observed in the present study, where reaction of the precursors occurred during milling. This difference in reaction mechanism can be attributed to the use of a hydrated exchange reagent. Previous studies have shown that incipient water can significantly influence the kinetic behaviour of mechanochemical reactions.[10,11] For example, it has been found that $ZrCl_4$ reacts with $Ca(OH)_2$ during milling but only during post-milling heat-treatment with CaO.[10] Similar behaviour has also been observed for mechanochemical reaction of $FeCl_3$ with $Ca(OH)_2$ and CaO.[11]

4.2. Particle size and agglomeration

Combustive reaction of $ZrCl_4 + 4LiOH$ was found to yield a highly agglomerated ZrO_2 powder with an aver-

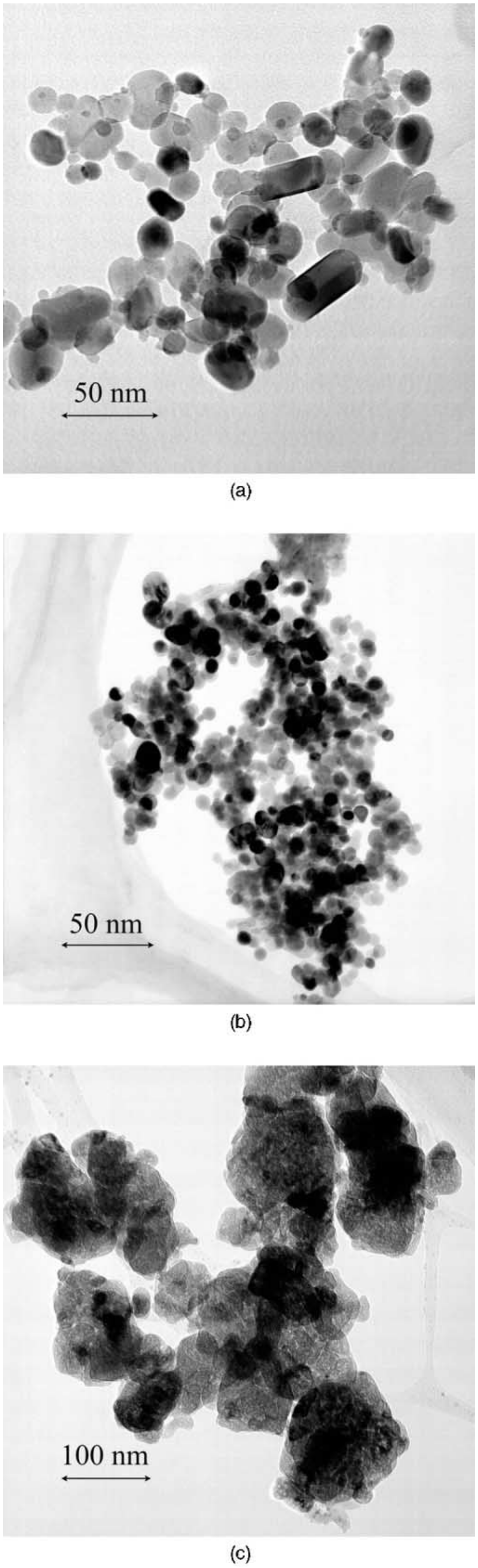

Fig. 10. Bright field TEM images of washed ZrO_2 synthesized from $ZrCl_4+4LiOH+4LiCl$ using milling times of (a) 10 min, (b) 30 min, and (c) 3 h.

age crystallite size of approximately 9 nm. The highly agglomerated state of the ZrO_2 powder is likely due to the high temperatures reached during combustive reaction. The adiabatic reaction temperature for the formation of ZrO_2, LiCl, and H_2O vapour is approximately 620 °C, which is sufficient to cause complete melting of the LiCl by-product phase. As a result, the salt matrix would have been unable to maintain effective separation of the particles, thus allowing the formation of hard agglomerates through interparticle sintering.

The average particle and crystallite size of the ZrO_2 product formed by the diluted reaction system was found to depend strongly upon the milling time. For short milling times, the majority of chemical reaction occurs during the post-milling heat treatment. As a result, the scale of the as-milled microstructure should determine the average particle size of the ZrO_2 product.[9] The initial decrease in particle size with milling time can therefore be attributed to increased refinement of reactant microstructure. Beyond this initial stage, the majority of the ZrO_2 reaction product is formed mechanochemically during milling, thus allowing growth of aggregates through interparticle welding during collision events. At long milling times, a steady-state particle size was developed as a result of the competing processes of particle aggregation and fracture.

A previous study of the synthesis of ultrafine ZrO_2 by mechanochemical reaction of $ZrCl_4+2MgO$ found that the particle size decreased with milling time down to a lower limit, which indicates that aggregation of the particles did not occur to any significant extent. This difference in behaviour compared to the present case can most likely be attributed to the presence of incipient water, which would have promoted aggregation of the ZrO_2 particles. A previous study by Murase and Kato[14] found that water increases the mobility of ZrO_2 at crystal surfaces, which facilitates particle growth and sintering.

4.3. Phase formation and stability

Combustive reaction of the undiluted reactant mixture was found to yield a nanocrystalline ZrO_2 powder with the high-temperature tetragonal structure. However, continued milling after the combustion event resulted in a progressive transformation to the equilibrium monoclinic structure. This behavior is consistent with previous studies of the effect of mechanical processing on the phase content of metastable tetragonal ZrO_2. For example, Bailey et al.[15] found that vibratory milling of metastable tetragonal ZrO_2 resulted in rapid transformation to the monoclinic form.

Garvie[16] attributed the stability of the tetragonal structure in nanocrystalline ZrO_2 to the lower specific surface energy of the tetragonal phase compared to the equilibrium monoclinic phase. As a result of this surface energy differential, the tetragonal phase should be stabilized below a critical particle size for a given temperature. This critical particle size has been estimated to be approximately 10 nm at 298 K.[16] However, it has subsequently been shown that a variety of other factors are also important in determining the phase content of nanocrystalline ZrO_2, including domain boundary stresses[17] and adsorbed hydroxyl anions,[18] both of which could reasonably be expected to play some role in the present case.

Gradual reaction of the diluted reactant mixture resulted in the formation of an amorphous ZrO_2 gel that crystallized with the tetragonal structure on calcination at 500 °C for 1 h. The crystallization of tetragonal ZrO_2 from amorphous gels has been attributed to structural similarities between the amorphous and tetragonal structures.[19]

5. Summary and conclusions

Reaction of $ZrCl_4 + 4LiOH$ to form nanocrystalline ZrO_2 powders has been shown to react during milling, either combustively or gradually depending on the presence of LiCl as an inert diluent. Combustive reaction resulted in the formation of a highly agglomerated ZrO_2 powder with the tetragonal structure. Gradual reaction of the diluted reactant mixture yielded a hydrated gel with amorphous structure that crystallized as tetragonal ZrO_2 during subsequent calcination.

The particle size and degree of agglomeration of the ZrO_2 product was found to depend strongly on the milling duration. For the undiluted reaction system, continued milling of the powder charge after the combustion event resulted in a progressive loss of specific surface area, which was due to compaction of the particle agglomerates. The diluted reaction system showed an initial decrease in particle size as a consequence of increased microstructural refinement of the reactants. Further milling resulted in aggregation of the particles before the attainment of a steady-state particle size.

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