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$LiNO_3$ molten salt assisted synthesis of spherical nano-sized YSZ powders in a reverse microemulsion system

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Abstract

Spherical nano-sized YSZ (yttria stabilized ZrO_2) powders were successfully synthesized via a reverse microemulsion system. The water droplets in the microemulsion system of yclohexane/water/span85/Triton X-100/hexyl alcohol can act as the nano-reactors which solubilize zirconium oxychloride and ammonia water separately. The minute original reactors are favor to the formation of nano-sized spherical YSZ powders and the dispersibility of the powders can be controlled effectually by adjusting the weight ratio of the $LiNO_3$ molten salt to the precursor. The phase transformation from cubic to monoclinic starts at and 500 °C and finally monoclinic and cubic phase with increased crytallinity coexist at 800 °C. The effect of $LiNO_3$ molten salt in the formation of YSZ powders was also discussed.

Keywords: Nanomaterials; X-ray techniques; Yttria stabilized ZrO_2; Reverse microemulsion; $LiNO_3$ molten salt

1. Introduction

Zirconia (ZrO_2) exists in three polymorphic modifications, these are monoclinic (m), tetragonal (t) and cubic (c). Among them tetragonal and cubic phases are metastable forms but monoclinic is the stable form at room temperature. So many hypotheses have been proposed regarding the factors which control the stabilization of the tetragonal and cubic phase relative to the thermodynamically stable monoclinic phase at room temperature [1,2]. In the literature the high temperature metastable forms can be partially or fully stabilized at room temperature by the addition of a small amount of oxides (e.g. MgO, CaO, and certain rare earth oxides) [3–5]. YSZ (yttria stabilized ZrO_2) powders are used in many advanced structural, high temperature and electrical ceramic applications due to their low thermal conductivity, high fracture toughness with a relatively high thermal expansion coefficient [6]. Therefore, many different methods such as conventional aqueous precipitation, hydrothermal processing, sol–gel and reverse emulsion were developed to prepare nano-sized YSZ powders. Although the sol–gel method is successful in the preparation of spherical ceramic nanoparticles, the raw materials of metal alkoxide in the process are too expensive to use in a large-scale production. Thermal hydrolysis needs a high temperature and a long reaction time.

Over the past few decades, microemulsion technique has attracted particular attention because the aqueous phase dispersed into the oil phase can form specifically a transparent microemulsion. Mixed two emulsion solutions, in which content metal-containing aqueous solution or aqueous ammonia are suspended in the oil phase to form emulsion by adding surfactant. The well-dispersed aqueous droplets allow any precipitation reaction to occur only within the droplets, herein the droplets serve as nano-reactors. Uniform spherical powders can be obtained after the precipitation [7–8]. Ai and Kanga [6] took octane/Span-80/zirconium (yttrium) oxychloride aqueous solution to form the microemulsion system. Approximate 20–40 nm spherical powders were obtained. Ma et al. [9] prepared ultrafine spherical YSZ using the cyclohexane/water/Triton X-100/hexyl alcohol microemulsion system. Ultrafine zirconia powders of tetragonal crystalline with the diameter of 30–40 nm were prepared.

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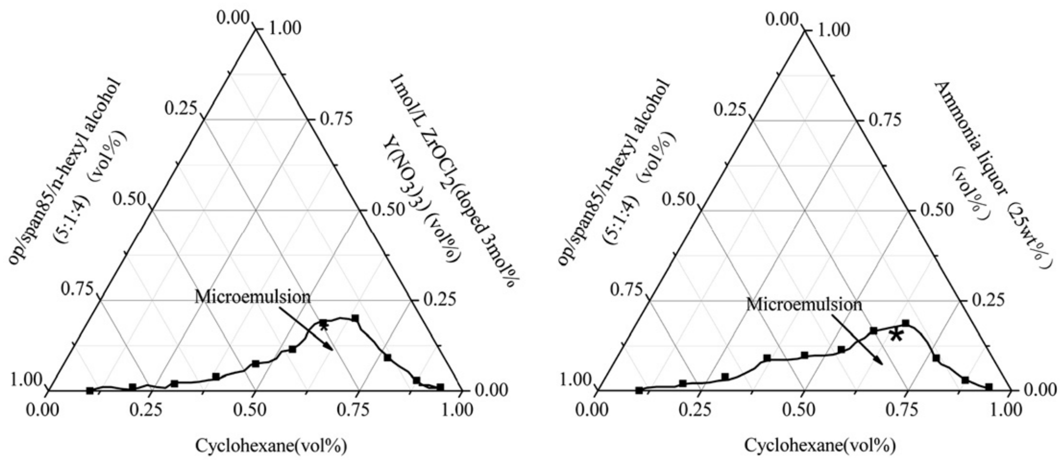

Fig. 1. Phase diagrams established at room temperature for the systems consisting of oil phase (cyclohexane), as well as surfactants (op/span85/*n*-hexyl alcohol) and various aqueous solution.

In this work, a new water/oil microemulsion consisted of cyclohexane/water/span85/Triton X-100/hexyl alcohol is utilized to prepare ultrafine spherical YSZ powders. Compared with traditional microemulsion systems, this inverse microemulsion system has demonstrated to be more stable and exhibited superior solubilization capability. Furthermore, well-dispersed nano-sized YSZ powders were successfully prepared with the addition of $LiNO_3$ molten salt. In our previous work [10], the $NaNO_3$–KNO_3 eutectic system was successfully employed as the effective medium to synthesize NiO nanopowders.

2. Experimental

2.1. Definition of the oil/water/surfactant ternary phase diagram

Microemulsion is thermodynamically stable mixtures of water, oil, and surfactant, where the water regions are separated from oil by a monolayer of surfactants. Due to the amphiphilic nature of the surfactant, numerous disordered or partially ordered phases are formed, depending on temperature and surfactant concentration [11]. In order to acquire the solubilization capability of such system on the water phase, the oil/water/surfactant phase graph is studied. In this experiment, the content of oil phase (cyclohexane) is certain, the content of surfactant (Triton X-100+span85+hexyl alcohol) changes gradually. The water phase ($ZrOCl_2$), 3 mol% $Y(NO_3)_3$ and 25 wt.% ammonia are titrated into the system via micropipette. As a result, the ternary phase graph is acquired as shown in Fig. 1. It can be seen that microemulsion can be obtained in the enclosed area. The symbol asterisk (*) refers to the adopted data in the experiment.

2.2. Preparation of nano-sized YSZ powders

During the preparation of nano-sized YSZ, mixture surfactant (mixture of span85, TX-100 and *n*-hexyl alcohol in the volume ratio of 1:5:4) was firstly dissolved in cyclohexane. This solution was mixed with 1.0 M $ZrOCl_2$ and 3 wt.% mol $Y(NO)_3$ aqueous solution and 2.0 M ammonia solution, respectively, to prepare two microemulsions under magnetic stirring. The two transparent microemulsions were first mixed and stirred for 30 min followed by refluxing for 2 h. Then the microemulsion was destroyed after addition of appropriate amount of ethanol, leading to the precipitation of the precursor. The precipitate was collected and washed successively with anhydrous ethanol and distilled water, and the wash water was checked by $AgNO_3$ solution until no negative Cl^- can be detected. After being dried by azeotropic distillation process and in vacuum at 120 °C, the precursors were calcined with $LiNO_3$ molten salt in different temperature. Then the resultants were washed with anhydrous and distilled water again, white products were ultimately achieved.

2.3. Characterization

High temperature X-ray powder diffraction (HTXRD) pattern was obtained on a Rigaku D max-gA X-ray diffractometer with Ni filtered CuKα radiation (V=40 kV, I=120 mA) at a scanning rate of 4°/min. The morphology of YSZ nanocrystals

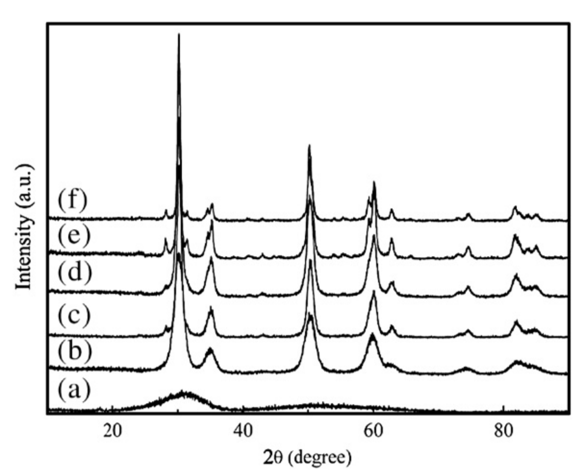

Fig. 2. HTXRD patterns of the as-prepared products in different temperatures: (a) 350 °C; (b) 400 °C; (c) 500 °C; (d) 600 °C; (e) 700 °C; (f) 800 °C.