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Preparation of Nanocrystalline Mesoporous ThO_2 via Surfactant Assisted Sol-gel Procedure

N. Mohseni, S. Janitabar, S. J. Ahmadi, M. Roshanzamir, M. Thaghizadeh

Abstract**—**In this research, thorium dioxide mesoporous nanocrystalline powder was synthesized through the sol-gel method using hydrated thorium nitrate and ammonium hydroxide as starting materials and Triton X100 as surfactant. ThO_2 gel was characterized by thermogravimetric (TGA), and prepared ThO_2 powder was subjected to scanning electron microscopy (SEM), X-ray diffraction (XRD), and Brunauer-Emett-Teller (BET) analyses studies. Detailed analyses show that prepared powder consisted of phase with the space group Fm3m of thoria and its crystalline size was 12.6 nm. The thoria possesses 16.7 m^2/g surface area and the pore volume and size calculated to be 0.0423 cc/g and 1.947 nm, respectively.

Keywords**—**Thoria, sol-gel, mesoporous, nanocrystalline.

I. Introduction

DEACRESE of economically accessible uranium resources motivates consideration of breeding of fertile elements such as thorium [6]. ^{233}U bred in the thorium fuel cycle, exhibits the highest neutron yield of all fissile materials when used in reactors with a thermal neutron spectrum. So in the last two decades extensive R&D has been carried out on the thorium fuel cycle [7]. The established procedures have been used industrially for the production of ThO_2, UO_2, $(U, Pu)O_2$, $(U,Th)O_2$, and pellets successfully. Powder metallurgical process is a very well established route [3]. As these fuels are associated with radiation exposure problems, the sol-gel processes that use liquids ideally suited for fuel manufacturing. The sol-gel process is an excellent method for controlling the properties of metal oxide materials on the nanometer scale. Historically, the sol-gel method utilizes metal alkoxides precursors that readily undergo catalyzed hydrolysis and condensation reactions to form a metal oxide gel, comprised of particles with nanoscale dimensions (1-100 nm). This synthetic route has been used to produce a variety of metal oxide materials with a range of physical properties. Preparation of thoria materials typically involves the aqueous precipitation of thorium oxalate followed by high temperature calcination. This approach allows for little control over the bulk properties of the resultant materials [1]. In a sol-gel process, droplets of metal nitrate solution or oxide sol are converted into hard gel particles by a suitable gelation process. These particles are dried and to obtain high density pellets, calcined, pressed, and sintered [3]. The applications for sol gel-derived products are numerous. For example, scientists have used it to produce the world's lightest materials and also some of its toughest ceramics. In the process of precipitation, ultra-fine and uniform ceramic powders can be formed which are powders of single and multiple component compositions of nanoscale particle size for dental and biomedical applications. Composite powders have been patented for use as agrochemicals and herbicides. Powder abrasives, used in a variety of finishing operations, are made using a sol-gel type process. One of the more important applications of sol-gel processing is to carry out zeolite synthesis. Other elements (metals, metal oxides) can be easily incorporated into the final product and the silicate sol formed by this method is very stable [10].

Nanocrystals represent fundamental building blocks in nanoscience and nanotechnology. The small size of nanocrystals modifies their physical and chemical properties and size and shape effects are generally observed at the nanoscale [2]. Hence, nanocrystals in the range of few to tens of nanometers exhibit unusual properties which are different to the once of their bulk counterparts [5]. Investigating the fundamental chemical and physical properties of these nanoscale building blocks opens up the way to the design of functional nanomaterials with innovative properties and high expectations in different fields [4].

In nuclear fuel pellet fabrication, the control of composition, porosity, surface area and particle size of powder is important. The manner and mechanisms involved on the sintering process are essential investigation to achieve the required microstructure and final properties in solids. During the conventional sintering of a compacted powder, densification and grain growth occur simultaneously through atomic diffusion mechanisms. Many researchers have been working on reducing the grain size below 1 μm aiming to improve some properties, such as strength, toughness and wear resistance in ceramics. In order to obtain ultra-fine ceramic microstructures, nanocrystalline powders can be used. Although the sinterability of nanoparticles is superior to that of fine particles due to the higher sintering stress, densification of these powders is often accompanied by grain growth [11]-[14].

The main aim of this research is to investigate the physical properties of thorium fuel pellets fabricated by thoria nanocrystals which prepared by our sol-gel route. But in this paper, manufacturing of pellets is not considered.

N. Mohseni is with the Nuclear Science & Technology Research Institute, NFCRS, (corresponding author to provide phone: 0098-82063623; fax: 0098-88221116; e-mail: nmohseni@aeoi.org.ir).

S. Janitabar, S. J. Ahmadi, and M. Taghizadeh are with the Nuclear Science & Technology Research Institute, NFCRS (e-mail: sjanitabar@ aeoi.org.ir, sjahmadi@gmail.com, mtaghizadeh@ aeoi.org.ir).

M. Roshanzamir is with the Shahid Beheshti University (e-mail: manroshanzamir@yahoo.com).

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We have developed a new sol-gel technique for the synthesis of thoria powder using TritonX100 surfactant.

II. Experimental

In an Erlenmeyer flask, 5 cm^3 TritonX100, $C_{14}H_{22}O(C_2H_4O)_n$ (n=9-10), was dissolved in 50 cm^3 absolute ethanol and stirred for 20 hours. Then in a beaker, 8.45 g thorium nitrate pantahydrate, $Th(NO_3)_4.5H_2O$, was dissolved in 15 cm^3 absolute ethanol. Then 2.25 cm^3 ammonium hydroxide 25% was slowly added dropwise to the beaker. With each drop of ammonium hydroxide, a white precipitate formed. This precipitate must be allowed to dissolve before the next drop of NH_4OH added. Then the contents of beaker transferred to the Erlenmeyer and the mixture was stirred for 3 hours. The solution was allowed to age in room temperature for 72 hours. At this stage a turbid gel was produced. The prepared gel was dried at room temperature and finally calcined at 773 K for one hour.

III. Characterization

The prepared gel was subjected to thermogravimetric analysis (TGA) studies in an argon atmosphere using Rheometric Scientific STA 1500 machine. X-Ray Diffraction (XRD) experiments were performed in the 2θ range from 20^0 to 80^0 with a STOE-Stidy-mp XRD. Surface area determination and pore volume & size analyses were performed by Brunauer-Emett-Teller (BET) and Barret-Joyner-Halenda (BJH) methods using an Nova 2000 Convantocrom surface area analyzer. SEM images were taken with a COXEM scanning electron microscope.

IV. Results

The TGA curve recorded for the dried gel sample is depicted in Fig. 1. The weight loss up to 473K corresponds to loss of water from the sample. Moreover, the weight loss from 473 to 573 K is due to surfactant egress. After that, the weight remains approximately constant as observed from Fig. 1. The prepared gel was calcined at 773 K.

Figs. 2 and 3 show the nitrogen adsorption/desorption isotherms and BJH method desorption for the nanocrystalline thoria respectively. Isotherms of prepared mater are of type IV which indicates the presence of mesopore [8]. The surface area of powder after calcination is found to be 16.7 m^2/g. The pore volume and size was 0.0423 cm^3/g and 1.947 nm respectively.

Thorium dioxide exists in only one stable crystalline form, a cubic phase with the fluorite structure (Fm3m space group) [1]. The average crystallite size of the synthesized thoria, is calculated by the XRD data (Fig. 4) and Scherrer's equation [9]. According to Scherrer's equation (1), the average crystallite size of pure ThO_2 sample is 12.6 nm.

$$\tau = \frac{\lambda K}{\beta cos\theta} \quad (1)$$

τ: The mean size of crystalline. **K:** A dimensionless shape factor, with a value close to unity but varies with the actual shape of the crystallite. The shape factor for cubic structure is 0.9 but varies with the actual shape of the crystallite. **λ:** X-ray wavelength. **β:** the line broadening at half the maximum intensity. (FWHM) after subtracting the instrumental line broadening, in radians. **θ:** Brag angle.

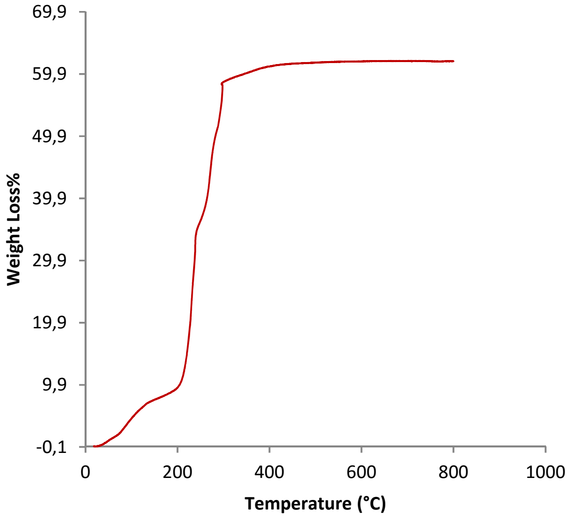

Fig. 1 Thermal Analysis (TGA) of thoria dried gel

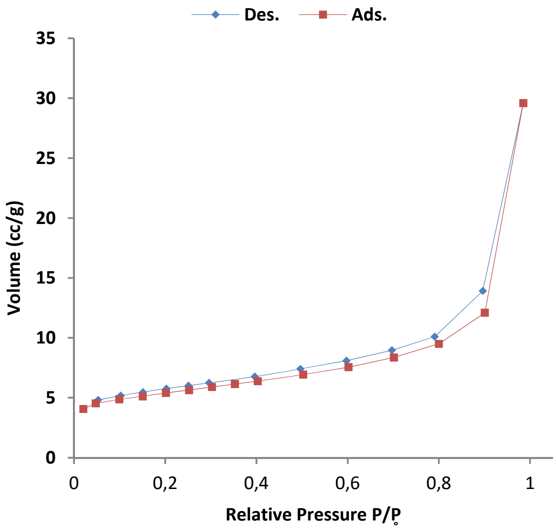

Fig. 2 Nitrogen adsorption/desorption isotherm for the nanocrystalline thoria powder

SEM images show the agglomeration in thoria powder that corresponds to high calcination temperature. The average agglomerated particle size is 1 μm as shown in SEM photograph (Fig. 5).

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V. Conclusion

Nanocrystalline ThO_2 successfully prepared through surfactant assisted sol-gel procedure. According to the nitrogen adsorption/desorption analyses, the thoria is mesoporous solid with relatively high surface area. The high surface area and mesoporosity of the thoria might exhibit improved sinterability of this nuclear fuel material. Sol-gel method not only is a dust free technique to prepare alpha emmiter radioactive fuel material, but also produce beter sinterable powder that causes the reduction of sintering temperature. Calcination in high temperature results in agglomeration in particles, but the particles were spherical and the powder was so soft. This powder has acceptable pressing and sintering characteristics.

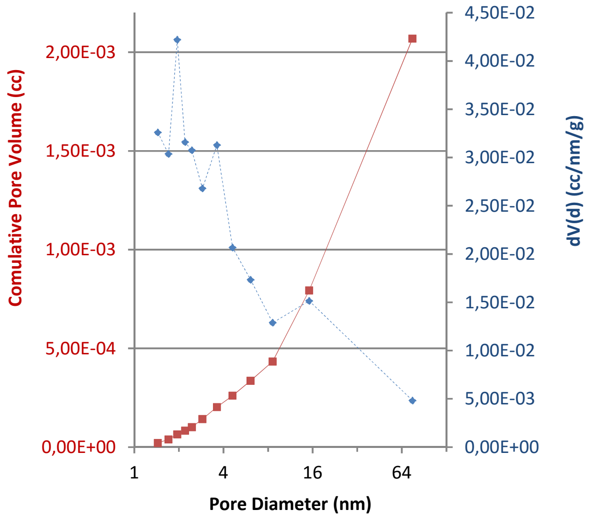

Fig. 3 Nitrogen adsorption/desorption BJH method desorption for the nanocrystalline thoria powder

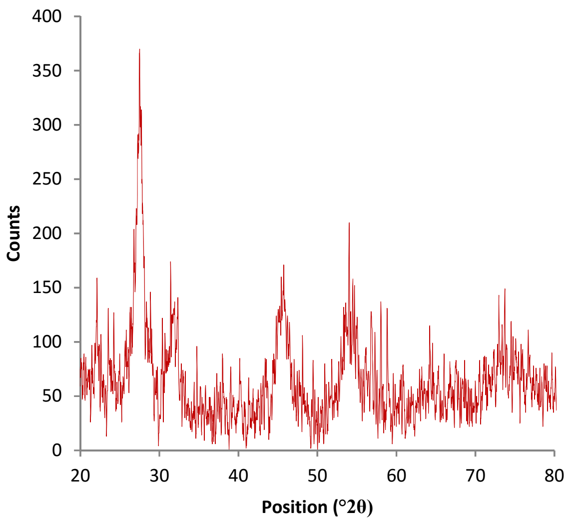

Fig. 4 XRD analysis of prepared thoria powder

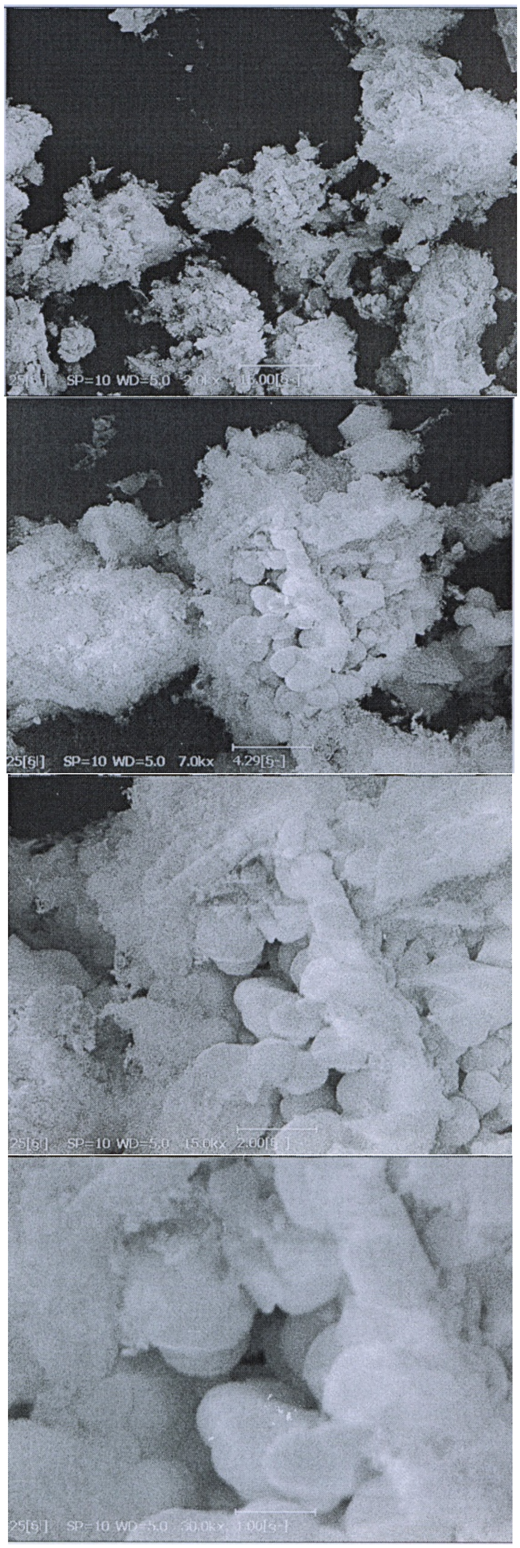

Fig. 5 SEM images of prepared thoria powder in different magnifications

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REFERENCES

[1] R. A. Reibold, J. F. Poco, T. F. Baumann, R. L.Simpson, J. H. Satcher Jr., "Synthesis and characterization of nanocrystalline thoria", *Journal of non-crystalline solids* , vol. 341 , pp. 35–39, 2004.

[2] N. Kumar, R.K. Sharma, V.R. Ganatra, S.K. Mukerjee, V.N. Vaidya, D.D. Sood, "Studies of the preparation of thoria and thoria-urania microspheres using an internal gelation process ", *Nuclear fuel Cycles*, vol. 96 , pp. 164–177, 1991.

[3] V.N. Vaidya, "Sol-gel process for ceramic nuclear fuels", *BARK newsletter*.

[4] V.N. Vaidya, "Status of sol-gel process for nuclear fuels", *J Sol-Gel Sci.*, vol. 46, pp. 369–381, 2008.

[5] V.G. Balakhonov, V.A. Matyukha, N.P. Saltan, E.A. Fillipov, A.N. Zhiganov, "Technology of getting of microspheric thorium dioxide", *Jurnal of physics*, vol. 49 , pp. 897–901, 1999.

[6] S.A.H.Feghhi, Z.Gholamzadeh, L.Sotani, C. Tenreiro," Comparison of (Th-233U) O2 and (Th-235U) O2 fuel burn up into a thermal research reactor using MCNPX2.6 code", *International Journal of Radiation Research*, vol. 11, No. 1, pp. 29-33, 2013.

[7] E. Zimmer, C. Ganguly, "Reprocessing and refabrication of thorium-based fuel", *IAEA-TECDOC-412*, pp. 89-109, 1987.

[8] M. Kruk, M. Jaroniec, "Gas adsorption characterization of ordered organic−inorganic nanocomposite materials", *Chem. Mater.*, vol. 13 , pp. 3169–3183, 2001.

[9] A. Monshi, M. R. Foroughi, M. R. Monshi "Modified scherrer equation to estimate more accurately nano-crystallite size using XRD", *World Journal of Nano Science and Engineering*, vol 2, pp.154-160, 2012.

[10] V. Uche. Don Okpala, "Sol-gel technique: A veritable tool for crystal growth", *Advances in Applied Science Research*, vol. 4, pp.506-510 ,2013

[11] A. L. Greer, "Nanostrucuture Materials – from Fundamentals to Applications", *Mat Sci. Forum*, vol. 269-272, pp.3-10, 2013.

[12] A. Inoue, T. Masumoto, "Nanocrystalline alloys produced by crystallization of amorphous alloys", *Current Topics in Amorphous Materials: Physics and Technology*, pp.177-184, 1993.

[13] D. G. Morris, "What have we learned about nanoscale materials? The past and future", *Mat Sci. Forum*, vol. 268-272, pp.11-14, 1998.

[14] C. Suryanarayana, "Nanocrystalline Materials", *Int. Mat Reviews*, vol. 40, No. 2, pp.41-64, 1995.