SYNTHESIS OF NANOCRYSTALLINE ZIRCONIA POWDER

Nabile Hassine, Abdalraof Bakeer, and Reiad Abo-Shrenta

Department of Materials and Metallurgical Engineering,
Faculty of Engineering, University of Tripoli
E-mail: nabs65@hotmail.com

الملخص

تم في هذا البحث تحضير مسحوق من النانو زركونيا بواسطة عملية ترسيب أجريت عند درجة حرارة منخفضة وذلك بخلط محلول حمضي من زركونيم أكسي كلورايد ($ZrOCl_2$) ومحلول من هيدروكسيد الأمونيوم. المحلول الحمضي تم تحضيره باذابة 8 جرام من زركونيم أكسى كلورايد المميئة ($ZrOCl_2\ 8H_2O$) في حمض الهيدروكلوريك والمحلول الناتج أضيف الى محلول من هيدروكسيد الأمونيوم بعد تحريكه بشكل جيد.

شملت هذه الدراسة تغيير كل من تركيز الحمض وأيضا ترتيب اضافته لمحلول الأمونيوم وبالتفاعل بينهما تم الحصول على راسب من هيدروكسيد الزركونيوم والذي تم ترشيحه وغسله بالايثانول وتجفيفه عند درجة حرارة 110 درجة مئوية و لمدة 12 ساعة. أخيرا أجريت عملية الكلسنة عند درجة حرارة 600 درجة مئوية ولمدة ساعتين لغرض تحويل حبيبات هيدروكسيد الزركونيم الى زركونيا.

تم فحص عينات مسحوق الزركونيا المتحصل عليها باستخدام أشعة اكس ومجهر المسح الالكتروني وذلك لتحديد شكل و حجم الحبيبات الناتجة. حيث أظهرت نتائج أشعة اكس أن الحبيبات في المدى النانومتري بحجم يتراوح بين حوالي 15 الى 28 نانومتر وأن مضاعفة تركيز الحمض أدت الى الحجم الأصغر. ولكن نتائج الفحص المجهري كشفت عن وجود نسبة عالية من الحبيبات المتكتلة نظرا لتضاؤل قوى التنافر الكهروستاتيكي بين حبيبات المسحوق مع التجفيف.

ABSTRACT

Nanocrystalline zirconia powder was prepared via a low temperature precipitation process involving the mixing of an acidic solution of $ZrOCl_2$ and ammonium hydroxide solution. The acidic solution was prepared by dissolving 8 g of $ZrOCl_2.8H_2O$ in HCl acid and the resultant solution added to a well stirred ammonium hydroxide solution. The acid concentration and the order of adding acid to the ammonium solution were both varied. Upon reaction between the two solutions, a precipitate of zirconium hydroxide formed, which was then filtered, washed with ethanol and dried over night at 110 °C. Finally, calcination at 600 °C transformed the $Zr(OH)_4$ particles to ZrO_2 particles.

The resultant powder samples were characterized via the use of X-ray diffraction and scanning electron microscopy techniques.

The XRD results obtained showed that the crystallite size was in the nanometer range from approximately 15 to 28 nm, with the smallest size being achieved by doubling the used HCl acid concentration.

SEM micrographs of the produced powder samples, however, revealed a high degree of agglomeration. This may possibly be due to diminishing electrostatic repulsion between powder particles upon drying.

KEYWORDS: Synthesis; Nanocrystalline; Zirconia; Ultrafine Powder; Zirconium Oxychloride; Precipitation Technique.

INTRODUCTION

Zirconia (ZrO_2) is a well - known ceramic oxide material used for a variety of applications. It has three stable forms: monoclinic, tetragonal and cubic. The physical and chemical properties of zirconium oxide are closely related to its different crystal phases and they determine its applications in industry. For example, the martensitic transformation of tetragonal zirconia into monoclinic zirconia improves the mechanical properties of composite materials. The high ionic conductivity of ZrO_2 in the cubic form at high temperatures permits its use for sensing oxygen. Tetragonal ZrO_2 is used as a catalyst and catalyst support for various gas phase reactions. It has also been used as a ceramic membrane instead of silica, titania or alumina due to its better alkaline resistance and biocompatibility. It is now well recognized that the mechanical, electrical, chemical as well as catalytic properties of zirconia can be improved by using nanocrystalline instead of conventional micron-sized zirconia[1].

Ultrafine zirconia (ZrO_2) particles are of particular interest because of their unique set of properties which include: high refractoriness, corrosion resistance, mechanical strength, fracture toughness and ion conduction. ZrO_2 is one of potential materials for the fabrication of dense nanocrystalline zirconia ceramics that could be applied in many different fields such as sensors, batteries, capacitors, and especially in fuel cells [2].

The methods that have been reported in the literature for synthesizing ultrafine zirconia particles include the following: sol - gel processing via hydrolysis and condensation of zirconium alkoxides [3-7], forced hydrolysis of zirconium in organic salt solutions [8, 9], precipitation from solutions of inorganic salt or alkoxide complexes[10], hydrothermal and plasma decomposition methods[11], microemulsion and electrodispersion techniques combined with precipitation reactions[12,13], combustion synthesis techniques[14], and electric explosion and oxidation of zirconium metal wires[15]

The present work involved the use of a precipitation based technique to prepare nanocrystalline ZrO_2 powder particles from a solution of zirconium chloride. The technique used was investigated in two ways; firstly by using hydrochloric acid of different concentrations, and secondly by changing the order of adding the NaOH and HCl solutions to each other , i.e. by adding NaOH to HCl and vice versa.
Characterization of the produced powder particles was then carried out via the use of X - ray diffraction analysis and scanning electron microscopy.

EXPERIMENTAL WORK

Materials

The materials used in the present work included the chemicals zirconium oxychloride, $ZrOCl_2.8H_2O$ with a purity of 99%, hydrochloric acid (HCl), ammonium hydroxide (NH_4OH), ethanol and distilled water. The chemicals were obtained from the Department of Chemistry, Tripoli University.

Preparation Procedure

The salt ($ZrOCl_2.8H_2O$) was dissolved to make a very acidic solution containing Zr^{4+} ions and this was then introduced into a well stirred ammonium hydroxide

solution. Considering the very high concentration of (OH^-) ions present in the second solution, the Zr^{4+} ions readily react to form $Zr(OH)_4$. Once the hydroxide was formed, it was filtered, washed with ethanol and dried overnight in an oven at 110 ˚C. The washing step was very important, as it replaced the particles' surface hydroxyl groups with ethanol molecules. After the zirconia precursor powder was thoroughly washed and dried, it was calcined at 600˚C for two hours to transform the $Zr(OH)_4$ particles to ZrO_2 particles.
The preparation procedure described above involved four experimental variants as shown in Table (1) given below;

Table 1: Experimental parameters of the preparation method

Powder Sample Number	Experimental solutions	Method of Solutions mixing
1	8 gm of $ZrOCl_2.8H_2O$ was dissolved in 4M HCl	NH_4OH solution was added to the acid solution
2	8 gm $ZrOCl_2.8H_2O$ was dissolved in 2M HCl	NH_4OH was added to the acid solution
3	8 gm $ZrOCl_2.8H_2O$ was dissolved in 4M HCl	The acid solution was added to NH_4OH solution
4	8 gm $ZrOCl_2.8H_2O$ was dissolved in 2M HCl	The acid solution was added to NH_4OH

The obtained four powder samples were characterized via the use of X-ray diffraction (XRD) in order to determine the phase composition and estimate the grain size of the produced powders.
The crystallite size of a powder sample can be estimated from the X-ray broadening by using the well-known Scherrer equation;

$$B = \frac{0.9\lambda}{t\cos\theta}$$

Where B is the width of the X-ray pattern line at half peak-height in radians, λ is the wave length of the X-ray (1.540 A° for the Cu K_α), θ is the angle between incident and diffracted beams in degrees, and t is the crystallite size of the powder samples in angstroms. Scanning Electron Microscopy (SEM) was used to investigate the powder morphology and measure the powder particle size of the produced zirconium oxide, ZrO2, samples.

RESULTS AND DISCUSSION

The calculated crystallite size of the obtained powder samples, together with the values of θ and B for each powder sample, are given in Table (2) below;

Table 2: XRD Crystallite Sizes

Sample Number	θ (degrees)	B (radians)	t (nm)
1	15.387	0.00858	16.77
2	14.33	0.006178	23.20
3	15.28	0.005146	27.96
4	14.30	0.00956	14.98

Powder sample number 1 is taken as an example for the calculation of the crystallite size using the Scherrer equation and the values of θ and B obtained from XRD analysis of the produced powder samples (see figures 1 and 2).

$\theta = 15.387$ and $B = 0.492° = \frac{0.492 \times 3.14}{180} = 0.00858\, radians$

Hence;

Crystallite size $t = \frac{0.9 \times 1.542}{0.00858 \times \cos 15.387} = 167.76\text{A} = 16.77 nm$

The other values of crystallite size were obtained in a similar way.

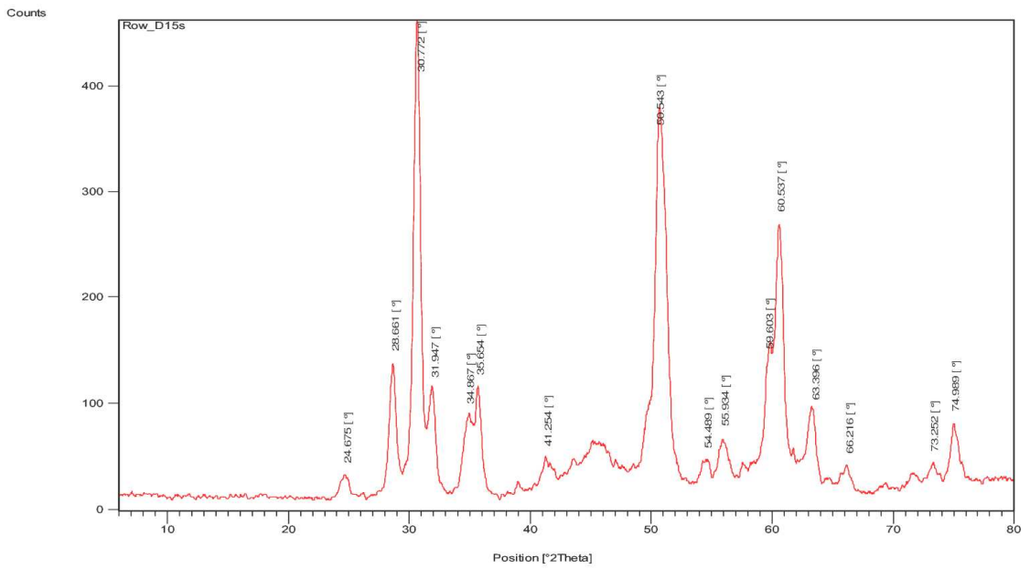

Figure 1: 2θ values for sample 1

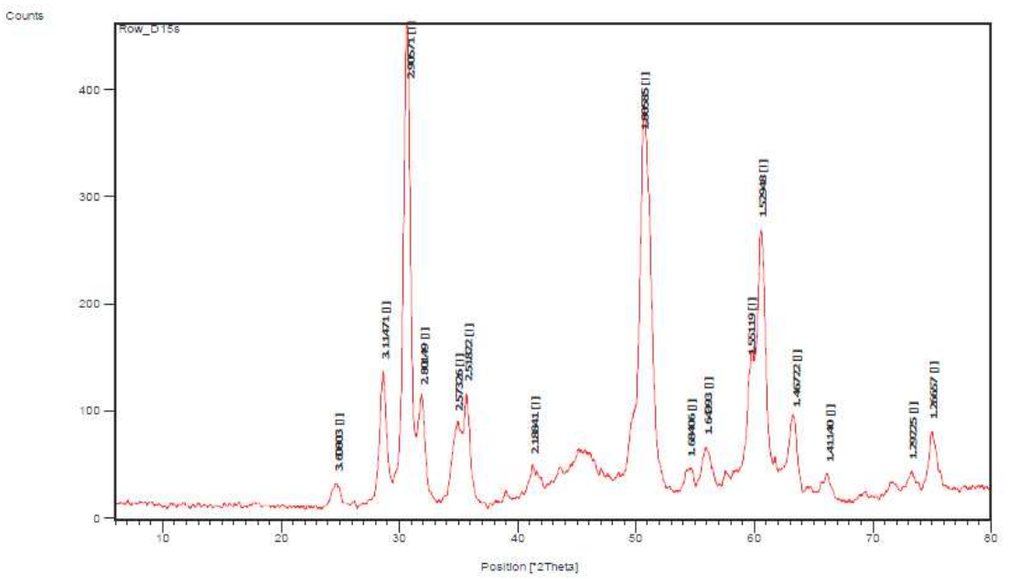

Figure 2: Inter planar spacing (d) values for sample 1

As can be seen from the figures listed, all the powder samples obtained were in the nanometer size range with sample 4 being the smallest. This shows that the acidic solution is best be prepared by dissolving 8 gm of $ZrOCl_2$. $8H_2O$ in 2M HCl and, then to add this acidic solution to a well stirred ammonium hydroxide solution.

The results also show the influence of both increasing the acid concentration used and the changing of the order of mixing the acid and the ammonium hydroxide solutions on the size of the produced powders. For example, doubling the molarity of the acid led to the observed increase in powder particle size from 15 nm to about 28 nm.

The obtained SEM images of the produced samples generally showed a high degree of agglomeration, as figure 3 below shows.

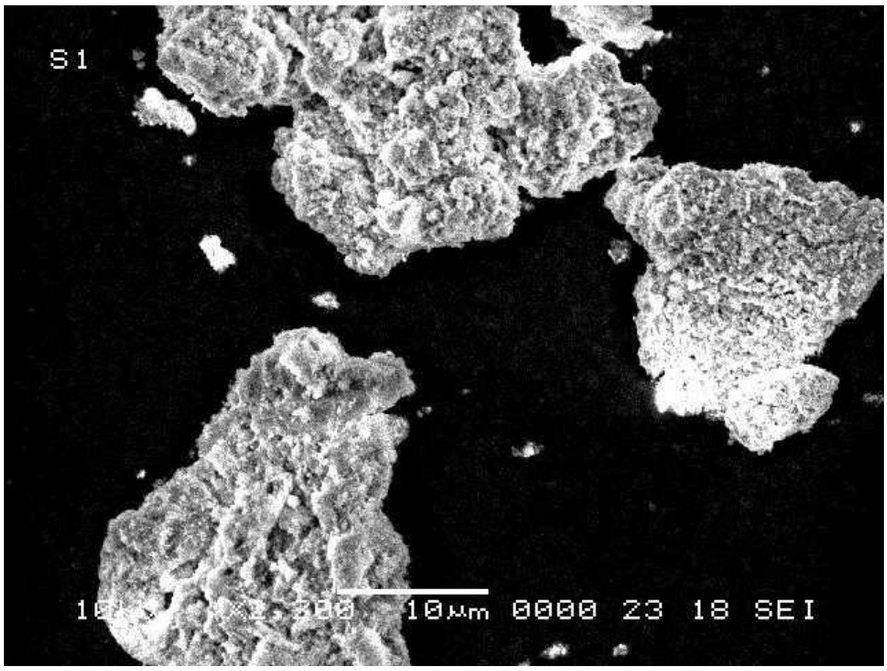

Figure 3: SEM image typical of the produced powder samples showing large agglomerates.

This made it very difficult to use the SEM micrographs to estimate the particle size of the produced powder samples. The problem of agglomeration is particularly acute in the nanometer–size range due to both heightened powder dissolution and diminishing electrostatic repulsion in drying suspensions. Powder dissolution is thought to assist agglomeration through the re–precipitation of dissolved matter at particle contact points, thereby forming inter particle necks. Electrostatic repulsion, on the other hand, is an original feature of the suspension; it stems from the fact that like–charged clouds of dissolved ions exist around each suspended particle, thereby leading to mutual repulsion between particles.

Agglomeration occurs when the electrostatic repulsion is no longer sufficient to counter the ever – present, attractive London – Van der Waals forces that also exist between particles [16].

CONCLUSIONS

Based on the present work the following conclusions may be drawn;

- Nanocrystalline zirconia powder, with a particle size ranging from about 15 to 28 nm, was successfully prepared via a low temperature precipitation process involving the mixing of an acidic solution of $ZrOCl_2$ and ammonium hydroxide solution.
- It appears that the smallest particle size would be obtained by dissolving 8 gm of $ZrOCl_2$. $8H_2O$ in 2M HCl and, then to add this acidic solution to a well stirred ammonium hydroxide solution.
- The concentration of the acid and the order of mixing the acid and the ammonium hydroxide solutions both have an influence over the size of powder particles produced.
- SEM images showed the particles to be highly agglomerated due to the fact that when particle size decreases to the nanometer scale van der Waals forces and electrostatic forces will far exceed single particle weight. Moreover, agglomeration will increase as particle size decreases.

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