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Physical and morphological properties of zirconia produced at different precipitating conditions

Julie Andrianny Murshidi, Nurasiah Umor, Mohd Khairul Tazril and **Meor Yusoff M.S.**

Malaysian Institute for Nuclear Technology Research (MINT), Bangi, 43000 Kajang, Selangor, Malaysia.

ABSTRACT Zirconia is an important advanced material due to its structural as well as functional properties. Hydrothermal technique is one of the more common methods to produce this material and this can be achieved by precipitating zirconium hydroxide from zirconyl chloride solution. In this study, pH 8 had been selected for the precipitating condition and the zirconia was produced at different concentrations. The ratio of tetragonal to monoclinic zirconia crystalline phases was determined using X-Ray Diffraction technique. Scanning Electron Microscopy was used for analyzing the morphological structure. Other characterization techniques used include particle size analyzer for size distribution.

(Hydrothermal, Tetragonal, Monoclinic, XRD, SEM)

INTRODUCTION

Zirconium element was named after either an Arabic word 'zargun' to mean gold color or a French word 'zerk' to mean precious stone. Zirconium had been discovered in 1800, but was later commercialized in 1940's, the decade when the advent technology in the nuclear energy started. One of the modern materials originate from this element is zirconia ceramic. Zirconia is used in a number of applications such as solid electrolyte, catalytic material and structural ceramic [2,3]. Zirconia can exist in monoclinic, tetragonal and cubic crystalline phase but at room temperature only the monoclinic is stable. Applications of zirconia are normally associated with its crystalline phases and of late tetragonal zirconia particulate (TZP) has become a more important structural material. Hence the conditions for control formation of crystalline phases have been subject of important studies by several researchers [4, 6]. In this study, characterization of the crystalline phase developed from different zirconyl chloride concentrations has been done.

EXPERIMENTAL

25% ammonia solution was diluted to its 10% concentration with distilled water. Zirconia products with varying weights of zirconyl chloride were produced by dissolving the zirconyl chloride in 4M HCl. 5, 10, 15, 20 and 30% (w/v) of the zirconyl chloride solutions were then obtained. 100 ml of each zirconyl chloride solutions was then placed in a beaker with the 10% ammonia solution dropwise until pH 8 is obtained. After the precipitation process, the zirconyl hydroxide precipitate was then filtered using Buchner filter and dried in an oven at 100°C for 3 hours. The weight of each precipitate before and after drying was measured.

The dried precipitate was then calcined at 800°C for 3 hours in a furnace. After the calcinations process, zirconia precipitate was grinded into a finer form. Every sample was analyzed using SEM (for morphological structure), XRD (for calculation of tetragonal ratio of zirconia phase) and Particle Size Analyzer (for identification of the powder size).

RESULTS AND DISCUSSION

The results show that there was an increase of weight loss from 5% to 15% concentration (Table 1). But this weight loss decreases, as further concentration is used. There is no conclusive evidence on the effect of weight by different zirconyl chloride concentrations but earlier study had shown that loss of water vapor during drying and calcinations increase the rate of crystal growth and reduced the critical size for transformation [1].

Table 1: Precipitate weight at different zirconyl chloride concentration.

Percentage of zirconyl chloride concentration (%)	Before drying process at 100°C (g)	After drying process at 100°C (g)	After calcinations process at 800°C (g)
5	13.16	11.44	1.719
10	30.33	26.72	3.606
15	45.74	40.59	5.146
20	74.36	46.60	6.818
30	97.71	64.34	10.10

Particle size plays an important role in determining the quality of zirconia product produced by the hydrothermal process. The effect of different zirconyl concentrations on the particle size of zirconia can be seen in Table 2 below. The use of more concentrated zirconyl chloride solution will result in the formation of smaller zirconia particle size.

Table 2: Particle size of zirconia at different zirconyl hydroxide concentration.

Particle Size (μm)	% Pass				
	5% $ZrOCl_2$	10% $ZrOCl_2$	15% $ZrOCl_2$	20% $ZrOCl_2$	30% $ZrOCl_2$
352	0.43	0	3.59	0	4.14
176	5.71	0	9.46	4.25	17.01
88	12.98	1.04	16.21	10.87	18.29
44	19.05	9.47	19.5	17.38	16.20
22	14.17	26.99	12.18	14.01	13.97
11	10.98	21.55	10.73	12.96	10.77
5.5	11.84	16.18	9.86	11.90	8.55
2.75	10.35	10.74	8.66	11.4	6.43
1.375	7.94	7.18	5.93	8.73	3.25
0.687	5.74	5.92	3.53	6.61	1.39
0.43	0.81	0.93	0.35	1.84	0

This can be seen from the zirconia product produced by 5% zirconyl chloride which has most of it at 22-88 μm. With higher zirconyl chloride concentration there is an increase of the smaller particle product especially that of using 20% zirconyl chloride. The result also shows an increase in the sub-micron scale zirconia.

SEM micrographs (Figure 1, 2 and 3) obtained from this study show that the morphological structure is similar to that observed in commercial zirconia product. The structure shows group of agglomerates with no single crystal present. Sizes of these particulates are also consistent with results obtained from particle size analyzer (Table 2).

Figure 1. SEM micrograph for 5% zirconyl chloride concentration (X3700).

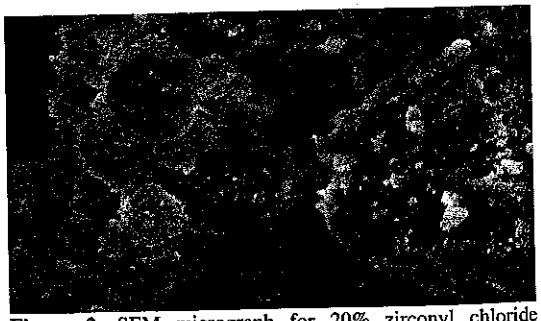

Figure 2. SEM micrograph for 20% zirconyl chloride concentration (X2300).

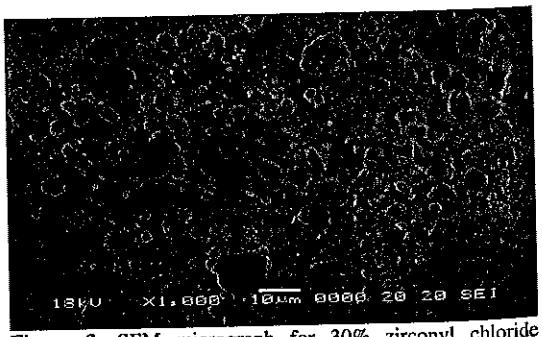

Figure 3. SEM micrograph for 30% zirconyl chloride concentration (X1000).

Another aspect considered was the tetragonal ratio in the zirconia products. The XRD diffractograms of these zirconia products show the presence of two different forms of crystalline phases (Figure 4). These are monoclinic peaks namely the $(11\bar{1})$ plane at $2\theta=28°$ and (111) plane at $2\theta=32°$. Tetragonal crystalline phase is also present and this is identified by the (111) plane at $2\theta=30°$. Of these two zirconia crystalline phases, only the monoclinic is stable at room temperature while the presence of tetragonal at this temperature was said to be due to its metastable properties [1].

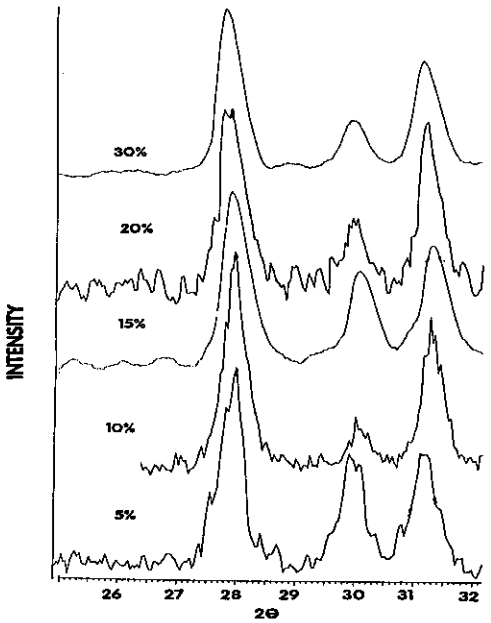

Figure 4. X-ray diffraction patterns of zirconyl chloride at different concentration.

The tetragonal phase ratio in the zirconia product can be derived from the following relationship [5];

$$\text{Tetragonal zirconia phase ratio} = \frac{I_{T(111)}}{[I_{M(111)}+I_{T(\bar{1}11)}+I_{M(11\bar{1})}]}$$

where $I_{M(111)}$ = Intensity of monoclinic plane $(11\bar{1})$

$I_{T(111)}$ = Intensity of tetragonal plane (111)

$I_{M(111)}$ = Intensity of monoclinic plane (111)

The tetragonal zirconia phase ratio was calculated for the different zirconia products and a graph between this value and zirconyl chloride concentration was plotted as shown in Figure 5. It is apparent that this value is highest at the lowest zirconyl chloride concentration and as the concentration increases, the value tends to decrease.

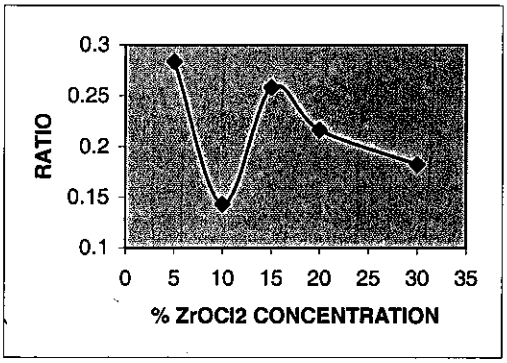

Figure 5. Ratio of zirconia tetragonal phase at different % of $ZrOCl_2$ concentration.

CONCLUSION

Zirconia powder precipitated at pH 8 produces wide size of particles including considerable amount of nano-size particles. Most of the zirconia powder produced is a mixture of both monoclinic and tetragonal phases rather than an absolute single crystalline phase.

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