Synthesized Zirconia Powder from Australian Zircon Sand

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***Abstract*— Zirconia (ZrO_2) is one of the bioceramic materials widely used in dental restorations in surgical applications. The Zirconia powder is synthesized using Australian zircon sand using the caustic fusion method at 500°C, 600°C, 700°C and 800°C of calcination temperature. The synthesized Zirconia are being analysed using X-Ray Diffractometer (XRD), particle size distribution, Scanning Electron Microscopy (SEM) and Brunauer–Emmett–Teller (BET). The results showed that synthesized zirconia are monoclinic phases and the surface area of the synthesized zirconia based on the calcination temperature for 500°C, 600°C, 700°C and 800°C are 0.0635 m^2/g, 0.135 m^2/g, 0.0268 m^2/g and 0.0288 m^2/g. For BET surface area are 1.0721 m^2/g, 0.6811 m^2/g, 1.8915 m^2/g and 1.5074 m^2/g. Based on SEM images, the surface structure of the powder has been determined and at zirconia that been calcined at 600°C showed the similarity with commercial zirconia. Due to the structure of zirconia are not stabilized, dopant zirconia with yttrium oxide (Y_2O_3) is done using ball milling to produce 3 mole % yttria stabilized zirconia (YSZ). The several tetragonal structure is determined in 3 mole % YSZ. The similarities of synthesized zirconia and commercial zirconia showed that the synthesized of zirconia powder from zircon sand is successful.**

Keywords*— Zirconia, 3 mole % YSZ, Zircon Sand, Monoclinic, Caustic Fusion Method

I. INTRODUCTION

Zirconia (ZrO_2) powder is white crystalline known as zirconium oxide. This powder is chemically inert and withstand with high temperatures, corrosion and thermal shock (Sommers et al., 2010). There several conditions of the zirconia which are in natural form or process form. Zirconium oxide is the condition when the zirconia is in the natural form and is known as mineral baddeleyite. In the process form, the zirconia is being processed by a thermal treatment called calcination to produce zirconia oxide with high temperature. Many researchers interested to do a study about zirconia powder because it is widely used in ceramic materials and used in many applications such as in the hard ceramics production in dentistry, application in scaffold bone tissue engineering and enamels. Melting point of zirconia is high which 2715°C and the boiling point is 4300°C make the toughest of zirconia is very high. Zirconia have unique properties because it's complex and temperature-dependent phase transitions. Pure zirconia exists 3 crystal phase, monoclinic, cubic and tetragonal depends on the temperature. The material can have sharp edges and very smooth surface when the powder in fine grain size. However, the weakness of the zirconia is shown during phase change in its physical characteristics when heated (Daou, 2014). The addition of stabilizer can overcome this problem. Yttria partially stabilized zirconia when the trial or yttrium oxide is added as stabilizer is one of the problems that have been solved (Hjerppe, 2015).

Yttria stabilized zirconia (YSZ) is a zirconium oxide in crystal structure with addition of yttrium oxide as stabilizer at room temperature and produce ceramic. (Abd El-Ghany & Sherief, 2016).YSZ is strongest ceramic because it is purely tetragonal phase and have highest strength between zirconia-based materials. (De Aza, Chevalier, Fantozzi, Schehl, & Torrecillas, 2003). Then, growth is hinder, and the fracture toughness is developed when crack is put into compression. This process considerably prolongs the lifetime and consistency of product made with stabilized zirconia. (Abd El-Ghany & Sherief, 2016). It also high in chemical and erosion resistant. Besides, in biomedical used especially orthopedics and dentistry are preferring to use YSZ because it excellent stability and shock and wear resistance (Apratim et al., 2015). Hence, the unique characteristics of the YSZ make it suitable use in orthopedic because of it excellent in mechanical properties and physicochemical (Afzal, 2014). The example application of the YSZ is zirconia ceramic scaffolds and bone graft substitutes. Bone tissue regeneration an bone defects fill used porous bone scaffolds and materials substitution are usually used in bone tissue engineering (Hutmacher, 2000). Composite scaffolds using YSZ and hydroxyapatite (Hap) is 70/30 ratio is the best result of microporous zirconia/Hap and the strength of composite scaffolds is same to cortical bone. It also have cell and tissue is affinity and showed adsorption of protein is high (Matsumoto et al., 2011). Thus, the by doping the yttria with zirconia make the application of zirconia become wide and characteristics of zirconia should be investigating to find the best condition of the YSZ.

There are several methods to produce zirconia powder such as hydrothermal oxidation, thermal decomposition and precipitation and hydrolysis (Sōmiya & Akiba, 1999). The method that used to produce different characteristics of zirconia powder based on the desired product. The best result to obtained zirconia powder is using chemical routes, but it is not an economic method for industrial manufacturing compared to conventional milling method (Kljajević et al., 2011). However, the high-quality nanometre sized powder is obtainable using technology of precipitation, but these powers are relatively expensive even though it's high chemical purity. Zircon can be used to overcome the problem because it's main mineral precursor. Zircon is the main in heavy mineral where the beach along the coast Brazil is happening (Yamagata, B. Andrade, Ussui, Lima, & Paschoal, 2008). In industrial mineral, zircon is commercially important. The uses of zircon in the production of zircon is quickly increasing because it resists high temperature and chemical attack creates it good refractory for furnaces and steel ladles and foundry sand used (Götsch, Wallisch, Stöger-Pollach, Klötzer, & Penner, 2016). Thus, in this study to synthesize the zirconia powder, zircon will be used to produce high purity and economical of zirconia with doping with yttria to produce YSZ. The 3 mole % YSZ is synthesized because high demand and usage in dental applications (Isabelle & Holloway, 2010). The physical and chemical characterization of Zirconia using scanning electron microscopy (SEM), particle size distribution, Brunauer–Emmett–Teller (BET) and X-ray Diffraction (XRD) are determine to study the zirconia properties.

II. METHODOLOGY

A. Materials

The Australian zircon sand obtained from the manufacturer of zircon, which is Zircon Minerals Malaysia. Commercial zirconia powder is obtained from Vistee Techology Services and commercial 3 mole % YSZ from Inframat Advance Materials, USA.

B. Synthesized of Zirconia Powder

The Zirconia is synthesized by using the caustic fusion method (Apriany, Permadani, Syarif, Soepriyanto, & Rahmawati, 2016). Australian Zircon sand is obtained from Zircon Mineral Malaysia. NaOH is measured 30 g and Zircon is 33 g (Apriany et al., 2016). The weight is identified by calculating from mole, according to the chemical reaction below:

$$ZrSiO_4(s) + 4\,NaOH(s) \rightarrow Na_2ZrO_3(s) + Na_2SiO_3 + 2\,H_2O(g) \quad (1)$$

Next, the acid leaching method is used to produce the $ZrOCl_2$ by dissolving mixture in 5 M of HCl solution in 120 ml. The process is conducted at 85˚C for 30 minutes. Then, $ZrOCl_2$ that has been produced is reacted with NH_4OH at concentration 1 M until the pH of the solution at 9 to obtain the $Zr(OH)_4$. The process is done by stirring at 90˚C. The $Zr(OH)_2$ will produced after 24 hours and then filtered and washed using hot water to get the pH of solution 7. Before the zirconia powder is obtained by calcination process, the residue was heated to remove the moisture content at 150˚C for 3 hours (Apriany et al., 2016). The calcination process is done at 800˚C for 5 hours and repeated with different temperature at 500˚C, 600˚C and 700˚C.

C. Synthesized of 3 mole % YSZ

The stabilizer is added to zirconia produced. The stabilizer added is yttrium oxide that obtained from Sigma-Aldrich. The doping of the ZrO_2 and Y_2O_3 using the definite mole amount $Y_{0.03}Zr_{0.97}O_{2-d}$ to produce 3 mole % YSZ using a planetary mill machine with YSZ ball (Apriany et al., 2016). The process of powder milling is done in the Faculty of Chemical Engineering, UiTM. The ratio of ball of ceramic powder was 1:2 to 100 RPM in 8 hours with several pauses periods (Md Ani, Muchtar, Muhamad, & Ghani, 2014). 3 percent of dopant chosen because is synthesized because high demand and usage in dental applications (Isabelle & Holloway, 2010).

D. Characterization of As-Synthesized Powder

1. X-Ray Diffractometer (XRD)

Analysis of XRD was determined to identify the present phases of the as-synthesized and commercial zirconia powders. The principle of the XRD is X-Rays shoot at one point of the sample at specific degree. Thus, the crystalline substance and scatters can be obtained. The observation of diffraction ray and scattered peaks is done. Before XRD was performed, the samples were cut, ground and polished to attain good flat surface and perfect result is attained. Ultima IV Rigaku X-Ray Diffractometer was used at scan speed 2°C/min over scan range 10°-90° to examine the phase that presents in the as-sintered and commercial samples.

2. Particle Size Distribution

The particle size distribution of the as synthesized Zirconia powder was measured using Malvern Instrument type Mastersizer 2000. The particle size distribution analysis can determine the surface area and width of particle size of powder.

3. Scanning Electron Microscopy (SEM)

Image of sample is produce by scanning the surface using the focused of electron beam use in SEM analysis. Topography and composition of sample surface is obtain from the interaction of the electron and atoms in the sample that come from many signals that have information. The combination of position in beam with the signal detection to provide the image. The images of the synthesized zirconia, 3 mole % YSZ and commercial powders is determined. The SEM analysis is done at SIRIM Kulim.

4. Brunauer–Emmett–Teller (BET) Analysis

BET analysis is use to measure the specific surface area and the distribution of pore size. Dissolution rate prediction are related to the specific surface area by using the information. Bioavailability are measured by surface area and performance uniformity is evaluate by the information obtained. BET analysis also use in the measurement of the specific surface area and total pore volume and area of synthesized zirconia.

III. RESULTS AND DISCUSSION

A. The effects of calcination temperature on synthesized zirconia powder

The identification of m-ZrO_2 and t-ZrO_2 content and used XRD by the method of Garvie Nicholson (G-N) from the relations of the intensity diffraction pattern according the equation below (Gauna et al., 2015):

$$Im\,(111) + Im\,(\bar{1}11) = It\,(101) \quad (2)$$

The content of m-ZrO_2 molar fraction is known by:

$$x_m = \frac{I_m(111) + I_m(\bar{1}11)}{I_m(111) + I_m(\bar{1}11) + I_t(101)} \quad (3)$$

The intensity of the monoclinic phase are *Im* (111) and *Im* (ī11) parallel to plane 111 and ī11 correspondingly (Gauna et al., 2015). The intensity of the 101 plane is parallel with (101).

Figure 1 show the XRD patterns for synthesized and commercial zirconia powder respectively. The synthesized zirconia prepared at different temperatures are shown in figure A. XRD showed two phases monoclinic of nano crystalline zirconia 28.1° (111), 31.4° (111) (JCPDS card no.78 – 1807) and tetragonal 30.2° (101), 50.2° (112) and 60.2° (211) (JCPDS card 79 – 2769) (Gusain, Singh, & Sharma, 2016). Figure A (a) – (e) shows that XRD patterns for the samples prepared with different temperature of calcination process from 500°C to 800°C.

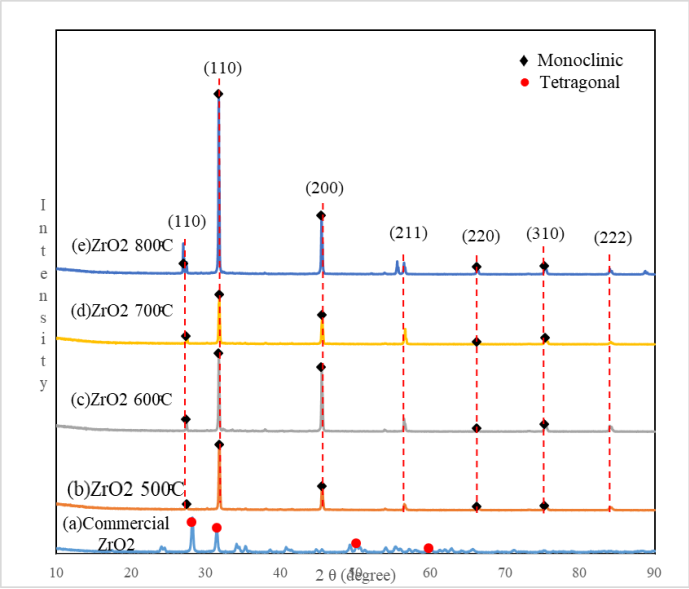

Fig.1: XRD Patterns for Commercial and Synthesized Zirconia at Various Temperature Values

In figure 1 (b) to (e), the synthesized Zirconia showed that the x-ray pattern on the line of the synchrotron beam based on samples are pure monoclinic (>95%) Zirconia (Srinivasan, De Angelis, Ice, & Davis, 1991). The synthesized zirconia does not involve of tetragonal structure because of the calcination temperature does not above 1170°C based on the xrd pattern obtained. The explanation of structure of zirconia change can be explain from figure 2. Three crystallographic structures occurred in pure zirconia are monoclinic form are stable until 1170°C, tetragonal form stable between 1170°C until 2370°C and cubic form stable above 2370°C showed in figure 2.2. The volumetric expansion of 3% to 5% related with both martensitic nature in considerable technological important in the changes of zirconia from tetragonal to monoclinic structure (Oliveira & Torem, 2001).The significant effect of calcination on the phase purity of the Zirconia powder has been determined. 32% from the total zirconia is monoclinic phase and above 1170°C will change totally in tetragonal form. Then, during calcination process, the presence of cations, from the migration of cation, if there is diffusion pathway existing like inactivated or not fully in phases crystalline because the situation of transformation stated peak of endothermic and irreversible (Gauna et al., 2015).

However, the preparation to synthesize zirconia can affect the structure of zirconia. The material was prepared using zircon sand and been produce around pH 10 when the precipitation form which it able to obtain a high percentage of monoclinic form. The medium pH (8-11) range could produce monoclinic zirconia while low pH (3-5) range and high pH (13-14) range produced tetragonal phase based on previous researches (Srinivasan et al., 1991). This is because of the initial zirconium species are well detached and probably it is monoatomic species of zirconium (Srinivasan et al., 1991). Thus, the application for monoclinic structure can be used for component in refractory materials, molten metal filters, additive to mixed oxide systems and nozzles and stoppers of transfer/holding ladles.

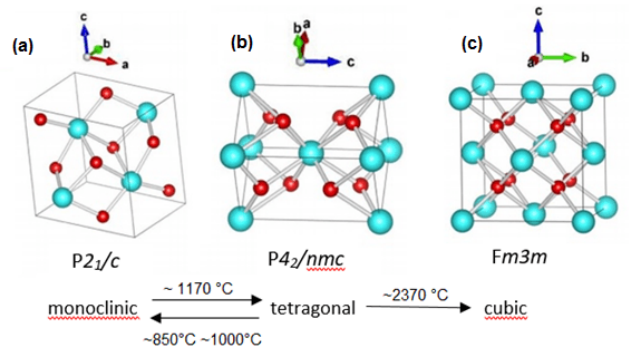

Fig 2: Zirconia phase transformations. As temperature increases, zirconia transforms from monoclinic (a), to tetragonal (b) to cubic (c) (Brog, Chanez, Crochet, & Fromm, 2013)

However, the commercial zirconia containing tetragonal zirconia with high percentages. The commercial zirconia changed fully from the monoclinic to tetragonal since the thermal treatment of the commercial zirconia above 1170°C. Within this the temperature of 1170°C until 2300°C the zirconia stable in tetragonal form (Ning, Zhan, Xie, Li, & Zhang, 2013). Effect on pH can be the main factor for Zirconia produce in the tetragonal phase because it be obtained either low pH (3-5) range or high pH (13-14) range (Srinivasan et al., 1991). Recently, the current researchers suggested the formation of crystal structure, transformation of polymorphic and growth of crystallinity become the main role for precursor of zirconia solution chemistry (Jada & Peletis, 1989).

The parameters of the particle size distribution of synthesized zirconia powder are shown in table 1. Usually, the most significant aspect in the particle size distribution is the three point distribution nominated as D_{10}, D_{50} and D_{90} using equation 4.

Table 1: Parameter of the Particle Size Distribution

ZrO_2 Powder	Particle Size (μm)			Particle Width Distribution (S_w)	Specific Surface Area (m^2/g)
	D_{10}	D_{50}	D_{90}		
ZrO_2 500°C	38.725	121.380	142.802	4.5170	0.0635
ZrO_2 600°C	21.928	153.055	299.111	2.2558	0.1350
ZrO_2 700°C	190.251	930.022	1546.454	2.8132	0.0268
ZrO_2 800°C	507.257	993.615	1473.014	5.5294	0.0288

$$S_w = \frac{2.56}{log_{10}\left(\frac{D_{90}}{D_{10}}\right)} \quad (4)$$

The ideal condition of the value S_w the be either less than 2 or greater than 7 show that very broad (S_w = 2 or D_{90} = 19D_{10}) or very narrow distribution (S_w = 7 or D_{90} = 2.3D_{10}) (Zauner, 2006). Based on the results tabulated on the table, synthesized zirconia samples are 4.5170, 2.2558, 2.8132 and 5.5294 respectively and the particle width distribution correspond to broad distribution because less than 7.

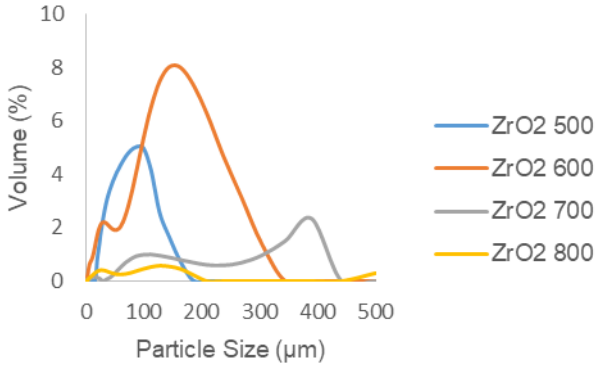

Fig.3: Particle Size Distribution for Synthesized Zirconia Powder of Different Temperature of Calcination

The figure 3 showed, the temperature increases make the particle size distribution become less narrow except for synthesizing zirconia at temperature 600°C. Calcination temperature influenced the size of zirconia and densification of samples. However, in this result, the value of specific surface area are not consistent. Smaller the size, the larger specific surface area. The particle size of the powder directly depends on calcination temperature because the high temperature, shrinkage happen (Yaqub, Savaniu, Janjua, & Irvine, 2013). The observation can made the lower calcination temperature, the narrower the distribution. Primary particles of the distribution broaden with equivalent volume fraction decreases as the increases of the calcination temperature (Yaqub et al., 2013). In figure 4, the influence of the particle size on the phase of zirconia is shown when the calcination to produce zirconia is done. The calcination temperature affect the size of the distribution. The surface area of the calcination at temperature 600°C is most high. Probably the zirconia is define as amorphous zirconia because have high surface area because the presence of small particles and can presence of the surfactant can be induced (Stichert & Schüth, 1998). However, the particle size probably be the factors because the nuclei embryonic were responsible with the nature of the phase obtained. The improvement of digested zirconia increases the resistance too thermal calcination up to 800°C when compared to the undigested zirconia. The time of digestion increases, the loss in surface area

decreases with calcination temperature up to 800°C (Chuah & Jaenicke, 1997). Hence, the smallest particle size width is 2.2558 which is synthesized zirconia at 600°C with largest specific surface area is 0.1350 m^2/g.

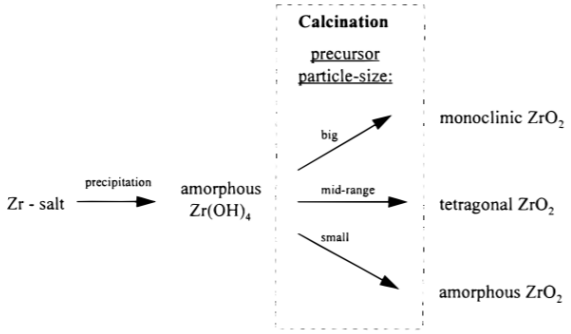

Fig. 4: Influence of the Precursor Particle Size on the Phase of Zirconia (Stichert & Schüth, 1998)

In BET analysis, specific surface area, S_{BET} and pore distribution are determined. In table 2, parameter of BET analysis of synthesized zirconia is been stated.

Table 2: Parameter of the BET Analysis

ZrO_2 Powder	BET Surface Area, S_{BET} (m^2/g)	Total Area in Pores(m^2/g)	Total Volume in Pores (m^3/g)
ZrO_2 500°C	1.0721	0.239	0.00147
ZrO_2 600°C	0.6811	0.329	0.00439
ZrO_2 700°C	1.8915	0.546	0.00205
ZrO_2 800°C	1.5074	0.750	0.00268

The highest BET surface area of synthesized zirconia is 1.8915 m^2/g that been calcined at 700°C and lowest surface area at 600°C which is 0.6811 m^2/g. For total volume in pores, the highest is 0.00439 m^3/g of synthesized zirconia at 600°C and lowest is 0.00147 m^3/g. However, the increasing the calcination temperature, the total area in pores of synthesized zirconia increases.

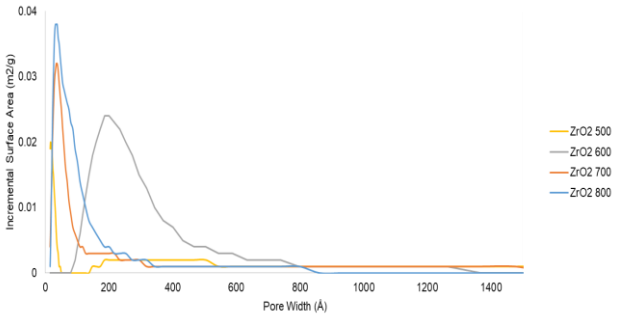

Fig.5: Surface Area against Pore Width of Synthesized Zirconia at Different Calcination Temperature

In figure 5 showed that surface area against pore width of synthesized zirconia calcined at 500°C, 600°C, 700°C and 800°C. The pore width is become widen with increasing the calcination temperature except for the synthesized zirconia calcined at 600°C. The pore width is largest with incremental surface area at 600°C when synthesized zirconia calcined. The pattern of graph for synthesized zirconia at 600°C, 700°C and 800°C are unimodal and for synthesized zirconia at 500°C is bimodal. The synthesized powders contained voids or pores in addition to particle slower growth direct to loose porous structure and sustain its nature of amorphous during calcination up to 500°C (Nayak & Nayak, 2016). At 600°C, the intermediate temperature for zirconia transform phase from amorphous to crystalline nature of t-zirconia and at 800°C, stabilization was found for t-zirconia with porous structure (Nayak & Nayak, 2016). The assumption can be made the ceramics with spherical shape near to existence of large pores causes of presence of particle with hollow spherical in source powders since average size of powder corresponding with large pores with average size in calcined material (Buyakova, Sablina, & Kulkov, 2015).

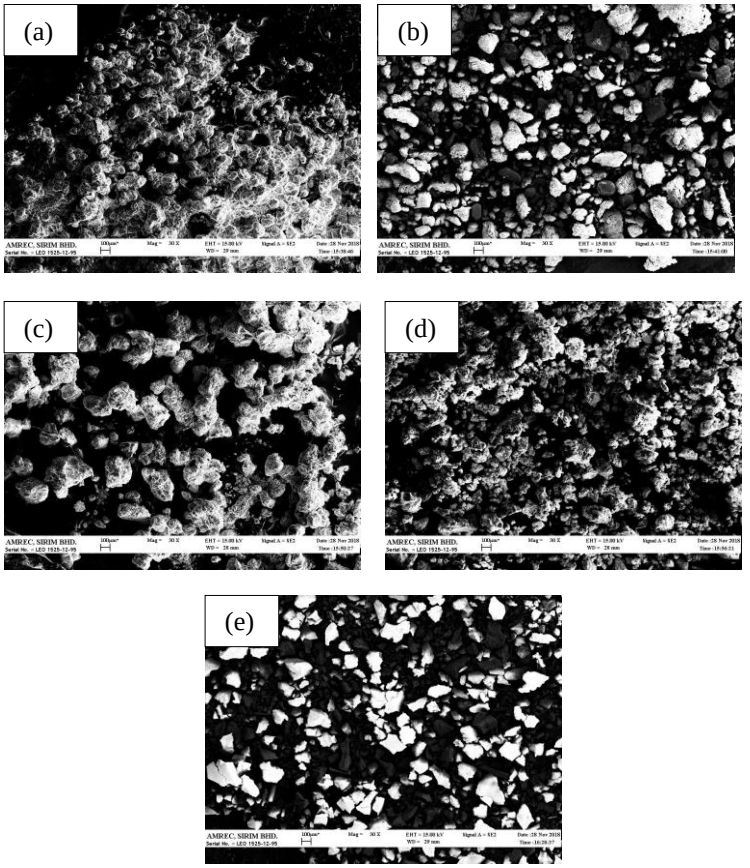

Fig. 6: SEM Images of (a) Synthesized Zironia at 500°C (b) Synthesized Zironia at 600°C (c) Synthesized Zironia at 700°C (d) Synthesized Zironia at 800°C (e) Commercial Zirconia

In figure 6, SEM images are resulted from SEM analysis for surface and topography of zirconia that been synthesized at different calcination temperature and commercial zirconia. The particle size found in this BET method are at (a) is 75.92 µm, (b) is 214.4 µm, (c) is 178.6 µm and (d) is 58.06 µm. The particle size at (b) showed the seemed to be with particle size in particle size distribution. These observations of quantity phase of crystallized being mostly dominant with narrowness of the line profile showed in the pattern of XRD are in perfect agreement (David, Trolliard, Volkringer, Loiseau, & Maître, 2015). The structure in (a) showed like amorphous because it not apparently like crystalline. However, it difference in images in (c) and (d), the shape of agglomeration of the powder reduces when the temperature of calcination increases but for images in (b) showed the similarity shape with (e). The powder in calcined at 600°C have same shape with commercial zirconia. Based on this observations, the synthesize of zirconia powder can be determine using Australian zircon sand when calcined at 600°C.

Based on previous study, the calcination temperature of the local zircon sand from Indonesia with same method of synthesized using caustic fusion method that been calcined higher than 500°C gives good ionic conductivity (Apriany et al., 2016). The slopes of zirconia calcined at 600°C to 700°C showed the greatest ionic conductivity based on their researches (Apriany et al., 2016). However, the application of the zirconia differ with the previous study, the synthesize of zirconia using different raw material which Australian zircon sand can be synthesized with same method. The results obtained also showed that zirconia calcined at 600°C gives the almost same structure with commercial zirconia and the other characteristics such as surface area and volume pore is the greatest when compared with others zirconia.

B. The effects of dopant of yttrium oxide on as-synthesized zirconia

In figure 7, the XRD pattern of synthesized 3 mole % YSZ and commercial 3 mole % YSZ are been showed.

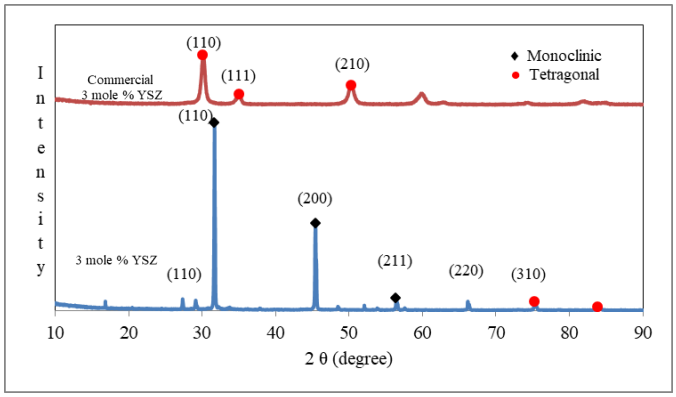

Fig.7: XRD Patterns for Commercial and Synthesized 3 mole % YSZ

The addition or dopant the yttria is done by using planetary ball milling to mix the powder. XRD pattern of 3 mole % YSZ has structure tetragonal zirconia that been confirm by ICDD 072-7115 in figure 7 (Gafur, Saifur, Sarker, Zahangir Alam, & Qadir, 2017). However, the structure of the monoclinic zirconia more than tetragonal structure because as-synthesized zirconia at 800°C is used. The structure of tetragonal can be increases when the sintering of 3 mole % YSZ is done to stabilize the structure. Few peak of before the dopant are reduce and narrow it showed the particle size should be fine. The commercial powder can be observed the peak is not sharp and the phase are tetragonal. The phase can be obtained because commercial 3 mole % YSZ are been sintered probably at temperature more than 1170°C. Thus, the diffusion between the yttria and zirconia can happen during sintering to ensure the phase stable (Gibson, P. Dransfield, & Irvine, 1998).

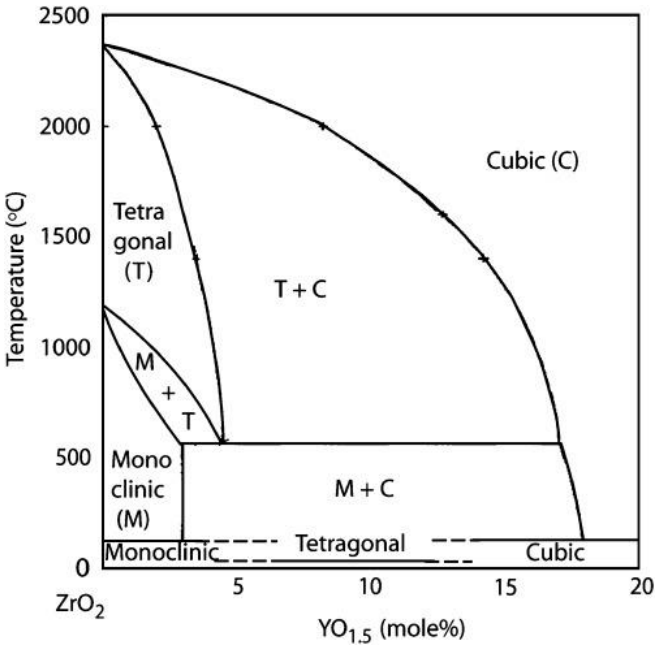

Fig. 8 Phase Diagram of Yttria-Stabilized Zirconia (YSZ) (Witz, Shklover, Steurer, Bachegowda, & Bossmann, 2007)

The phase of the zirconia actually depends on the amount of stabilizer dopant and the sintering temperature of YSZ referred in figure 8. The 3 mole % YSZ that been synthesized should be sintering more than 1170°C to obtain fully tetragonal form while the fully structure of cubic form can determine when dopant of yttria more than 17 mole %. Hence, the sintering temperature and amount of ytttria dopant with zirconia are main factor of the structure of zirconia.

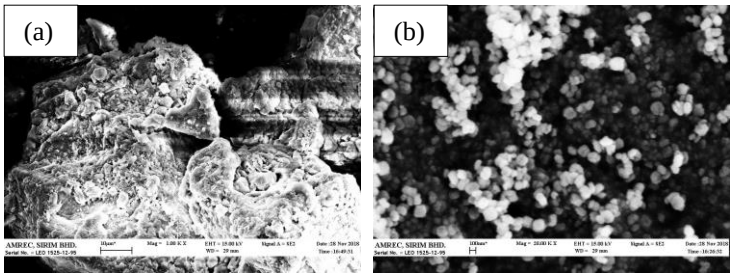

Fig. 8: SEM Images (a) Synthesized 3 Mole % YSZ (b) Commercial 3 Mole % YSZ

SEM images of the synthesized and commercial of 3 mole % YSZ are showed in figure 8. The structure of the both of powder are different. For the synthesized powder the sample higher agglomeration but commercial sample is smooth. The sample seen that many microcracks and fine pores exists (Liang, Ding, Liao, & Coddet, 2009). The ball milling should reduce the agglomeration of zirconia based on previous researches. Ball milling can effectively reduce the agglomerate of zirconia powder, the particle size distribution can improve, specific surface area increases and formation hard agglomerates can be prevent (Zhang, Wang, & Hu, 2013). Hence, the improvement of ball milling to synthesize 3 mole % YSZ should be improve in order to obtain best results.

IV. CONCLUSION

The synthesized of zirconia at different calcination temperature gives different results. In XRD analysis, all synthesized zirconia give monoclinic structure and the commercial zirconia is tetragonal structure. In particle size distribution, the small the particle width distribution resulted larger specific surface area. The highest specific surface area is 0.1350 m^2/g and lowest particle width distribution is 2.2558 of synthesized zirconia at 600°C. The specific area of BET decreases when the total volume increases. The highest total volume pore is 0.00439 m^3/g in BET analysis which obtained zirconia calcined at 600°C and the graph also obtained is perfect unimodal. However, the porosity of the samples can affected when the calcination temperatures increases. Based on the SEM images, the agglomeration of the structure decreases with higher temperature and the amorphous structure can be seen at temperature 500°C. The SEM images synthesized calcined at 600°C corresponding with the SEM images of commercial zirconia. It can be concluded, that Australian zircon sand successful synthesize the zirconia powder based on the results achieved. However, the improvement is needed to synthesized 3 mole % YSZ to achieve comparable results with commercialize samples.

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