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Microstructure Analysis of Zirconia-Alumina-Silica Particles Made from Indonesia Natural Sand Synthesized Using Spray Pyrolysis Method

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Abstract. Zircon sand is one of Indonesian natural resource that is potential to be used as composite filler. Natural zircon sand can be found in several places in Indonesia, i.e. Riau Islands, Bangka-Belitung, and the Borneo. Zircon sand contains zirconia compound; while ZrO_2 is the oxide crystal of zirconia compound. The mechanical and esthetical supremacy of zirconia is the reason why the usage of zirconia as nanocomposite filler mixed with alumina and silica increases. Spray pyrolysis method was used to synthesized natural zircon sand of Indonesia with temperature variety of 400˚C, 500˚C and 600˚C. Spray pyrolysis decomposed zircon sand into powder in nano-sized. Microstructure analysis conducted were SEM, EDS, and XRD. SEM analysis showed that the morphology of particle was spherical, uniform, and regular with size of 100-500nm. EDS and XRD showed best results at the temperature of 400˚C. Analysis result of EDS indicated that the largest atomic percentage was owned by sodium with ratio of Zr:Al:Si of 1:2:54 at temperature of 400˚C. The XRD pattern of 400˚C revealed that the crystal structure of zirconium silicate ($ZrSiO_4$) was tetragonal, the structure of quartz (SiO_2) was trigonal, and the structure of corundum aluminum oxide (Al_2O_3) was rhombohedral. Synthesis of zirconia-alumina-silica particles from natural zircon sand of Indonesia could be used as composite filler based on the characterization results.

Introduction

Indonesia has natural resources that could potentially be used as manufacturing materials for dentistry concerning that expensiveness of current imported materials. Some of these natural resources are cocoa, kaolin, feldspar and zircon sand. Zircon sand contains zirconia compounds. Zirconia (ZrO_2) is a crystalline dioxide form of Zr compound. This material has mechanical properties, durability, and stability, as well as high biocompatibility. Moreover, zirconia is highly resistant to corrosion and scratches. Zirconia is also an excellent aesthetics because of its color that resembles the color of teeth, it is also frequently chosen for the restorations that require aesthetic. Currently, zirconia is used as a filler in nanocomposite with a mixture of alumina and silica. Zirconia has varied different crystallographic structure that's called polymorphism. There are three phases of crystalline zirconia, which is monoclinic, tetragonal and cubical.[1,2] Metastability of zirconia in a tetragonal structure may increase its susceptibility to aging. This is due to the stress induced transformation from tetragonal to monoclinic form, along with an increase in volume and the formation of compressive stress on the surface, thus modify the phase integrity. Increasing volume may impede crack propagation, called transformation toughening.[3,4] Alumina acts as a stabilizer in zirconia, keeping the tetragonal form at room temperature.[5] Beside as a stabilizer, the addition of alumina to the zirconia as a composite material can increase the resistance to fracture.[6] Silica is added to the filler that can enhance the translucency, thus improving the esthetic on restoration results.[7] Nanocomposite is a composite material that contains filler in nano size, ie ≤100 nm. Nano-size materials have several advantages, such as better physical properties and mechanical properties, higher hardness, flexural strength, longer wear resistance, better end result of restoration, reduce shrinkage when curing, reduces discoloration, and reduce bacterial penetration.[8,9] The formation of nanoparticles can be made using spray pyrolysis as well as geo polymerization method. Spray pyrolysis and geo polymerization were top bottom technique of synthesized of ceramic particles. [12]

Materials and Method

The materials used in this study were zircon sand from Kalimantan, acid fluoride (HF), sodium hydroxide (NaOH), nitric acid (HNO_3), and distilled water obtained from a chemical store in Bandung. The tools used were Ohaus' digital scales, spatula, Ougang's mesh, ball mill, KSR's milling, teflon, YDP's hotplate stirrer, magnetic strirrer bar, beakers, pipettes, funnel burner, Yenaco's oven for burning, pyrolysis sprayer, 93 Whatman filter paper, and test tubes. This study was conducted using a spray pyrolysis method. Spray pyrolysis was one of bottom-up methods (chemical). This method was an aerosol process that atomized and heat the solution to produce solid particles. Previous research showed that the synthesis of zirconia with a spray pyrolysis method produces a solid homogeneous nano-size particle structure.[10,11] In addition, spray pyrolysis was also a simple method, in which, when controlled properly, produced high quality particles at a low price.[14] There were several stages in this research, including characterizations of natural Indonesian zircon sand using SEM, EDS and XRD. Purification of the sand was then conducted to remove the content of Ti and Fe with a solution of HF 20%, continued with manufacturing of a precursor solution i.e zirconil nitrate ($ZrO\ (NO_3)\ _2$), aluminum nitrate ($Al\ (NO_3)\ _3$), and sodium silicate ($Na2SiO_3$), as well as the synthesis of particles using spray pyrolysis method at a temperature of 400°C, 500°C and 600°C. The last stage was the characterization of particle synthesis product.

Results and Discussion

The results of the characterization test of natural Indonesian zircon sand using SEM, could be seen on fig. 1a, while fig. 1b, 1c, and 1d showed the result of particle synthesis product characterization.

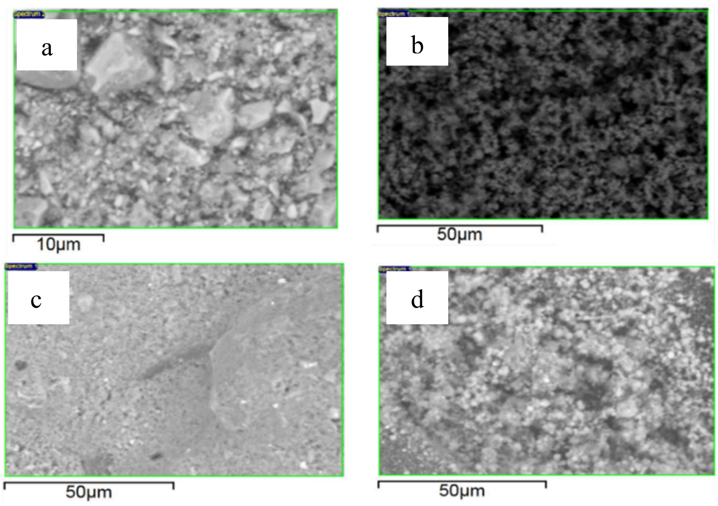

Fig. 1. SEM analysis result of natural Indonesian Zircon sand (a); Particle Synthesis (b) Temperature of400^{o}C; (c) Temperature of 500^{o}C; (d) Temperature of 600^{o}C

Figure 1 (a) showed that the particles was less than 8 μm in size and surface morphology of the sample had irregular sizes and shapes. Figure 1 (b), (c) and (d) showed that the result particles were uniform, dense, rounded with size of 100-500 nm (fine particles). At a temperature of 600^{o}C, the particle looked slightly larger than the particles at a temperature of 400^{o}C and 500^{o}C. Particles produced was influenced by several factors, including temperature and the concentration of precursor solution. Temperature played an important role in the morphology of particles produced because temperature affected the rate of solvent evaporation. The lower the concentration of precursor solution, the smaller particle produced with higher mechanical properties, physical properties, and aesthetic.[9,15,16]
Table 1 showed the results of EDS characterization test analysis of natural Indonesian zircon sand with the addition of 20% HF which showed that Fe content disappeared and Ti were decreased. This occured because HF dissolved both elements [17]. The presence of Na in three particles derived from synthesis results from the addition of NaOH solution which served to dissolve Si that form of sodium silicate (Na_2SiO_3).

Natrium atomic percentage decreased along with temperature increase. Natrium became more decomposed at high temperature. Na atomic percentage

Table 1. Percentage of Sample Content Based EDS Analysis

/No.	Sample	Atomic [%]							
		O	Zr	Al	Si	Ti	Fe	Na	K
1	Natural Indonesian zircon sand	63,403	7,411	0,299	7,825	6,203	3,3	-	-
2	Natural Indonesian zircon sand+ HF 20%	63,653	10,165	0,563	9,777	2,021	-	-	-
3	Temperature of 400^{o}C	54,618	0,034	1,838	0,083	-	-	26,762	
4	Temperature of 500^{o}C	59,829	0,059	2,585	0,130	-	-	19,517	0,392
5	Temperature of 600^{o}C	55,327	0,078	7,571	1,125	-	-	6,474	0,288

decreased causing the atomic percentage of Al and Zr to increase. Zr atomic percentage in three particles from synthesis product was lower than that of Al, while the EDS data of natural Indonesian zircon sand showed that Zr atomic percentage was higher than Al. This occured because Al was more soluble in HNO_3 compared to Zr, so that not all particles of Zr were sprayed [20].

Synthesized product at a temperature of 500^{o}C and 600^{o}C contained potassium. This occured because potassium was not identified at early initial EDS testing. Potassium were probably located in the particles (not surface), while the EDS testing could only identify the elements on the surface. After the leaching process in HNO3, potassium dissolved in the solution to form potassium nitrate (KNO_3), sprayed and was identified in EDS analysis.

XRD analysis results in Table 2 showed that the three particles and compounds synthesized had different crystal structures. Particle synthesis results showed that the percentage of sodium silicide (Na_4Si_{23}) were higher with increasing temperature. This was due to aluminum (Al) contained in corundum aluminum oxide (Al_2O_3) compound at a temperature of 400^{o}C was being decomposed at a temperature of 500^{o}C forming sodium aluminum silicate nepheline ($NaAlSiO_4$), so that the percentage of sodium silicide (Na_4Si_{23}) increased. Aluminium tended to bind with Si compared to Zr because the atomic radius were both fairly close. Aluminum had the atomic radius of 1.3607 Å, silica of 1.1476 Å, whereas zirconium's atomic radius was 3.3598 Å [20]. At a temperature of 600^{o}C, Al was decomposed back and lost its bond with silica, thus forming aluminum oxide hydroxide ($AlHO_2$).

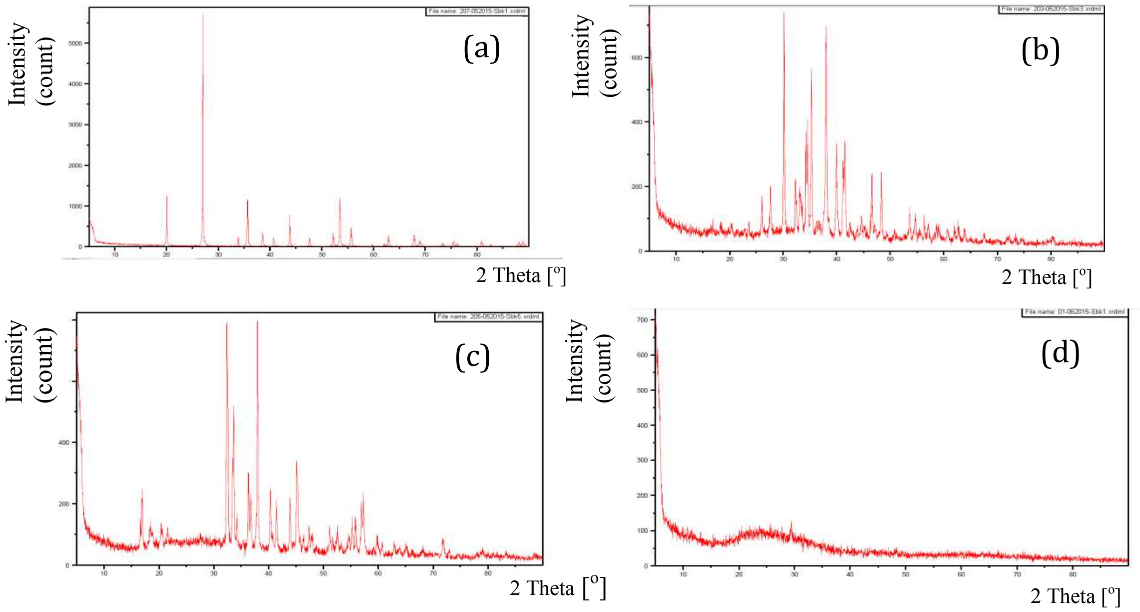

Fig. 2. XRD Diffractogram (a) Natural Indonesian Zircon sand; Particle Synthesis (b) Temperature of 400°C; (c) Temperature of 500°C; (d) Temperature of 600°C

At a temperature of 400°C zirconium silicate zircon crystals formed ($ZrSiO_4$) with tetragonal structure, corundum aluminum oxide (Al_2O_3) with rhombohedral structure, and quartz (SiO_2) with trigonal structure. Three structures of the resulting crystals had high physical and mechanical properties [1,20,21,22,23]. The structure of zirconium silicate zircon ($ZrSiO_4$) and quartz (SiO_2) did not change the crystal structure at the three different temperatures, while aluminum oxide corundum decomposed at temperatures of 500°C and 600°C.

Tabel 2. Results of XRD Analysis (a) Natural Indonesian Zircon sand; Particle Synthesis (b) Temperature of 400°C; (c) Temperature of 500°C; (d) Temperature of 600°C

A

No	Material	Chemical Formula	Quantity [%]	Crystal Structure
1	Quartz	SiO2	30.8	Trigonal
2	Zircon	ZrSiO4	66.3	Tetragonal
3	Aluminium oxide corrundum	Al2O3	1.8	Trigonal
4	Calcium titanate perovskite	CaO3Ti	1.1	Ortorombik

B

No	Material	Chemical Formula	Quantity [%]	Crystal Structure
1	Aluminium oxide corrundum	Al2O3	66.5	Rhombohedral
2	Zirconium oxide (1/2.12) arkelite	ZrO2	14.5	Cubical
3	Natrium silicide	Na4Si23	8.8	Cubical
4	Zirconium	Zr	4.1	Cubical
5	Quartz	SiO2	3.6	Trigonal
6	Zirconium silicate zircon	ZrSiO4	2.7	Tetragonal

C

No	Material	Chemical Formula	Quantity [%]	Crystal Structure
1	Natrium aluminium silicate nepheline	Na4AlSiO4	19.7	Hexxagonal
2	Quartz	SiO2	6.9	Trigonal
3	Natrium silicide	Na4Si23	50.8	Cubical
4	Zirconium silicate zircon	ZrSiO4	11.3	Tetragonal
5	Zirconium	Zr	5.6	Hexagonal
6	Zirconium Oxide Baddeleyite	ZrO2	5.8	Monoclinic

D

No	Material	Chemical Formula	Quantity [%]	Crystal Structure
1	Quartz	SiO2	5.7	Trigonal
2	Natrium silicide	Na2.9Si36	79.9	Cubical
3	Zircon	ZrSiO4	10.7	Tetragonal
4	Zirconium oxide	ZrO2	2.6	Monoclinic
5	Aluminium oxide hidroxide	AlHO2	0.2	Orthorhombic
6	Zirconium	Zr	1	Cubical

Conclusions

SEM and XRD analysis suggest that the alumina-zirconia-silica particles synthesized from natural Indonesian zircon sand at a temperature of 400°C can be used as filler composites. The particle composition did not meet the original design according the ratio of Zr: Si: Al of 1: 2: 54. Further study is necessary in order to determine material ability as filler composites as well as the utilization of natural Indonesian zircon sand from different sand origin and methods, as well as the need to test the characterization of the precursor solution prior to synthesize, to obtain the components contained within.

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