Journal of Materials Science and Engineering B 3 (2) (2013) 122-127

Characteristics of Water-ZrO_2 Nanofluid Made from Solgel Synthesized ZrO_2 Nanoparticle Utilizing Local Zircon

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Received: August 27, 2012 / Accepted: September 22, 2012 / Published: February 25, 2013.

Abstract: This work was carried out in order to study the possibility of applying nanofluid for nuclear reactor coolant. Nanofluid is a mixture of fluid and nanoparticle forming a stable suspension. Here ZrO_2 nanoparticle or nanopowder was synthesized using solgel method from $ZrOCl_2{\cdot}8H_2O$ (ZOC) utilizing sucrose as a chelating agent. The powder of ZOC was derived from local zircon using caustic fusion method. Data of X-ray diffraction (XRD) showed that the nanoparticler contains one phase of monoclinic with crystallite size of 14 nm. Transmission electron microscope (TEM) data showed that the particle size was about 25 nm. It was known that the produced nanofluids were stable until 20 days observation. Zeta potential of the nanofluid was 53 mV. According to the PSA data the average particle size of a typical nanofluid was 66 nm. Thermal conductivity of a typical nanofluid with concentration of ZrO_2 of 1 weight% was 5.5% larger than that of water.

Key words: Nanofluid, nanopowder, ZrO_2, local zircon, solgel.

1. Introduction

There is a need to enhance nuclear reactor safety by improving thermal management [1]. This need is related to attempts to step up the performance of nuclear power plants. Water as a conventional coolant has been being used in cooling system of many nuclear power plants. However, it is considered that the heat transfer performance of water is low. So, the capability of water as a coolant needs to be increased. The low heat transfer performance of the coolant will affect the performance of the nuclear power plant. Considering this situation, it is necessary to improve the capability of water in heat transfer. Nanotechnology may be applied in improving the heat transfer capability of water. One way to improve the performance of water in heat transfer is by applying nanofluid as a new coolant. Nanofluid is a product of the application of nanotechnology which is a mix of nanoparticle with water forming a stable suspension. Research on nanofluid has been widely being done in the world [2-7]. Nanofluid is possible to be applied as primary coolant of pressurized water reactor (PWR) and standby safety systems [5]. In production of nanofluid, synthesis of nanoparticle is the key.

Nanoparticle may be produced using many methods, one is solgel [8-10]. In this work, the nanoparticle of ZrO_2 was produced using a sol-gel method and the nanopowder was then utilized for producing nanofluid. Good nanofluid has some criterion and one of them is that the nanoparticle should not precipitate for long time. Application of water-ZrO_2 as a nanofluid for the nuclear reactor cooling system is a good choice due to small neutron absorption of ZrO_2. Especially when the water-ZrO_2 nanofluid is applied for the coolant of the primary cooling system.

Mineral of zircon ($ZrSiO_4$) is relatively abundant in Indonesia, however, utilization of it for advance materials is rare. So, in order to step up the added

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value of local zircon, here ZrO_2 was extracted from the local zircon and was used for production of the water-ZrO_2 nanofluid. Powder of ZrO_2 was extracted from zircon by caustic fusion and the ZrO_2 nanoparticle was synthesized using a solgel method utilizing sucrose as a chelating agent. Characteristics of our ZrO_2 nanoparticle was compared with the nanoparticle synthesized by other researchers and the nanofluid produced from the ZrO_2 nanoparticle was characterized.

2. Experiments

2.1 Synthesis of $ZrOCl_2{\cdot}8H_2O$ (ZOC) Crystal

Powder of local Zircon ($ZrSiO_4$) with chemical composition of Table 1 was mixed with NaOH. Diffraction pattern of the local zircon is shown in Fig. 1. The concentration of NaOH was varied so that the weight ratios of NaOH/Zircon were 1.33 and 1.7. The mixed powder was heated at 700 °C for 2 h for fusion. Frit from fusion process was leached using water. Solid part was separated from liquid part by filtration. The solid part was subjected to x-ray diffraction (XRD) analyses to know whether or not the concentration of NaOH was enough. The solid part already free from zircon was leached using HCl 5 M. After about 24 h kept at room temperature, the solution was filtered. The filtrate was heated at 60 °C to get $ZrOCl_2{\cdot}8H_2O$ (ZOC) crystal. The crystal was washed using ethanol and again heated at 60 °C to get white ZOC.

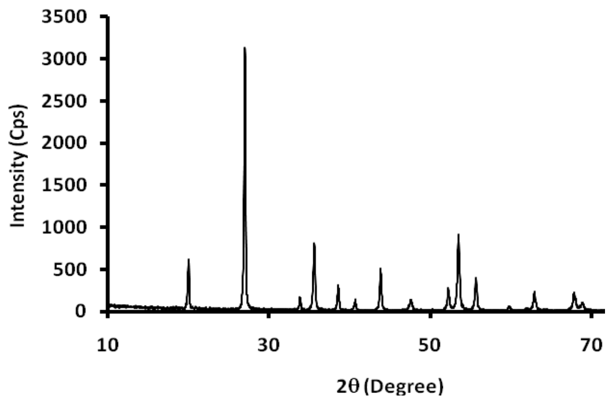


Fig. 1 XRD pattern of the local zircon.

Table 1 Chemical composition of local zircon used as raw material.

No.	Component	Concentration (weight %)
1	SiO_2	34.13
2	ZrO_2	65.22
3	Al_2O_3	0.083
4	Fe_2O_3	0.054
5	K_2O	0.004
6	Na_2O	0.029
7	LOI	0.48

LOI = lost of ignition

2.2 Synthesis of ZrO_2 Nanopowder

Powder of ZOC was dissolved in water. Sucrose was put into the solution. The sucrose and Zr^{4+} ion mole ratio was 0.75. NH_4OH was used to control the pH of the solution (sol) at 5. The sol was heated at 80 °C for 24 h to form gel. The gel was heated at 400 °C to form a xerogel. The xerogel was then calcined at 800 °C for 4 h to get ZrO_2 nanopowder/nanoparticle. The nanopowder was analyzed using XRD. Particle size of the powder was calculated using Debye Scherrer formula [11] from the XRD data. The nanopowder was then utilized to produce nanofluid.

2.3 Synthesis and Characterization of Nanofluids

The nanofluid was made by mixing the ZrO_2 nanopowder with aquadest and ultrasonicating the suspension. 1 g of ZrO_2 nanopowder was mixed with 100 mL of aquadest, shacked and ultrasonicated for 1 h. The nanofluids were observed visually time to time by taking picture using a digital camera. The decrease of the surface of the nanofluid was measured at every certain time. A particle size analyzer from Horiba was used to know the distribution of particle size as well as the average particle size. Viscosity and zeta potential of the nanofluids was measured using a vibro viscometer and Zetasizer (from Malvren), respectively. Thermal conductivity of the nanofluids was measured using a thermal conductivity meter of KD2 Pro.

3. Results and Discussion

3.1 Synthesis of ZOC and ZrO_2 Nanopowder

Diffraction patterns of solid part resulted from water leaching were depicted in Fig. 2. Upper pattern is that of the solid part containing zircon. At NaOH/zircon ratio 1.33 the concentration of NaOH is not enough for complete fusion. When the concentration of NaOH is enough for the fusion, the zircon peaks does not appear in the XRD pattern as shown in Fig. 2 (lower part) for NaOH/zircon ratio of 1.7. This means that the NaOH/zircon ratio of 1.7 can be made as the minimum value to ensure that the caustic fussion will work well. The solid part that free of zircon was leached by using HCl 5 M. After recrystalization, ZOC was formed. The XRD pattern of the ZOC is shown in Fig. 3. The pattern is in agreement with JCPDS No. 32-1498 for ZOC. No peak from $ZrSiO_4$ was observed indicating that the process of caustic fusion succeded.

The produced ZOC was processed using a solgel method utilizing sucrose as a chelating agent to produce ZrO_2 nanoparticle. Pectin was used by Suciu, et al. [8, 9] and Kashani-Motlagh, et al. [10] for modification, however, it was not used here. The XRD pattern of the ZrO_2 nanoparticle is depicted in Fig. 4. No peak from SiO_2 was observed indicating that utilizing local zircon for production of ZrO_2 is possible in order to step up its added value. The nanopowder crystallizes in monoclinic with crystallite size is 14 nm as calculated using Debye Scherrer method [11]. This crystallite size is comparable to that synthesized by Suciu et al of 22.91 nm at 900 °C [8] and by Kashani-Motlagh, et al. [10] of 17 to 31 nm at 700 °C. Suciu, et al. [8] and Kashani-Motlagh, et al. [10] synthesized ZrO_2 base material using the method as used in this work, however, they modified the method by adding pectin. Although, the pectin was not used here, however, the result is comparable to their results, even better than that of Kashani-Motlagh [10].

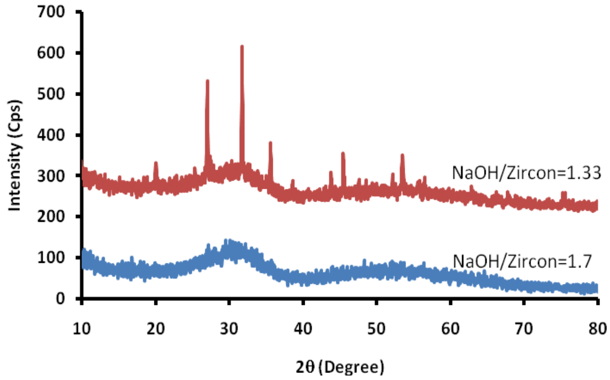


Fig. 2 XRD pattern of solid part of water leached frit.

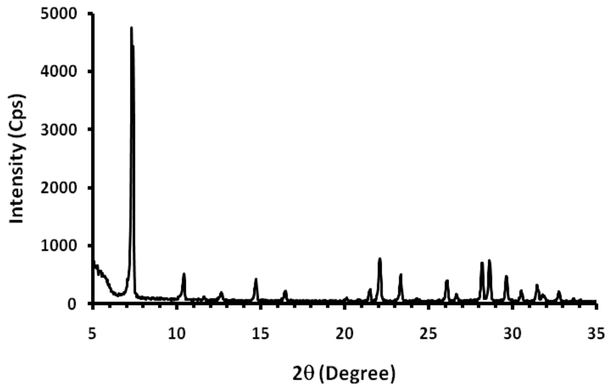


Fig. 3 XRD pattern of ZOC powder.

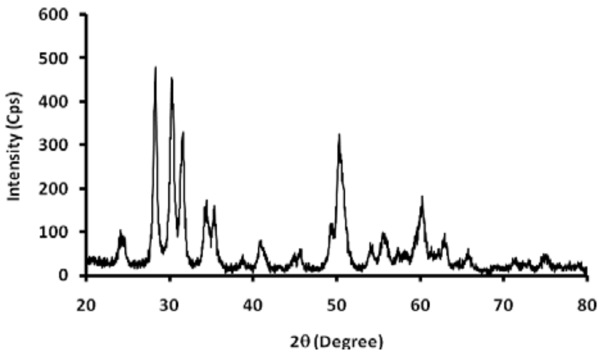
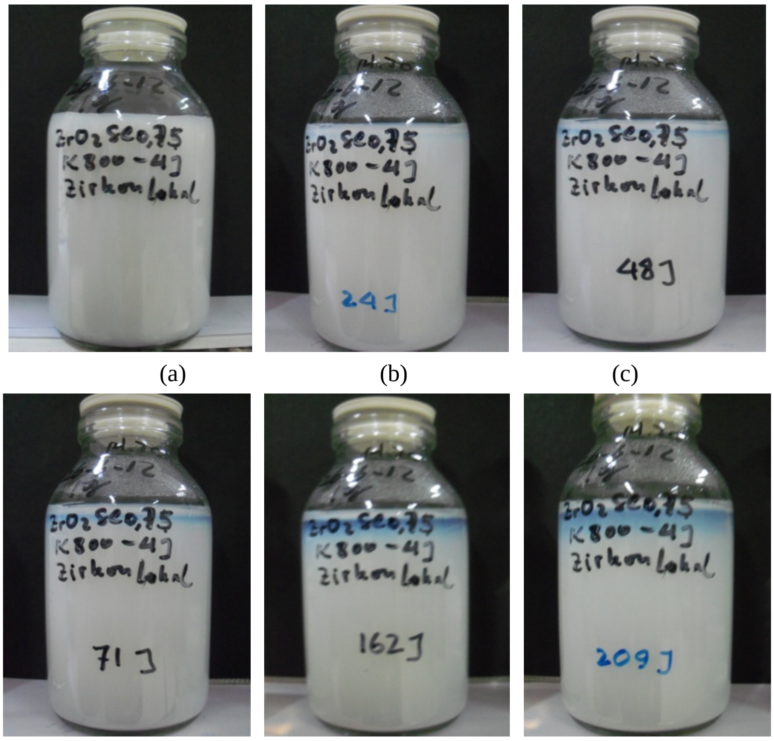


Fig. 4 XRD pattern of ZrO_2 nanoparticle calcined at 800 °C for 4 h. Crystallizes in monoclinic with average crystallite size of 14 nm.

3.2 Synthesis and Characterization of Water-ZrO_2 Nanofluid

3.2.1 Visual Appearance and Sedimentation

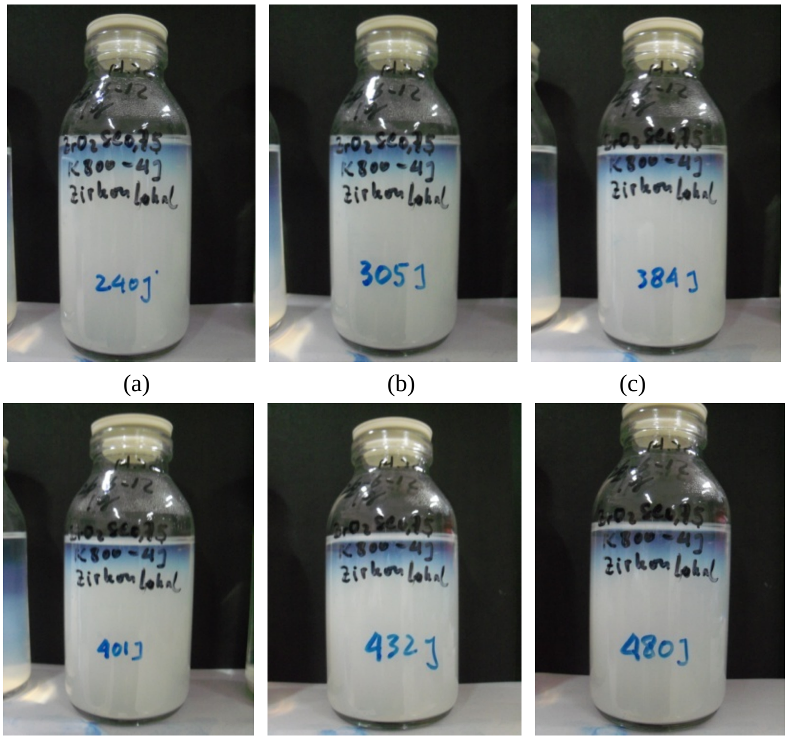
Visual appearance of nanofluids made of water (aquadest) and ZrO_2 nanopowder which then called as water-ZrO_2 nanofluid is shown in Figs. 5 and 6. After ultrasonicated a part of nanopowder was precipitated



(a) (b) (c)

(d) (e) (f)

Fig. 5 Nanofluid made from ZrO_2 nanopowder calcined at 800 °C. Initial (a) and after (b) 24 h, (c) 48 h, (d) 71 h, (e) 162 h and (F) 209 h.



(a) (b) (c)

(d) (e) (f)

Fig. 6 Nanofluid made from ZrO_2 nanopowder calcined at 800 °C. After (a) 240 h, after (b) 305 h, (c) 384 h, (d) 401 h, (e) 432 h and (f) 480 h.

at the bottom of the bottle and another part of the nanopowder forms nanofluid. After certain time the height of nanofluid in the bottle decreases (sedimentation process). The height of the nanofluid was observed after 24 to 480 h observation and the picture of the nanofluid was taken using a digital camera. The nanofluid made is relatively stable. After 480 h observation, the height of the nanofluid made decreases only 20% from the initial height. The relation between the height of the nanofluid surface and observation time is depicted in Fig. 7.

3.2.2 Viscosity, Thermal Conductivity and Particle Size

Particle size of the nanoparticle in the nanofluid was measured using TEM and PSA. TEM image of nanoparticle can be seen in Fig. 8. As one can see, the particle size is about 25 nm. This means that the particle consists of about two crystallites. PSA can be used to check whether the particle in the nanofluid forms agglomerate or not. Particle size of a typical nanofluid after 305 h measured by PSA is about 66 nm. This data shows that the ZrO_2 particles tend to form agglomerate in the nanofluid. The agglomerate consists of about three particles. The formation of agglomerate is one cause of the precipitation of the nanoparticle in nanofluid.

Thermal conductivity of nanofluids with concentration of 0 to 1 weight % was measured. Effective thermal conductivity as function of ZrO_2 nanoparticle concentration is shown in Fig. 9. The effective thermal conductivity is the ratio between thermal conductivity of nanofluid and that of water. The effective thermal conductivity increases as the increase of the ZrO_2 nanoparticle concentration. The thermal conductivity for a typical nanofluid with 1% nanoparticle increases 5.5% compared to that of water indicating the potential benefit of nanofluid to be applied as a coolant especially for nuclear reactor. Recapitulation of the characteristics of a typical nanofluid was depicted in Table 2.

4. Conclusions

Nanoparticle of ZrO_2 has been well synthesized using solgel method utilizing sucrose as chelating agent from local zircon with calcination temperature of 800 °C. The nanoparticle crystallized in monoclinic with crystallite size of 14 nm measured using Debye Scherrer method. Nanofluid of water-ZrO_2 could be well produced from the synthesized nanoparticle. The nanofluid was relatively stable after 20 days observation where the height of the nanofluid just

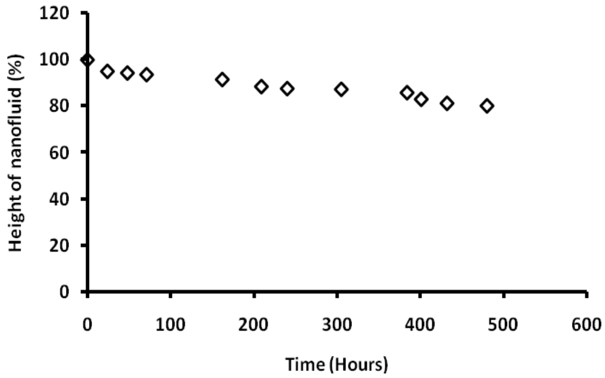


Fig. 7 The height of nanofluid as function of time.

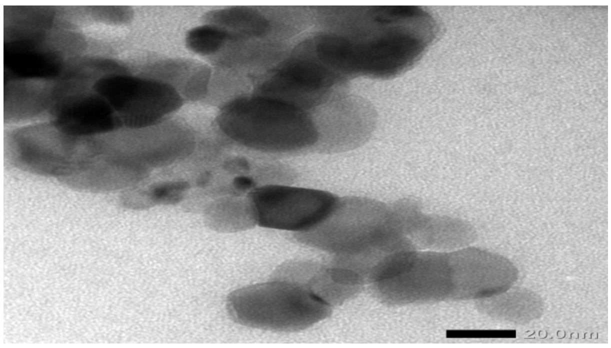


Fig. 8 TEM image of typical Water-ZrO_2 nanofluid.

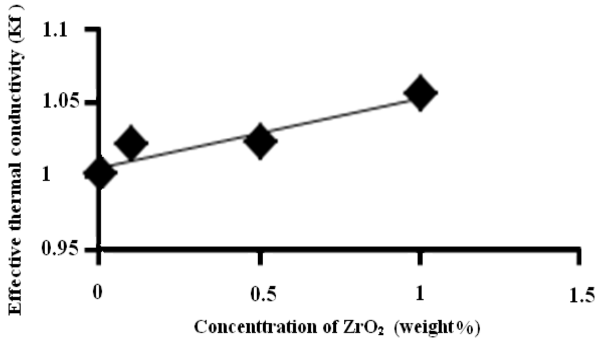


Fig. 9 Effective thermal conductivity of water-ZrO_2 nanofluid as function of ZrO_2 concentration.

Table 2 Recapitulation of the characteristic of a typical water-ZrO_2 nanofluid.

No.	Characteristic	Value
1	Average particle size measured by PSA (after 305 h observation)	66 (nm)
2	Height of nanofluid after 20 days (480 h)	80%
3	Particle size measured by TEM (after 305 h observation)	25 (nm)
4	Zeta potential (after 305 h observation)	53 (mV)
5	Thermal conductivity ratio of nanofluid (at concentration of 1 weight% ZrO_2) and water	1.05
6	Viscosity (at concentration of 0.7 weight % ZrO_2 and 28.7 °C)	1.4 (m·Pa·s)

decreased about 20% from the initial height with zeta potential of 53 mV. Particle size of a typical nanofluid measured by TEM was 25 nm consisting about two crystallites. The average particle size of a nanofluid measured by PSA was 66 nm showing that the particle of ZrO_2 in the nanofluid formed agglomerate. The thermal conductivity of the nanofluid with 1% ZrO_2 nanoparticle is 5.5% higher than that of the water. Production of ZrO_2 from local zircon is possible and beneficial. In addition, the produced nanofluid had a possibility to be applied for nuclear reactor coolant.

Acknowledgments

This work was funded by Ministry of Research and Technology through PKPP program year 2012. Thanks to Mr. M. Yamin for his help in synthesis of ZrO_2.

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