Intensive Study of Ceria Microsphere Stabilized with Zirconia by The External Gelatin Method

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Abstract. One of the keys to success in the process of fuel synthesis for pebble type high temperature nuclear reactors is mastery in kernel synthesis technology which is the core of the fuel itself. In this paper, the results of a comprehensive study of the preparation of a kernel microsphere from ceria stabilized zirconia (CSZ) using the external gelatin method in BATAN will be discussed. Important parameters obtained from this experiment will be the basis for the actual manufacturing of nuclear fuel kernels. Analysis based on measurement data using the Small Angle Neutron Spectrometer (SANS) provides a deep understanding of the mechanism of CSZ microsphere formation, so that at the end it can provide an understanding of how to avoid possible cracks during heat treatment.
Keywords: Kernel, Ceria stabilized Zirconia, Small Angle Neutron Scattering

1. Introduction
Fuel for gas-cooled high temperature nuclear reactors (HTGR) was researched and developed to support the operation of HTGR in the UK in 1956 and the simultaneous but independent operation of the 'pebble bed reactor' in Germany in 1967 [1]. The fuel consists of three layers of carbon and one ceramic based layer as a containment layer of fission products with a kernel core in the form of uranium oxide, or later known as TRISO. The initial challenge in the TRISO fuel manufacturing process is how to obtain a kernel with a uniform size, high density and free from cracks.

Based on various considerations, BATAN as a research institution in the field of nuclear technology in Indonesia has adopted a policy to explore the potential implementation of high temperature power reactors with helium gas coolers (Gas Cooled High Temperature Reactors, HTGR). The choice of HTGR was based on various considerations, apart from the main factors related to safety, and also efficiency in terms of heat exchange which was ultimately expected to support various aspects of industrial activities in Indonesia. The HTGR type chosen is the 'pebble bed' type with a TRISO-based fuel. The TRISO type fuel is the most advanced type of nuclear fuel at this time. The choice of TRISO-coated particles could reduce fission product release, extended burnup and higher fuel temperature applications [1].

Considering that in the future, Indonesia is expected to be able to meet HTGR fuel needs independently from within the country, so one of the activities in preparation for the first HTGR implementation in Indonesia is to prepare facilities to carry out research in the field of pebble fuel manufacturing processes. The research began with preparing the kernel using NUKEM technology-based facilities, Germany. The method used is an external gelation system. The mastery of
manufacturing technology is carried out through intensive collaboration of several research centers within BATAN, namely the Center for Nuclear Fuel Technology (PTBBN) and the Center for Science and Technology of Advanced Materials (PSTBM).

Although research on Ceria stabilized Zirconia (CSZ) has been widely carried out, both aiming at developing biocompatible materials [2], as well as relating to the study of the development of high temperature nuclear fuel reactors. Systematic research to obtain uniform CSZ particle sizes with small deviations has been carried out by varying the broth flow velocity according to the nozzle size used in the dropping process. It was also found that microspheres with low Zr content were more oblique compared to high Zr concentrations, apart from that the measurement results also showed that the density increased with increasing Zr concentrations [3]. Another challenge in the synthesis of microspheres with the external gelatin method is size uniformity. Uniformity in size and shape is also an important parameter in obtaining high-quality nuclear fuel. The results showed that the uniformity of shapes of a certain size was greatly influenced by the large vibration vibrational frequencies that functioned for liquid jet breaking up into uniform droplets with a certain nozzle size. The optimal frequency is found to follow Raleigh's theory [4]. The microsphere formed is composed of crystallites with a size of about 200 micrometers.

As discussed in previous research, it has succeeded in providing a clear picture on the micrometer scale about the microsphere, however it has not yet discussed what happened from the early stage of the crystallization process. It has also been explained about several parameters that must be controlled to get the kernel (microsphere) with the external gelatin method as desired. However, by understanding the process of forming the microsphere from the formation of the crystallite core, it is hoped that the possibility of failure in the manufacturing process of nuclear fuel will be reduced. One method that can be used for characterization is the small angle scattering technique, both using x-rays or neutrons as probes. These two facilities, Small Angle X-ray Scattering (SAXS) and Small Angle Neutron Scattering (SANS) complement each other. SAXS can be used to see crystallite sizes in the range 0.1-0.2 nm, while SANS can see sizes up to micrometers [5,6]. Actually, with this facility it is very possible to follow the dynamics of phase growth related to changes in temperature or caused by other external influences both chemically and physically.

In this paper, intensive studies of the crystallization process of Ce-Zr surrogate-based kernels have been carried out using small-angle neutron scattering facilities located at the Center for Advanced Materials Technology, BATAN and also small-angle X-ray scattering installed in BL.3 in. SLRI, Thailand. The research is focused on understanding the mechanism of kernel formation, especially with regard to the phase transformation from the polymeric system to the ceramic system through the heat treatment process. The heat treatment in the formation of the kernel plays an important role, because with the right heat treatment can avoid cracking in the kernel. The neutron scattering technique can be used to understand how the agglomeration patterns of the polymer metal molecules are deformed by the heating process and then followed by the formation of the kernel crystallite core.

2. Experimental

2.1. Sample Preparation

CSZ synthesis process with the external gelatin method, as has been discussed in many papers, starts with making broth which is the result of mixing a salt of Z(NO$_3$)$_4$ and a salt of Ce(NO$_3$)$_3$, which is dissolved in 250 ml of demineralized water and then while stirring heated at 80°C, so that a homogeneous solution is obtained. After part of the salt is completely dissolved, 8% PVA (Polyvinyl alcohol) and 50 ml THFA (Tetra Hydro Furfuryl Alcohol) are added to form the sol. The solution is stirred continuously until it reaches a pH of 2.67 and the viscosity is close to 60 mPa.s. The soles that have been formed are left in place for one night, so that the gas bubbles formed can come out perfectly. The preparation of the sol solution is in line with what has been done by Guogao W et.al [7].

The sol liquid that has been obtained is placed in a container that is ready to be dispersed with a nozzle inner diameter 1.0 mm and in this experiment the vibration frequency was setting follow Haas
[8], by regulating using a frequency generating facility [4]. To check whether the sol liquid dispersion rate through the nozzle is stable, a frequency-adjusted strobe light is used so that the sol is distributed in the form of a stable sphere. Schematically, it can be seen in Figure 1 a and 1 b. Like a gelatin external process, the liquid that comes out of the nozzle has passed through the passage of air flow, ammonia gas flow before falling into the gelatin column containing ammonia solution [9]. Gel that has been hardened on the outer skin in ammonia solution with a concentration of 3 mol/l and allowed to stand for 2 hours, then separated with a sieve and then washed using 0.5 M NH4OH solution 2 times with an interval of aging 30 minutes, followed by washing using demineralized water six times and followed by washing using propylene glycol monomethyl ether (PGME) four times with an interval of soaking for 30 minutes.

After the systematic washing process is completed, the microsphere gel granules are then dried at 60°C for 12 hours using a Rotary Vacuum Evaporator. To ensure the kernel is free from water content, the drying process is continued at 120°C for 4 hours.

2.2. Heat Treatment

As explained earlier, the heat treatment process plays an important role in the formation of the kernel. Basically, it can be said that the formation of metallic kernels occurs through the deformation process of gelatin and is followed by the formation of crystallites of Ce and Zr oxides. The deformation process of the gelatin system can be clearly seen from the thermal analysis data using DTA, see Figure 1.

The thermal data measured by DTA is very important, as shown in Figure (above), there is a change in enthalpy and mass at 231°C due to the decomposition of organic materials that function as a matrix of the gelatin system, namely PVA (Poly vinyl alcohol) and THFA (tetra hydro furfuril alcohol). Therefore, from the effect of this decomposition, there was a significant reduction in the relative mass of 28.2%. The mass change in the second stage is very important, because at this stage the calcination process occurs. However, it must be admitted that the measured DTA data are not very detailed, because at around 400°C-500°C the-Zr2O3 [9] phase formation should be detected which is very much influenced by pH. To complete the thermal data, a series of measurements using FTIR has been carried out for a range of temperatures of 60, 120, 200, 400, 600, and 1200 °C, as shown in Figure 2. Based on this FTIR data, the decomposition mechanism of chemical compounds the gelatin process can be analyzed. As shown in Figure 2, at a temperature of 60-200 °C, the water evaporation process occurs and the OH group associated with the alcohol compound used in the gelatin synthesis also disappears, according to the wave numbers 1099 cm⁻¹, 2941 cm⁻¹ and 3258 cm⁻¹. Meanwhile, at a temperature of 400 °C, FTIR data.

Figure 1. Thermal analysis data measured by DTA [10].
shows that the absorption wave numbers around 1340 cm\(^{-1}\) and 1577 cm\(^{-1}\) have not been detected, this is related to the decomposition process of the nitro (NO) group, according to the reaction:

\[
\begin{align*}
(NH_4)_2ZrO_3 (s) \rightarrow & \text{ ZrO}_2 (s) + NO \text{ (g)} + H_2O \text{ (g)} \\
(NH_4)_2CeO_3 (s) \rightarrow & \text{ CeO}_2 (s) + NO \text{ (g)} + H_2O \text{ (g)}
\end{align*}
\]

So that at a temperature of 400 °C, the \(\alpha\)-Zr\(_2\)O\(_3\) oxide compound began to form in accordance with the observations of very fine crystallites [2].

Based on the results of measurements with DTA and also analysis using FTIR, the CSZ system phase formation process is carried out according to the heating pattern as shown in Figure 3.

![Diagram of heat treatment of CSZ](image)

**Figure 3.** Diagram of heat treatment of CSZ

The heating process is carried out with a heating speed of 0.5°C/minute, by holding the temperature stable at 120, 200, 400, 600, and 1200 °C for 4 hours, with the aim of providing sufficient time for the decomposition process to occur perfectly.
3. Results and Discussion

Based on the heat treatment process, qualitatively the metal oxide formation phase system from the gelatin process by an external method can be evaluated. In Figure 4, it can be seen clearly the results of the heat treatment process of the microsphere according to the X-ray diffraction measurement data.

![Figure 4. X-ray diffraction patterns for each heat treatment performed on CSZ [10]](image)

Based on X-ray diffraction data, it can be seen that at temperatures below 400ºC, no diffraction peaks are formed according to FTIR data. The main process that occurs is in the form of decomposition of organic groups as part of the formation of sol-gel. After the polymer matrix has completely decomposed, at 400ºC it begins to enter a very fine crystallization phase of the oxide system, such as \( \alpha-Zr_2O_3 \). This is shown from the diffraction peaks that are still wide with low diffraction intensity. Apart from the crystallization process, it is also hoped that a microsphere will be formed without cracks. So the decomposition mechanism followed by crystallization must run simultaneously. Using a small angle scattering technique using X-ray beams and neutrons, the assembly process can be observed in stages.

The scattering pattern of X-rays and neutrons is generally described as the intensity versus the amplitude of the scattering vector or momentum transfer, which is expressed by:

\[
q = \frac{4 \pi \sin \theta}{\lambda} \tag{3}
\]

where \( \lambda \) represents the wavelength of the radiation beam hitting the sample, and \( \theta \) is the angle formed between the incident beam and the normal scattering plane. Remembering as long as the measurement \( \lambda \) is fixed, and assuming the scattering occurs in a small angle, the relationship between intensity and the angle of scattering can be stated

\[
I(q) = \langle \left[ (\rho(\vec{r}) - \rho_s) e^{i \vec{q} \cdot \vec{r}} \right]^2 \rangle \tag{4}
\]

here \( \langle \rangle \) represents the rotational average and \((\rho(\vec{r}) - \rho_s)\) is the difference in scattering density between a particle volume at the position indicated by the vector \( \vec{r} \) in the solvent which contributes to the background count. So that with the small angle scattering method, we can distinguish the scattering originating from particles (solids) and the media from the system in the form of a liquid, or what is known as \( \Delta q \) contrast. As seen in the wide-angle X-ray diffraction data in Fig.4, we cannot see any diffraction peaks (high irregularity effect), but based on SAXS measurement data, see Fig.5, the results showed that there was regularity on a very small scale with an average particle size of 3.2 nm. This regularity is of course related to the distribution of CSZ in the very initial phase, namely after the drying process at 60ºC. What is very interesting about the measured SAXS data, it appears that the intensity of the scattering continues to decrease as \( q \) (0.002) increases. Measurements of samples that have been aged at 200ºC, polydispersity of about 3.6 nm, see Fig. 6. Based on these data, it will be possible to
combine small particle clusters so that they are measured as particles with a larger size. This gives an indication that in addition to the distribution of fine particles, there are also larger particles.

Figure 5. SAXS scattering profile of the kernel after drying at 60°C

Figure 6. SAXS scattering profile of the kernel after drying at 200°C [12]

However, considering that the measurement range with SAXS is very limited, to identify larger particle sizes, the Small Angle Neutron Scattering (SANS) facility available at the Center for Advanced Materials Science and Technology (PSTBM) -BATAN has been used, see Figure 7.

Figure 7. Small Angle Neutron Scattering (SANS) at Center for Science and Advanced Material Technology.
Using SANS, the observed particle size is up to 12 nm. The measurement parameters are used by selecting a wavelength (λ) of 3.9 nm using the velocity selector, while the distance between the detector to the sample varies from 3, 6, 13 and 18 m, the measurement time is 24 hours per detector position. Data of measurement results for samples heated at 400 ºC can be seen in Figure 8.

![Figure 8. Small-Angle Neutron Scattering (SANS) intensity profile corresponding to kernel heated at 400ºC](image)

As shown in the measurement data using the X-ray diffraction method at 400ºC, the crystallization process has begun to form. Based on the results of the analysis, it shows that in addition to the diameter of about 3.5 nm, it is also spherical with a uniformity level of 0.3 as shown in Figure 9.

![Figure 9. Profile log normal of uniformity of kernel after heating at 400ºC](image)

Based on the results of the analysis using both SAXS and SANS, the stages of crystallite phase formation in the Zirconia kernel stabilized system by Ceria can be illustrated as follows:

![Figure 10. An illustration of the process of kernel formation, heated at 60 ºC to 400 ºC based on the results of SAXS and SANS data analysis.](image)
What is seen from SAXS is the presence of a cluster of tiny crystals scattered in the polymeric system, which after heating to a higher temperature the clusters then coalesce to form particles with higher density but with smaller size. Therefore, in the early stages of handling the CSZ gelatin system it will be very sensitive to changes in temperature. It is estimated that a very fast temperature increase can cause the crystallite phase formation process in the kernel system to not run properly. The irregularity of the fractal arrangement in the formation of kernel crystals is very likely to trigger micro cracks from the kernel system.

Based on the results of observations using SEM, the morphology of the CSZ kernel as a result of the heating process from temperatures of 60, 120, 200, 400, 600 and 1200 ºC can be seen in Figure 11. SEM observations show that the CSZ-based kernel has been formed without have a crack.

![Figure 11](image)

**Figure 11.** SEM photos of surrogate kernel samples after various heat treatments, at the stage (a) Drying 60°C, (b) Heating 120°C, (c) Heating 200°C, (d) Heating 400°C, (e) Heating 600 °C and (f) 1200 °C heating.

It can be seen that the higher the heating temperature, the smaller the kernel and without any cracks, thus the higher the calcination temperature. It can be estimated that the density of the kernel will increase. Just as a note, in terms of the density of UO$_2$ as a nuclear fuel the theoretical one is 10.96 g/cm$^3$ and experimentally it can be reached up to 10.59 g/cm$^3$.

4. **Conclusions**

A study on the synthesis of ceria stabilized zirconia (CSZ) as a nuclear fuel surrogate for high temperature reactors has been carried out. CSZ kernels were synthesized by external gelatin method. The fractal form of crystallite growth process from the outset can be identified using SAXS in the size range below 2nm and distributed polydispersity in the organic matrix system as a solvent. At higher calcination temperatures, deformation of the organic matrix is accompanied by fractal agglomeration to form a perfect kernel without cracks. The proper heat treatment process allows the fractal arrangement of CSZ crystallites in the formation of the kernel to not develop defects which are thought to be the main cause of kernel cracking since the calcination process.

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