R&D on Surrogate Kernel Fabrication in Support of Reaktor Daya Eksperimental (RDE) Project

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Abstract. R&D program on HTGR fuel to support the RDE project has been outlined and is aimed to develop national capabilities on nuclear fuel technology. The external sol-gel technology has been adopted for the fabrication of kernels. Laboratory scale work has been ongoing at the Center for Nuclear Fuel Technology (PTBBN) BATAN to study various parameters involved in the process of kernel fabrication including tuning of parameters related to droplet formation (feed flow rate, vibrator frequency, NH3 gas flow rate), optimizing chemical formulation in broth preparation, various treatments in aging, washing, drying process, and thermal treatment for densification of kernels. In this early stage, zirconium precursors were used to manufacture surrogate kernels of yttria-stabilized zirconia. The steps for kernel fabrication include chemical formulation of broth and droplet casting, aging-washing-drying of gel microspheres, calcination and sintering, and characterization of sintered kernels (surface morphology, density, diameter/sphericity, solid phase). Stable cast of droplets from 1 mm nozzle diameter was optimized by adjusting feed flow rate at 30 ml/min, viscosity at 45-60 cP, and vibrating frequency at 100 Hz. Presolidification of gel skin was optimized at a working NH3 flow rate of 3.5 - 4 L/min. Addition of urea with mole ratio urea/metal 2.5/1.0 gave the most preferable results based on SEM examination for crack and morphological structure. Control the opaqueness of the sol can be done by portioning addition of urea, where a portion of urea was added at decomposing temperature around 85°C, while another portion was added at a lower temperature. Addition of urea has a desirable effect on crack reduction during heat treatment of gel microspheres. Increase in metal concentration results in an increase in kernel diameter when other sol-to-gel conversion parameters were kept unvaried. Phase determination by X-Ray Diffractometer indicates that solid phase for ceria-stabilized zirconia prepared with precursor composition of 16% yttrium in zirconium-yttrium sol results in yttria-stabilized zirconia 8YSZ with cubic phase.

1. Introduction

The National Nuclear Energy Agency of Indonesia (BATAN) has established a plan to construct an Experimental Power Reactor of pebble bed HTGR type with a thermal output of 10 MWth as a demonstration purpose for the introduction of larger nuclear power plants of similar type in the country [1]. HTGR fuel R&D program for national capacity building has been outlined, where BATAN, national universities and related ministries are involved in the task of R&Ds on HTGR fuels under the coordination of the Ministry of Research, Technology and Higher Education. This HTGR fuel R&D
program is aimed to develop national capabilities on nuclear fuel research to support HTGR fuels for RDE operation [2].

The RDE fuel R&D program at this early step includes research in fuel kernel fabrication and designs of laboratory scale coater and pebble compaction facilities. The fuel manufacture technology employs the German Nukem external gelation process. The external gelation process (also known as the "gel-precipitation" process) is adopted for the fabrication of UO2 kernel for the HTR-10 (China), HTTR (Japan) and PBMR (South Africa) reactors.

Laboratory scale work is ongoing at the Center for Nuclear Fuel Technology (PTBBN) BATAN to study the chemical processes of surrogate (uranium-free) kernels fabrication. The surrogate kernels are necessary for utilization in the TRISO coating process development.

Tuning of parameters involved in gel casting process (such as viscosity of the feed solution, metal concentration, flowrate, nozzle frequency, and NH3 flowrate) requires repeated experiments of gel casting. For this purpose, surrogate materials are preferable to avoid the radiological hazards and the complexity of radioactive material handling. In this work, zirconia has been selected for the analogue material considering that nitrate precursors of zirconium are capable of being converted from a sol into a gel microsphere by the external gelation technique upon their reaction with ammonia solution. Further, stabilizing zirconia with yttria is also of interest to closely resemble urania in terms of crystallography and microstructure, i.e., fluorite crystal structure (face centered cubic, space group Fm-3m). Phase stabilization of zirconia is needed because three crystal structures of zirconia exist at different temperatures: cubic (c) (from 2680°C to 2370°C); tetragonal (t) (from 2370°C to 1170°C); monoclinic (m) (from 1170°C to room temperature) [3]. The monoclinic (m) phase is a more stable phase, but the cubic phase is preferred. Incorporation of cubic oxides like MgO, CaO, Y2O3 and CeO2 to zirconia can delay creation of the transformation phase to maintain the stability of the zirconia crystals in their tetragonal or cubic phase at room temperature [4]. These materials are referred to as stabilizers.

Presolidification of the surface of gel microsphere is required in the external gelation method in order to avoid spherical shape deformation during contact of droplets with the NH3OH column bath [5]. For this purpose, the metal solution needs to be preneutralized or be made acid deficient for rapid hardening of the droplets before reaching the NH3OH bath surface. In this way the spherical shape of gel microspheres can be maintained during gel casting process. Preneutralization can be performed by precipitation-redispersion upon dropwise addition of HN3OH to the metal solution. Another technique of preneutralization is by allowing urea to decompose in the metal solution. Raising the temperature of the solution above about 70°C will allow urea to slowly decompose in the aqueous system solutions. This will result in a homogeneous generation of hydroxyls in the solution and homogenous precipitation in the whole volume to convert the solution into sol. Some previous works have adopted this method in the preparation of sol for the fabrication of zirconia kernels [6, 7].

Unlike hydrous uranium oxide gel spheres that can be highly porous, Zr based gel spheres are amorphous, and cracking is a common problem with amorphous microspheres. The porosity of the amorphous microspheres is typically not sufficient to permit the gases that are formed during heat treatments to escape. The microspheres will crack if the internal pressure becomes too great [8]. The potential for microspheres fabricated through external gelation process to crack during thermal treatment exists because the gel spheres will contain ammonium nitrate (NH4NO3), organic additives such as PVA (polyvinyl alcohol) and THFA (tetra-hydrofurfuryl alcohol). PVA is used to control viscosity of the solution and serves as an organic frame to improve strength of the gelled microsphere. THFA is a kind of complexing agent for adjusting the performance of solution with PVA.

Decomposition of non-oxides components during thermal treatment, i.e., drying and calcining, will release various gases that add to the risk of defects in the final oxide microspheres. In view of the heat treatment process, higher porosity will facilitate the evaporation of water and the release of degradation products of additive components.

Readily decomposable additive materials, such as urea, are found to notably improve the surface area and porosity. Nohman, A.K.H. and H.M. Ismail [9] have examined the marked effect of the presence of
decomposable urea on the structure and surface texture of ZrO$_2$. They believed that decomposition of urea would lead to pore widening and/or pore creation.

It has been observed that serious cracking or damage would also occur in microspheres during heating steps if the gel microspheres are not washed clean enough. Attempts to overcome the heat treatment damages resulted from washing process include the use of propylene glycol monomethyl ether (PGME) as the washing alcohol [6, 7, 10, 11], instead of the commonly used isopropyl alcohol (IPA), to remove moisture and any remaining ammonium nitrate. This work aims to study the influence of chemical preparation routes on the morphological properties of the sintered yttria-stabilized kernels. The chemical preparation routes involve two parameters, i.e., preneutralization treatment and the use of urea as pore promoter. Pore widening and/or pore creation effects of urea on the structure and ZrO$_2$ has been reported by [9] through thermal analysis, X-ray diffraction and measurements of nitrogen adsorption. Preneutralization were done both by precipitation-redispersion upon dropwise addition of NH$_4$OH and by decomposition of urea. It is assumed that rapidness of gelation reaction can be controlled by the extent of acid deficiency caused by preneutralization treatment, and urea that will serve as pore promoter upon its subsequent decomposition during thermal treatment is expected to have a significant influence on the properties and structure of the resulting oxide kernels. Isopropyl alcohol as washing agent was used in this work considering that it is more affordable and widely available in Indonesian market.

2. Materials and Method
The schematic diagram for the fabrication of zirconia kernels is presented in Figure 1.

![Figure 1. Schematic diagram for zirconia kernel fabrication](image)

2.1. Materials
Zirconium The starting materials used were zirconium oxyxinate ZrO(NO$_3$)$_2$·6H$_2$O, Yttrium(III) nitrate hexahydrate (Y(NO$_3$)$_3$·6H$_2$O) 99.9 %, tetrahydrofurfuryl alcohol 98%, poly(vinyl alcohol) - Mowiol® 56-98, ammonia solution 25%, isopropyl alcohol ≥99.5%, demineralized water, and urea EMD Millipore.

2.2. Chemical formulation of broth and droplet casting
Zirconium and yttrium precursors were used as metal precursors. For preparation of zirconium-yttrium sol was prepared with 16% yttrium content. A certain amount of urea was decomposed to prepare sol. PVA solution (8%) was prepared as a viscosity modifier. Broth for casting feed was a mixture of sol, PVA solution, and THFA stirred for a certain time for homogeneity and finally stored in the feed tank overnight to release micro bubbles. The presence of micro bubbles in the feed flow, if not removed, may interfere with droplet sphericity during casting. Casting process of broth was carried out at adjusted feed flowrate, vibrating frequency and the amount of NH$_3$ gas flow.
2.3. Aging, washing and drying of gel microspheres
Processes of aging of gel in ammonia solution, washing sequentially with diluted ammonia solution, demineralized water, fresh isopropanol as well as recycled isopropanol and isopropanol drying at 80°C were carried out in a rotary flask. Water in gel, which is not chemically bonded, was removed by drying the gels in an oven at 90°C and 120°C for 4 hours each.

2.4. Calcination and sintering
Thermal treatment was aimed to decompose and remove additives, convert hydroxides to oxides and remove by process byproducts, and for densification of oxide kernels. The temperature profile for calcination and sintering process was set at 200°C, 400°C, 600°C and 1350°C for 4 hours each as can be seen in Fig. 2.

2.5. Characterization of sintered kernels
The sintered kernels were characterized for their diameter and sphericity, density, surface morphology (SEM) and oxide solid phase (XRD).

3. Result and Discussion
The gelation mechanism of mixed zirconium and yttrium or cerium sol is based on the precipitation of metal hydroxides by polymerization of hydrolysis species. In external gelation method, rapid presolidification of spherical droplets is a prerequisite to maintain spherical shape of gelled microspheres intact. Dropping of the casting sol through a nozzle will cause impact between the spherical droplets with the surface of the ammonia solution bath as gelation agent. The absence of presolidification of the sol droplets may cause will lead to droplet deformation. Although rapid gelation is preferable, however, it is anticipated to result in amorphous structure of the gel, which leads to the potential for cracked microspheres during subsequent heat treatment, i.e., drying, calcining and sintering. In this work, urea was used as an attempt to retard the occurrence of cracking of the crack-prone Zr based gel spheres.

In the fabrication of such multicomponent oxide microspheres, the preneutralization step poses a challenge because it involves metal aqueous solutions with different chemical properties. In this work the preneutralization was by the addition urea and allow it to decompose upon heating. In our preliminary experiment some difficulties were encountered, however, when this method was adopted. We found it difficult to control the precipitation, i.e., agglomeration took place readily in a few minutes, that such re-work of sample preparation was unavoidable to obtain visually clearer sols without precipitates. Attempts to preneutralize zirconium nitrate solution by urea decomposition with mole ratio urea/metal 2.5:1 were mostly unsuccessful, where we found that adding urea at that amount at 80-85°C resulted in visually murky suspension even in relatively short time of 10-15 minutes, resulting in a sol solution containing recoverable precipitates. The desirable casting solution should be a colloidal suspension or sol, namely a solution containing dispersed fine particles but possessing a slow (often negligible) settlement rate under normal gravity.
A workaround to overcome rapid sol settlement was by portioning the amount of urea used in the broth preparation. During preneutralization process the amount of urea was reduced to 1:1 and the other portion was added after sol preparation at lower temperature below the decomposition temperature of urea in water. This portioning method of urea decomposition exhibited change in opaqueness of the sol into murky solution in around 50 minutes at 85°C.

In the casting process, tuning of casting parameters showed that stable cast of droplets from 1 mm nozzle diameter was optimized by adjusting feed flowrate at 30 ml/min, viscosity at 45-60 cP, and vibrating frequency at 100 Hz. Presolidification of gel skin was optimized at a working NH₃ flow rate of 3.5 - 4 L/min at room temperature.

The morphological images of yttria stabilized zirconia (YSZ) sintered kernels prepared with varied mole ratio of urea/metal are presented in Fig. 3.

Figure 3. Morphological images of YSZ sintered kernel prepared with a mole ratio of urea/metal 0.0/1.0 (0.0-a and 0.0-b), 1.0/1.0 (1.0-a and 1.0-b), 1.5/1.0 (1.5-a and 1.5-b), 2.0/1.0 (2.0-a and 2.0-b), and 2.5/1.0 (2.5-a and 2.5-b)
We performed SEM image observation to study the most desirable characteristic of the sintered kernels in terms of crack issue and morphological pore that relates to the resulting density, and we found that the mole ratio of urea/metal 2.5/1.0 to be the most desirable, i.e., less crack and morphologically less pores. To further study the effects of other parameters on the resulting kernels, the broth was then prepared with mole ratio of urea/metal 2.5/1.0, where 1.0 mole ratio was used at 85°C for preneutralization and the other remainder of the urea was added at lower temperature.

**Figure 4.** Morphological images of sintered YSZ kernel prepared with preneutralization process by urea decomposition method (D-a and D-b) and by precipitation-redispersion (R-a and R-b)

We observed that both techniques of preneutralization (i.e., precipitation-redispersion and urea decomposition) gave satisfactory kernel product based on the morphological images of kernels prepared by both techniques, as shown in Fig. 4. However, we anticipated that the preneutralization by dropwise addition of NH₄OH in precipitation-redispersion technique may pose issues of repeatability since manual dropwise addition of NH₄OH may cause some portion of the NH₄OH to evaporate before reaction with the metal nitrates precursors. Therefore, the preneutralization by urea decomposition was preferable.

Diameter of the sintered kernels were controlled by metal concentration in broth. Figure 5 shows the correlation between concentration of metal and the resulted sintered diameter. Higher metal content tends to increase the resulted kernels.

**Figure 5.** Correlation between concentration of metal (mol/L) and the resulted sintered diameter (mm)
Figure 6 shows photo of sintered YSZ kernel, and the sphericity of the sintered kernel typically prepared with 0.812 mole metal/L broth is showed in Fig. 6. It is shown that the sphericity value (Dmax/Dmin) of the sintered kernels are below 1.1. It is well known that for gel casting by the external gelation method, higher concentrations may result in poorer sphericity.

The density measurement of sintered YSZ kernel prepared by different preneutralization routes is presented in Table 1.

Table 1. Density of sintered YSZ kernel

| Sol Preparation Route          | Kernel Density (gram/cc) | % Theoretical density |
|--------------------------------|--------------------------|-----------------------|
| Precipitation-Redispersion     | 5.85                     | 98.15                 |
| Urea Decomposition            | 5.56                     | 93.34                 |

Analysis of the XRD pattern of this composition shows that the resulted solid solution of yttria-zirconia with cubic structure, in compliance with ICDD database no. 00-030-1468 with chemical formula of Y_{0.15}Zr_{0.85}O_{1.93} or 92ZrO_{2.8}Y_{2}O_{3} (Fig. 8). According to literature, when 16 mol% of yttrium nitrate is added to a zirconium sol, a thermal treatment of this mixed solution will cause diffusion of Y_{2}O_{3} into the ZrO_{2} resulting in 8YSZ [12].
Figure 8. XRD pattern of YSZ sintered kernels with cubic phase in compliance with ICDD database no. 00-030-1468 with chemical formulation of $Y_{0.15}Zr_{0.85}O_{1.93}$ or $92\text{ZrO}_2.8\text{Y}_2\text{O}_3$.

4. Conclusion

Rapid gelation of zirconium nitrate solution will result in amorphous zirconia gel microspheres, and this structure may increase the risk of cracking during heat treatment of the gel microspheres. Urea can be used to serve both as agent for preneutralization process for preparing homogenous sol and as pore promoter for suppressing the occurrences of crack of the sintered kernels. Addition of urea with mole ratio urea/metal 2.5/1.0 gave the most preferable results based on SEM examination for crack and morphological structure. Portioning addition of urea can be employed to control the opacity of the sol by mole ratio of urea/metal 1.1, where opacity change occurred in about 50 minutes at 85°C, while the other remainder of the urea can be added at lower temperature. Both techniques of preneutralization (i.e., precipitation-redispersion and urea decomposition) gave satisfactory kernel product in term of morphological structure of the sintered kernels. Broth composition of 84% mole zirconium nitrate dan 16% mole yttrium nitrate precursors can be applied to produce solid-solution of $92\text{ZrO}_2.8\text{Y}_2\text{O}_3$ or also known as 8YSZ, which has cubic structure and is stable up to its melting point. Increase in metal concentration will result in kernels with greater diameter.

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