XRD study of ceria stabilized zirconia (CSZ) microsphere synthesized by external gelation

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Abstract. Ceria stabilized zirconia microsphere has been synthesized by external gelation. XRD investigations were carried out at each thermal treatment to study the process of zirconia oxide formation. The diffraction patterns at thermal treatment 60°C, 120°C and 200°C still appeared to be broadening because there were still amorphous hydrocarbon compounds. The peak of diffraction started to look at 400°C although it was always broadening, this was because the oxide has begun to form but has not crystallized. Perfect crystallization appears on heat treatment at 1200°C as the tetragonal ZrO₂ phase.

1. Introduction

Stabilized zirconia (CSZ)-based microspheres is a ceramic material which has excellent properties such as high mechanical strength and high thermal resistance. Because of these properties, CSZ was used as analogous nuclear material [1]. CSZ, as an analogue nuclear fuel has advantages such as chemical stability, high melting temperature, low neutron capture cross-section and stability under irradiation [2]. This research related to CSZ has been done by various methods, mole ratio, media and theoretical [3-6].

The most important part of the sol-gel high density ZrO₂ synthesis method is the preparation of a sol colloid solution containing ZrO₂ nano dispersion particles. The preparation of metal oxide nano dispersion colloid solutions can be done, among others, by controlled dispersion nano precipitation. Dispersion nanoparticle preparation can be prepared by controlling the precipitation kinetics, one of them by controlling the release of anions from organic molecules. The requirements for homogeneity of colloid solutions must be met, namely that the precipitation takes place slowly and that it is easy to control pH. From this point of view urea is an ideal organic molecular reagent.

The problem appears to be the formation of crack during heat treatment [7]. In this research, the purposes are to investigate the diffraction pattern on the crystal structure formed by the addition of 20% mole of cerium oxide into zirconia

2. Experimental Method

Samples were synthesized by external gelation [8]. 0.3240 mol Zr(NO₃)₄ and 0.0640 mol Ce(NO₃)₃ were dissolved into 250 ml of demineralized water at 80 °C. After all, was completely dissolved, 8% PVA (Polyvinyl alcohol) and 50 ml THFA (Tetra Hydro Furfuryl Alcohol) were added. The solution was stirred continuously until it reaches PH 2.67 and the viscosity is close to 60mPa.s. The solution was
then poured into a container on a fabrication device and allowed to stand for at least 12 hours to remove bubbles. After measuring its viscosity, the solution was dropped into a gelation tube containing an ammonia solution. The drained sample was treated with 3M NH4OH, washed with 0.5M NH4OH, demineralized water and PGME. Then the sample was dried at 60 °C for 12 hours using a Rotary Vacuum Evaporator. Thermal characteristic was measured by using TG/DTA and crystal structure analyzed by XRD. Heat treatment was carried out on temperature 120 °C, 200 °C, 400 °C and 600 °C with heating rate of 0.5 °C / min and held for 4 hours at each temperature, then sintered at a temperature of 1200 °C with heating rate of 1 °C / minute and held for 4 hours.

3. Result and Discussion

Figure 1 shows the thermogravimetric and the differential thermal analysis of ceria Stabilized Zirconia (CSZ) sample obtained using external gelation method. From Figure 1, it was known that there were several reactions to thermal treatment with changed in mass and enthalpy. The first stage was a change in weight and enthalpy at a temperature of 231.1-454.1 °C by 28.1985% and 775.73 J / g. At this temperature, the decomposition process of organic compounds as the media or matrix in the process of synthesizing samples, such as PVA (Polyvinyl alcohol) and THFA (tetrahydrofolic acid). The second phase at a temperature of 580-812 °C, there was a mass change of 2.2964%. At this temperature, the calcination process occurred. The third step, at a temperature of 991-1012 °C, a large-scale shift in 1.2780% occurred, which was a sintered process, where Zr(1-x)CeO2 crystallization occurred. This DTA data profile was the basis of the next heat treatment.

![Figure 1. Differential thermal analysis (DTA) curve of CSZ sample obtained using external gelation method.](image)

The diffraction pattern at each stage of thermal treatment was shown in Figure 2. Crystallization began at thermal treatment to 400 °C. At temperature below 400°C, organic compounds as media or matrix in the process or synthesizing samples, such as PVA and THFA were decomposed. Then in the subsequent thermal treatment occurred to form a perfect crystal at a temperature of 1200 °C. From the phase diagram it was known that the addition of 20% mol of CeO2 to ZrO2 and heated at temperatures above 1000 °C will get tetragonal zirconia[9].

![Figure 2. Diffraction pattern of CSZ sample obtained using external gelation method.](image)
Figure 2. X-ray diffraction patterns of CSZ heat treatment between 60 °C and 1200 °C.

The results of refinement using Full prof software it was found that the crystals formed were Zr$_{0.85}$Ce$_{0.15}$O$_2$ which had a tetragonal crystal structure with space group P 42/nmc, A lattice parameter of $a = 3.6327(78)$ Å and $c = 5.2337(80)$ Å. (Figure 3). This structure was close to the structure reported by Yashima M et al [10]. Where Zr and Ce atom occupy coordinate 0;0;0 and O atom at 0; 0.5; 0.205. (Fig.4). It was known that tetragonal ZrO2 has lattice parameters $a = 3.5781$ Å and $c = 5.1623$ Å [11]. This extension of the lattice parameter from tetragonal ZrO2 occurred because the Ce atom which occupied part of the Zr atom position has a larger atomic radius. The atomic radius of cerium is 181.8 pm, and Zirconium is 160 pm.

Figure 3. Refinement result of CSZ 1200.
Figure 4. Crystal structure of CSZ1200.

The addition of cerium to ZrO2 did not change the crystal structure but is expected to change physical properties. Zirconia which has brittle material can be derived agility so that it can be used in the next process as a surrogate kernel.

4. Conclusion
Ceria stabilized zirconia (CSZ) microsphere synthesized by external gelation was investigated in term of diffraction. This XRD study revealed that the cerium addition to zirconia may exhibit crystal structure transformation and physical properties.

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