CHARACTERISATION OF ThO$_2$-CeO$_2$ SINTERED PELLETS FABRICATED BY POP AND CAP PROCESSES USING IMPEDANCE SPECTROSCOPY TECHNIQUE

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ABSTRACT

Pellets of ThO$_2$-CeO$_2$ have been fabricated as a surrogate material for ThO$_2$-PuO$_2$ fuel being considered for use in Indian Advanced Heavy Water Reactor (AHWR). The green pellets were prepared by two different routes, namely, powder pellet route (POP) and coated agglomerate pelletisation route (CAP) and sintered in both oxidizing and reducing atmosphere. Preliminary investigations using impedance spectroscopy has been carried out on these samples. The electrical conductivity of sintered pellets was found to be significantly affected by the chemical inhomogeneity and porosity present in the pellets. Higher conductivity has been observed for the pellets sintered in reducing atmosphere compared to those sintered in air. The results indicate that impedance spectroscopy can be used as a tool for evaluation of pellets in terms of chemical homogeneity and non-stoichiometry.

Keywords: ThO$_2$-PuO$_2$ fuel, agglomerate, coating, impedance spectroscopy, electrical conductivity

1.0 INTRODUCTION

ThO$_2$ based fuels are expected to play a major role in the development of a proliferation-resistant fuel which exhibits higher performance under irradiation [1-2] and has the advantage of generating less spent fuel [3]. ThO$_2$ based fuel exhibits better performance than UO$_2$ based fuel due to its higher thermal conductivity and lower specific heat capacity and density. ThO$_2$ containing $^{233}$UO$_2$ and PuO$_2$ is the proposed fuel for the forthcoming Indian Advanced Heavy Water Reactor (AHWR). Various fabrication processes, such as, powder pellet (POP) process, pellet impregnation, sol gel microsphere pelletisation (SGMP), have been reported in literature [4-9]. In POP route, handling of dry fine powder is a concern for safety. The coated agglomerate pelletisation process (CAP) is the most recently developed concept in nuclear fuel fabrication in our laboratory. In this approach agglomerated particles of ThO$_2$ are made and subsequently coated with binder added powder of $^{233}$UO$_2$/PuO$_2$ and then sintered. Safety issues associated with handling of ThO$_2$ powder are less as compared to $^{233}$UO$_2$/PuO$_2$ powders and are carried out in unshielded facility.

CAP process has gained relevance especially in fabrication of AHWR fuel comprising of (Th,U$^{233}$)O$_2$ and (Th,Pu)O$_2$. Due to difficulties associated with PuO$_2$ such as radio toxicity, high specific activity and proliferation risk, exploration of fabrication process for desired objectives necessitates the studies to be conducted with substitute material. Sufficient works using CeO$_2$ as surrogate material for PuO$_2$ have been carried out and available in the literature [10-14]. Both Ce and Pu have similar atomic radii, in oxide form as CeO$_2$ and PuO$_2$ take valence states of 3+ and 4+ and possess fluorite structure (CaF$_2$, Fm3m).

In the present study, (Th,Pu)O$_2$ fuel fabrication for AHWR is being currently investigated using CeO$_2$ as surrogate material. Thermo-physical properties of sintered fuel pellets are influenced by the degree of chemical homogeneity and oxygen non-stoichiometry in composition. In (Th,Ce)O$_2$ system Ce valence state changes from +4 to +3 at higher temperature and also in reducing atmosphere. AC impedance spectroscopy can be a useful tool in determining the mechanisms of the processes that take place throughout the sample. Any intrinsic feature that influences the conductivity of a material system can be studied by impedance spectroscopy.

The impedance can be expressed as:

$$Z(\omega) = Z' + iZ''$$

The plots of the real and imaginary parts of the above equation as parametric function of frequency show distinctive features characterizing particular combinations of the circuit element. The complex plane (Argand diagram) plot of impedance, i.e., a plot of $-Z''$ vs. $Z'$ is known as impedance plot. It is possible to calculate the resistance and capacitance values from the intercepts on the real axis and highest point on the semicircle respectively. Further information regarding the principle is given elsewhere [15]. Interpretation of impedance...
spectra requires models that need to relate microstructural features. Some of the models that include grains, grain boundaries, differing phase composition, suspensions of one phase within another and porosity are discussed in the literature[16-18].

Although a RC element corresponds to a semicircular arc in an impedance plot, in practice however, there may be perturbations. The most common perturbation observed in the real systems are: (i) The center of an experimental arc is frequently displaced below the real axis. This is due to the presence of distributed elements in the material system. In this case the relaxation time (τ) is not single valued but is distributed continuously or discretely around a mean (τm = t_m^{-1}). The angle (φ) by which such a semicircular arc is depressed below the real axis is related to the width of the relaxation time distribution.

Fuel pellets prepared by different processing conditions shall have different electrical response. In the present study impedance spectroscopic study has been explored for characterization of fuel pellet samples fabricated by two different routes namely, conventional powder processing (POP) route and coated agglomerate pelletization (CAP) process.

2.0 EXPERIMENTALS

ThO2 powder prepared through oxalate route and CeO2 powder (99.5% purity) were used as starting material. ThO2-5 wt.% CeO2 composition pellets were prepared using two different techniques. In POP process, ThO2 powder was mixed with CeO2 powder in a ball mill, pre-compactad, granulated and pressed uniaxially to form green pellets. In CAP process, ThO2 powder was milled and mixed with an organic binder and extruded through perforated rollers. The agglomerates of ThO2 as extrude were in the form of rods of diameter corresponding to roller hole and nominally of 4 mm length. These extrude agglomerates were reduced in size and shaped to near spherical using a spherodiser. The agglomerates were sieved and subsequently dried to remove the organic binder. All these operations were carried out in an alpha tight glove-box facility. Weighed quantity of CeO2powder premixed with liquid binder and ThO2 spheroids were charged into a uniaxial mixer. The mixer was rotated at 120 rpm for 15 minutes. The discharge consisting of coated spheroids was collected and sieved through #40 mesh screen. After drying pellets were made by uniaxial die pressing.

The green pellets were sintered in batch type furnaces at 1550°C and 1650°C both in air and reducing atmosphere (Ar-H2) respectively. Densities of the sintered pellets were evaluated by water displacement method.

Sintered samples were prepared for metallography by grinding, polishing and thermally etching at 1650°C in respective sintering atmosphere for 4 hours. Microstructural study was carried out using a SEM (Model: Quanta 200). X-ray diffraction patterns of the sintered pellets were taken using STOE diffractometer (Diano XRD-8760) using the CuKα radiation and graphite monochromator.

Silver conductive paste was used to coat both the faces of pellets. Electrical measurements were carried out in a SOLARTRON (Model : 1260) frequency response analyser in the frequency range 0.01 Hz to 10 MHz and in the temperature range 250°C – 500°C. PROBOSTAT sample holder (Norwegian Ceramic Society, Norway) was employed for measurement.

3.0 RESULTS AND DISCUSSIONS

The densities of the pellets sintered in oxidizing and reducing atmospheres are given in Table 1. More than 90% of theoretical density has been obtained in each case. The density of POP pellets is found to be slightly more than that of CAP pellets under identical conditions of sintering. The microstructures of the POP and CAP pellets sintered in air and reducing atmosphere are shown in Fig. 1 and Fig.2 respectively. It was observed that microstructure is uniform in case of POP pellets. The microstructure of CAP pellets is featured with distinct coarse grained and fine grained regions. During sintering, solid solution formation results due to inter diffusion of ions. As the diffusion coefficient of cations is very low compositional in-homogeneity is resulted in the sintered pellets. Compositional gradient (concentration) occurs on micro scale along the progressive diffusion interface. In POP pellets due to homogeneity in starting powder mixture, ThO2 and CeO2 particles are in contact uniformly across the pellet matrix. Hence sintering leads to solid solution of uniform composition as diffusion lengths are very small. However, in CAP pellets the concentration of CeO2 being higher at the boundary of ThO2 agglomerate and interparticle distance are higher. This leads to high concentration gradient and solid solution formation of varied composition. At the interface of ThO2 agglomerate due to large concentration of defects grain growth is observed. The fine grained region has been identified to be primarily ThO2 rich phase.
Table 1: Sintered pellets densities

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sintering atmosphere</th>
<th>Temperature (ºC)</th>
<th>Density (g/cc)</th>
<th>% Theoretical density</th>
<th>O/M ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>ThO₂ -5%CeO₂ (POP)</td>
<td>Air</td>
<td>1550</td>
<td>9.18</td>
<td>93.1</td>
<td>2.00</td>
</tr>
<tr>
<td>ThO₂ -5%CeO₂ (CAP)</td>
<td>Air</td>
<td>1550</td>
<td>9.05</td>
<td>91.6</td>
<td>2.00</td>
</tr>
<tr>
<td>ThO₂ -5%CeO₂ (POP)</td>
<td>Ar-H₂</td>
<td>1650</td>
<td>9.11</td>
<td>92.3</td>
<td>1.978</td>
</tr>
<tr>
<td>ThO₂ -5%CeO₂ (CAP)</td>
<td>Ar-H₂</td>
<td>1650</td>
<td>9.03</td>
<td>91.4</td>
<td>1.987</td>
</tr>
</tbody>
</table>

Figure 1: SEM micrographs of (a) CAP and (b) POP pellets sintered in air atmosphere

Figure 2: SEM micrographs of (a) CAP and (b) POP pellets sintered in Ar-H₂ atmosphere

Expanded view of the most intense peaks of XRD patterns of sintered pellets is shown in Fig. 3. XRD peak of pure ThO₂ has also been included in the figures for comparison. The peak shift indicates CeO₂ has gone into the lattice of ThO₂ decreasing the lattice parameter. The decrease in lattice parameter may be attributed to lower ionic radii of Ce⁴⁺ compared to that of Th⁴⁺. The base of the peak showed broadening towards higher angle in case of CAP samples sintered in both air and reducing environment. XRD patterns reveal compositional inhomogeneity in the sintered sample with varying CeO₂ enrichment.

Figure 3: Expanded view of the most intense peaks of XRD patterns of pellets sintered in (a) air atmosphere and (b) Ar-H₂ atmosphere
For the analysis of electrical behavior of the samples real impedance ($Z'$) and imaginary impedance ($Z''$) data have been used. The data have been presented in the form of impedance plot ($Z''$ vs. $Z'$) to extract information on ionic conductivity. Impedance plots of POP and CAP samples at 500°C are given in the Figures 4(a) and 4(b) for illustration. The impedance values used in the plots have been normalized for unit cell constant. Analysis of impedance plots (Fig. 4) show that the semicircles corresponding to CAP samples were depressed by more than 23°angle. This indicates gross compositional inhomogeneity in the CAP samples. This observation corroborates with the results obtained from microstructural and XRD studies.

For the determination of resistances from the impedance plots the arcs have been fitted in semicircles. Resistances have been determined from the intercepts of the fitted semicircles with the real impedance axis. The conductivity is calculated using the following relation.

\[
\sigma = \frac{1}{\frac{1}{l} \cdot \frac{1}{A} \cdot R}
\]

(1)

where, \(l\) is the sample thickness, \(A\) is the flat area and \(R\) is the sample resistance of the sample.

\[\sigma = \sigma_0 \exp \left( \frac{-E}{kT} \right) \]

(2)

Thus the plot of log($\sigma_0$) vs. inverse of temperature (Arrhenius plot) should be a straight line with the slope equal to (-E/k), where ‘E’ is the activation energy for ionic conduction. The plot of log($\sigma_0$) vs. inverse of temperature is shown in Fig. 5.

The bulk conductivities of CAP samples are about one order of magnitude lower than that of POP samples. In the microstructural study, it has been discussed that non-uniformity of microstructure is due to concentration gradient of cerium ions in the ThO$_2$ agglomerates. In CAP pellets extent of CeO$_2$ in to the
The internal resistance of ThO₂ agglomerates was lower. Therefore, low conductivity may be attributed to smaller area of conduction path.

It was observed that the conductivity of pellets sintered in reducing atmosphere was significantly higher compared to air sintered pellets. From Table 1, it could be observed that O/M ratio was lower in case of pellets sintered in reducing atmosphere compared to air sintered pellets. Higher conductivity in pellets sintered in reducing atmosphere could be attributed to hypo-stoichiometry of the pellets. Sintering in reducing atmosphere leads generation of electronic defect (polaron) and oxygen vacancies as per the following defect reaction.

\[ O_{\text{O}}^{2-} + 2Ce_{\text{Fe}}^{3+} \rightarrow \frac{1}{2} O_{2} + V_{\text{O}}^{\cdot} + 2Ce_{\text{Ce}}^{4+} \]

Electrical conductivity arises due to polaron hopping between the Ce³⁺ and Ce⁴⁺ sites. The activation energies have been calculated from the slope of the Arrhenius plot (Fig. 5) and are given in Table 2. For samples sintered at oxygen atmosphere the slope increases at higher temperature and therefore, activation energies have been given in two temperature regions.

**Table 2: Activation energies for electrical conduction**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sintering atmosphere</th>
<th>Activation energy (eV) (below 600°C)</th>
<th>Activation energy (eV) (above 600°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ThO₂-5%CeO₂ (POP)</td>
<td>Air</td>
<td>0.94</td>
<td>0.50</td>
</tr>
<tr>
<td>ThO₂-5%CeO₂ (CAP)</td>
<td>Air</td>
<td>0.99</td>
<td>0.59</td>
</tr>
<tr>
<td>ThO₂-5%CeO₂ (POP)</td>
<td>Ar- H₂</td>
<td>0.46</td>
<td>0.46</td>
</tr>
<tr>
<td>ThO₂-5%CeO₂ (CAP)</td>
<td>Ar- H₂</td>
<td>0.52</td>
<td>0.52</td>
</tr>
</tbody>
</table>

The activation energies in the samples sintered in reducing atmosphere is lower compared to samples sintered in oxidizing atmosphere. The values are close to activation energy for polaron hopping. Therefore, in samples sintered in reducing atmosphere polaron hopping is the dominant mechanism of electrical conductivity. Oxygen ion conduction prevails at higher temperature in the samples sintered in air. The activation energy is higher in CAP samples compared to POP samples. In CAP samples the defect concentration (oxygen vacancy) is relatively higher in the narrow conduction path. Higher oxygen vacancy acts as barrier for polaron hopping.

**4.0 CONCLUSIONS**

This study reveals significant influence of sintering atmosphere on the conductivity behavior of (Th,Ce)O₂ pellets. The depression angle of the impedance curve gives an indication of the level of inhomogeneity of the sample. This study indicates that the impedance spectroscopy can be a useful tool in the analysis of chemical homogeneity and non-stoichiometry in samples.

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**Nomenclature:**

- \( Ce_{\text{Fe}}^{3+} \): Ce substituted at Th site
- \( Ce_{\text{Ce}}^{4+} \): Ce³⁺ (reduction of cerium from 4+ to 3+)
σ: Conductivity (S.cm⁻¹),
CAP: Coated agglomerate pelletisation route
POP: powder pellet route,
\( V_0 \) : Oxygen Vacancy

REFERENCES


