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Fabrication of CeO_2 pellet with controlled microstructure for the application as a spent fuel surrogate

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1. Introduction

The nuclear fuels are being irradiated to high burnup in order to reduce the amount of fresh fuel and the spent fuel inventories and to enhance the fuel economy as well. During irradiation, the nuclear fuel experiences changes of its initial microstructure including grain growth and fission gas release at the central region and porosity build-up and fuel restructuring into small grains at the periphery. The high burnup microstructure is mainly composed of two regions, i.e., the large grain size (~ 21 µm) and small porosity (~ 5 %) central region, and nano-size (~ 200-300 nm) and large porosity (20-30 %) outer region. [1]

Due to the radioactivity and toxicity of the spent nuclear fuel, several studies using nuclear fuel analogue (surrogate) under simulated test conditions have been performed [2,3] and several fabrication methods have been used to fabricate a spent fuel surrogate with a similar structure of the spent fuel [4–6]. Cruz et al [4] fabricated a structure similar to the rim microstructure that is composed of isolated individual pores of 0.5-1 µm in size immersed in a matrix of 200-300 nm size grains and porosity levels of 10-20 %. However, they did not fabricate the large grain size central region. Fernandez et al. [5] fabricated two regions microstructure with a mean grain size and porosity of ~ 30 µm and 4.5 % in the inner region and of ~ 10 µm and ~ 25% in the outer region. Torres et al. [6] fabricated a three region gradient microstructure with porosity levels of 6.2 %, 13.2 %, and 28.3 % in the inner, intermediate, and outer region, respectively, and with an average grain size of 24.7 µm, 22.8 µm, and 17.2 µm in the inner, intermediate, and outer region, respectively. However, they did not fabricate the sub-micron size outer region. The fabrication studies of the spent fuel analogue have controlled the microstructure of the spent fuel surrogate in terms of the grain size either by controlling the sintering conditions (time and temperature) or by using a nano-size powder [4,5], which makes difficult to fabricate the inner large grain size and the outer small grain size structure during the same step. One possible method is by using a doped CeO_2 in the central region and milled CeO_2 in the outer region. The porosity can be controlled by using a sacrificial agent.

The objective of this study is the fabrication of a spent fuel analogue with a similar microstructure of the high burnup UO_2 fuel. Firstly, the densification and grain size of CeO_2 after microwave (MW) sintering methods will be investigated. Then, the effect of milling, Fe_2O_3 doping, and sacrificial agent addition on the densification and grain size of CeO_2 will be analyzed. After selecting the optimum milling time, dopant and sacrificial agent amount, sintering conditions that result in a microstructure similar to that of the spent fuel surrogate, the CeO_2 pellet will be fabricated.

2. Experimental procedures

2.1 Starting materials

CeO_2 (Sigma Aldrich, < 5 µm), Fe_2O_3 (Sigma Aldrich, < 50 nm), and Polymethylmethacrylate (PMMA) (Good fellow, ~ 3 µm) were used as starting materials. PMMA was used as a sacrificial agent in order to control the porosity in the central and outer region of the fabricated CeO_2 pellet.

2.2 Experimental procedures

Pure CeO_2 and CeO_2 doped with 0.03 mol. % and 0.06 mol. % of Fe_2O_3 were fabricated by firstly mixing for 20 h with a milling speed of 143 rpm and a ball to powder ratio of 1:2 in ethanol. Then, the mixed powder was filtered and dried at 120°C for 12 in a vacuum oven. After that, the mixed powder was poured into a 10 mm in diameter steel mold and pressed under a pressure of 100 MPa using a uni-axial press followed by cold isostatic pressing under a pressure of 300 MPa for 5 min to make the green pellets. Then, the green pellets were sintered in a MW furnace in an air atmosphere with a heating rate of 50°C/min and a holding time of 10 min at 1300°C, 1400°C, and 1500°C, respectively.

To fabricate nano-size CeO_2, pure CeO_2 powder was milled with a milling speed of 143 rpm and ball to powder ratio of 1:10 in ethanol for 20 h, 40 h, and 60 h, respectively. Then, the milled powder was pressed into green pellets using the same pressing conditions used to fabricate the pure and Fe_2O_3 doped CeO_2 pellets. After that, the green pellets were sintered by a microwave sintering machine with a heating rate of 50°C/min in an air atmosphere for 10 min at 1300°C, 1400°C, and 1500°C, respectively.

The densification of all sintered pellets was measured using Archimedes principle method. A theoretical density of 7.13 g/cm^3 was used to measure the relative density of the sintered pellets. The microstructure of the sintered pellets was investigated using a scanning electron microscopy after polishing and thermal etching at by a

MW furnace at 1300ºC for 5 min with a heating rate of 50ºC/min.

3. Results and discussions

The densification of the MW sintered pure and Fe_2O_3 doped CeO_2 is shown in Fig. 1. Almost, a fully densified CeO_2 can be achieved with Fe_2O_3 doping amount as low as 0.06 mol. % and a sintering temperature of 1300ºC or above.

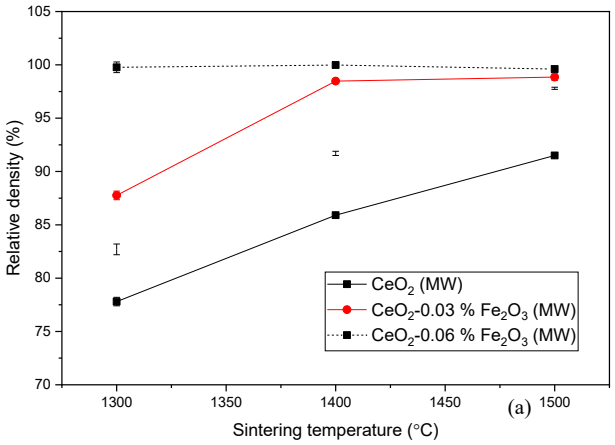

Fig. 1. The relative density of the pure and Fe_2O_3 doped CeO_2 after MW sintering.

The grain size as a function of the sintering temperature of the pure CeO_2 and Fe_2O_3 doped CeO_2 is shown in Fig. 2.

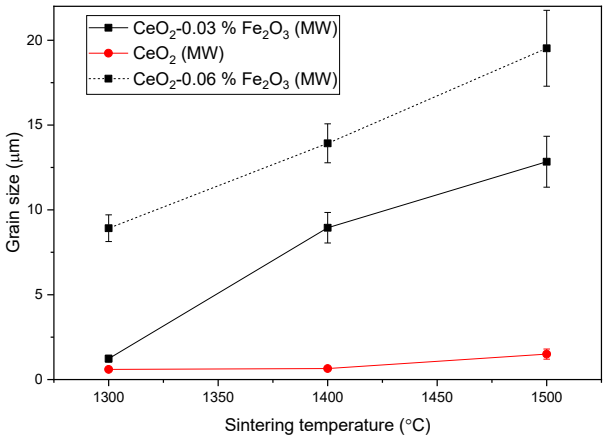

Fig. 2. The grain size of the MW sintered CeO_2 composites.

As can be seen from Fig. 2, The addition of a small amount of Fe_2O_3, as low as 0.03 %, resulted in a significant increase in the grain size of the sintered CeO_2. a grain size of about 20 µm (close to the grain size of the central region of the irradiated spent fuel) can be achieved with a 0.06 mol. % doping of Fe_2O_3 after MW sintering at a temperature of 1500ºC for 10 min. The microstructure of the pure and 0.03 % Fe_2O_3 doped CeO_2 after MW sintering at 1500ºC is shown in Fig. 3.

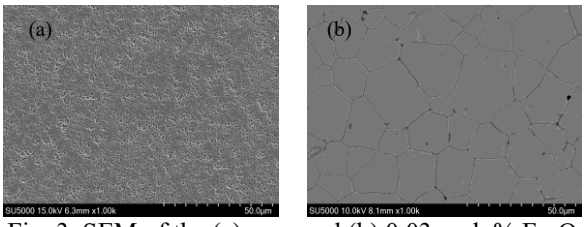

Fig. 3. SEM of the (a) pure and (b) 0.03 mol. % Fe_2O_3 doped CeO_2 after MW sintering at 1500ºC.

The effect of the milling time on the densification and grain size of CeO_2 sintered by MW sintering is shown in Fig. 4.

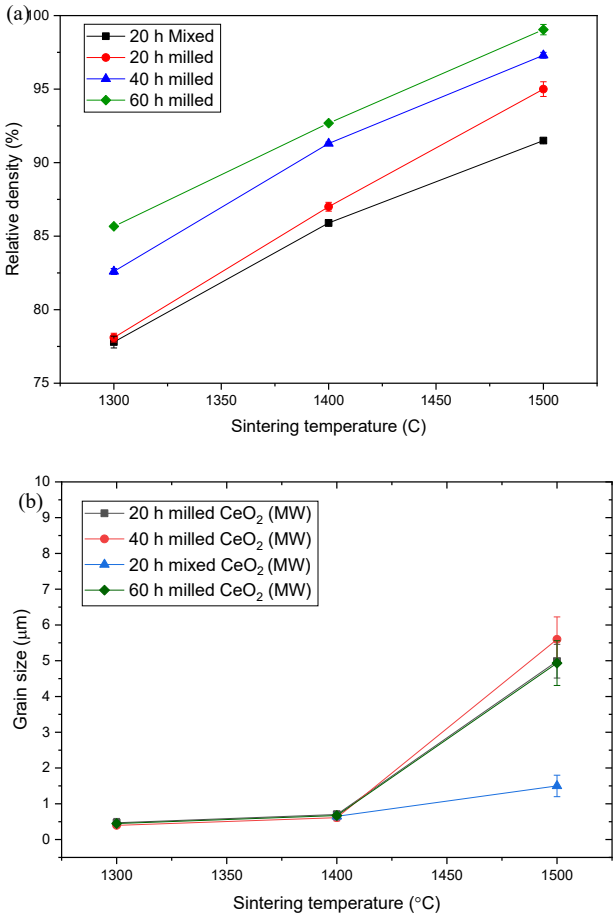

Fig. 3. (a) The relative density and (b) grain size of the mixed and milled CeO_2 after MW sintering at different temperatures.

As can be seen from Fig. 4, almost a 90 % relative density and sub-micron size CeO_2 can be achieved by milling the powder for 40 h and sintering by MW for 10 min at a temperature of 1400ºC.

As can be seen from the previous results, we have successfully fabricated a large gain size and sub-micron size CeO_2 by doping with Fe_2O_3 and milling and MW sintering. However, the sintered pellets have still higher densification than the densification of the spent fuel in the central region and outer region. One possible method to reduce the densification is by using a sacrificial polymer that decomposes at a low temperature. In this study, we used PMMA which fully decompose at a temperature of

400°C [7]. The PMMA powder was added to the 40 h milled CeO_2 powder and 0.06 mol. % Fe_2O_3 doped CeO_2 powder during the mixing process in order to reduce the densification of the milled and doped CeO_2 powder. Then, the mixed powder was fabricated with the same pressing conditions of the samples without PMMA. After that, the green pellets were sintered by MW furnace with a slow heating rate of 5°C/min up to 400°C and holding time of 1 h to evaporate PMMA followed by a faster heating rate of 50°C/min up to the sintering temperature and a holding time of 10 min. The effect of adding PMMA on the densification of both 40 h milled CeO_2 and 0.06 mol. % Fe_2O_3 CeO_2 is shown in Fig. 5.

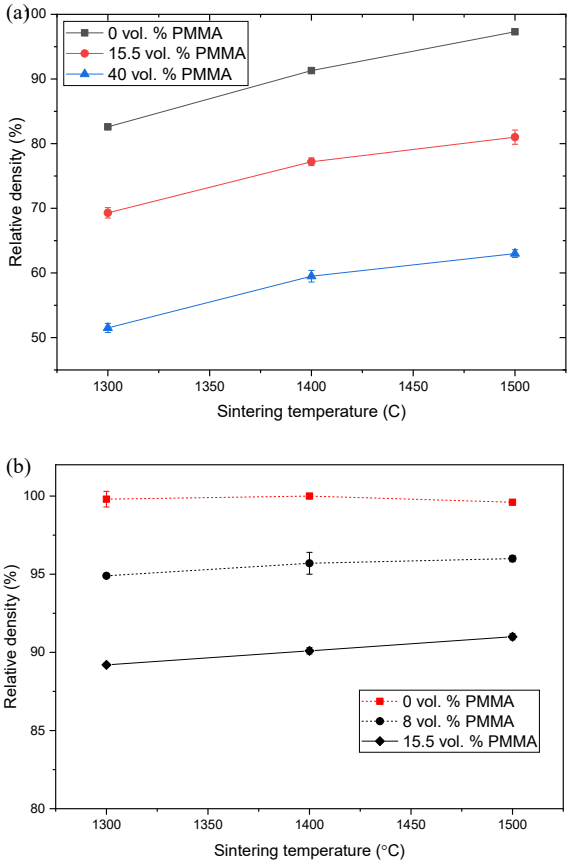

Fig. 5. the effect of adding PMMA on the densification of (a) milled and (b) 0.06 % Fe_2O_3 doped CeO_2 pellets.

As can be seen from Fig. 5, almost a 75 % relative can be achieved by adding 15.5 vol. % of PMMA to the 40 h milled CeO_2 and sintering by MW at 1400°C for 10 min. For the case of the 0.06 mol. % doped CeO_2, a relative density of about 95 % can be achieved by adding about 8 vol. % of PMMA to the 0.06 % Fe_2O_3 doped powder and MW sintering at a temperature of 1300-1500°C for 10 min. Therefore, 0.06 mol. % doped CeO_2 with 8 vol. % of PMMA mini-pellet were fabricated by pressing under a pressure of 300 MPa and sintering by MW at a temperature of 1400°C for 10 min by MW. Then, the fabricated mini-pellet wase inserted in a CeO_2 compact, composed of 40 h milled CeO_2 powder with a 15.5 vol. % of PMMA, and pressed under the same pressure and sintered under the same sinter conditions. The microstructure of the sintered duplex CeO_2 is shown in Fig. 6.

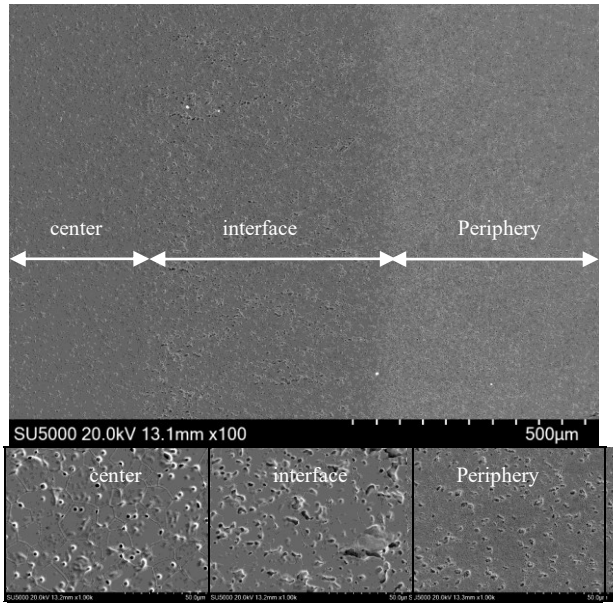

Fig. 6. Microstructure of the duplex CeO_2

As can be seen from Fig. 6, a large grain size central region and nano-size grain porous outer region were successfully fabricated.

4. Conclusions

The effect of milling, Fe_2O_3 doping, and the addition of PMMA on the densification and grain growth of CeO_2 by MW sintering was investigated in this study in order to find the optimized conditions for the fabrication of CeO_2 spent fuel analogue with a similar microstructure with that of the spent fuel. It was found that a milling time of 40 h, the addition of 15.5 vol. % of PMMA, and MW sintering at a temperature of 1400°C for 10 min is needed to fabricate the sub-micron grain size porous structure of the outer region of the spent fuel. For the fabrication of the large grain size and 5 % porous central region structure, 0.06 mol. % doping of Fe_2O_3, 8 vol. % addition of PMMA, and MW sintering at a temperature of 1300-1500°C for 10 min is needed. CeO_2 pellet with a structure similar to the spent fuel was successfully fabricated using the optimized sintering conditions.

Acknowledgments

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