The role of oxygen potential in the sintering of UO$_2$–5wt%CeO$_2$ powder mixed with M$_3$O$_8$ (M = U + Ce)

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Abstract

The sintering behavior of a UO$_2$–5wt%CeO$_2$ powder mixture was examined with different amounts of M$_3$O$_8$ (M = U + Ce) powder pulverized from a (U,Ce)O$_2$ pellet by oxidation and in atmospheres with different oxygen potentials. The analysis revealed that a higher oxygen potential in the sintering atmosphere and a higher amount of M$_3$O$_8$ contributed to a lower sintered density but the formation of a larger average grain size in the microstructure of the sintered specimens. Moreover, it was revealed that the weight change during sintering with different amounts of M$_3$O$_8$ had an influence on the microstructural evolution and sintered density due to the difference in the oxygen potentials. This behavior is discussed in terms of the oxygen potential–density relationship, thermogravimetric behavior and microstructure evolution in the specimens.
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1. Introduction

Uranium and plutonium oxides are widely utilized as fuel materials in nuclear reactors for power production. Technologies relevant to Pu-bearing uranium dioxide nuclear fuel, the so-called MOX (Mixed Oxide) fuel, have been pursued since the 1950s, firstly for fast breeder reactors (FBRs) as well as for the effective utilization of fissile fuel materials, coming from the already settled-upon spent fuel reprocessing process, in light water reactors (LWRs) because of the delay of the commercialization of the FBRs. During these periods, the process technologies concerning the MOX pellet fabrication have matured, and fuel pellets with high Pu contents up to 20 wt% are thought capable of production without any difficulty in meeting specifications.

Generation of dry scrap is one of the unavoidable aspects of the pellet production process. This requires process development in view of the homogeneity of the Pu distribution as well as the microstructure, via the oxidation–reduction or mechanical crushing of the pellet scrap. Oxidation of the scrap pellet and the successive admixing of the pulverized U$_3$O$_8$ powder with up to 15 wt% to the starting powder is the most commonly adapted method in the uranium pellet process to recover these scraps as well as to control the sintered density for a highly sinterable UO$_2$ powder [1], and this can be applied also to the Pu-bearing MOX pellet technology [2].

Recently, Lee et al. examined the possibility of sintering a U$_3$O$_8$ + CeO$_2$ powder mixture and its microstructure evolution in the N$_2$ + H$_2$, N$_2$ + H$_2$ + CO$_2$ and CO$_2$ atmospheres and incorporating several dopants,

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and found that the CO_2 atmosphere gave a lower sintered density but larger grains than the other sintering atmospheres [3]. In the present work, sintering of the UO_2–5wt%CeO_2 powder mixture was examined when sintered with different amounts of M_3O_8 (M = U + Ce) powder pulverized from a $(U, Ce)O_2$ pellet by oxidation and in oxidizing atmospheres. Sintering gases were CO_2/CO ratios (10/1, 1/1 and 1/10), together with pure CO_2 and H_2 gases for comparison. The purpose of this work is to observe a variation of microstructure in thermodynamic aspect in particular, having different sintering atmospheres with different oxygen potentials. CeO_2, which simulates PuO_2 to form solid solutions with UO_2, has been utilized to simulate the MOX pellet process [4].

2. Experimental

The UO_2 powder used in this study was IDR-UO_2 purchased from BNFL (British Nuclear Fuels plc) and the O/U ratio, average particle size and specific surface area of the UO_2 powder were 2.14, 2.2 μm and 2.36 m^2/g, respectively. CeO_2 powder with a purity of 99.9% was purchased from Aldrich Chemical Company and has a specific surface area of 9.46 m^2/g. UO_2–5wt%CeO_2 powder was mixed with a Turbula® mixer for 1 h and successively milled by a dynamic ball mill for 4 h. M_3O_8 powder was prepared by heating a UO_2–5wt%CeO_2 pellet at 500 °C in air with an oxidative pulverization technique, and then by passing it through a 30 mesh sieve in order to remove the large agglomerates. The milled UO_2–5wt% CeO_2 powder was mixed with weighed amounts of M_3O_8 powder, at concentrations of 10, 20 and 30 wt%, by a Turbula® mixer. Zinc stearate was used as a lubricant and admixed with the powder mixture. The milled UO_2–5wt%CeO_2 powder and those mixed with the M_3O_8 powder were compacted with a compaction pressure of 300 MPa and the green pellet specimens of 10 mm in diameter were sintered at 1700 °C in H_2 for 4 h and at 1450 °C in oxidizing atmospheres (pure CO_2, CO_2/CO = 10/1, 1/1, 1/10) for 4 h, respectively. The pellets sintered in the oxidizing atmosphere were reduced at 1450 °C for 1 h in a H_2 atmosphere to adjust the O/M ratio to 2.0. The weight change of the pellet specimens prepared from the UO_2–5wt%CeO_2 powder mixed with M_3O_8 during sintering was observed by thermogravimetry using a thermal balance (ATI Cahn, TG171). The same experimental conditions as the oxidizing sintering mentioned above were conducted in the thermogravimetric experiments. The sintered density including the open and closed porosity and the average grain size of the pellet specimens were measured by the water immersion method and the mean linear intercept (MLI) method, respectively.

3. Results and discussion

Fig. 1 shows the variation of the density as a function of the amount of M_3O_8 for the specimens sintered in different oxidizing atmospheres with various CO_2/CO ratios, and that for the specimen sintered in the H_2 atmosphere. Ceramographic observation revealed that there were no cracks all the specimens sintered in oxidizing and reducing atmospheres. The density variations for all the specimens show a linearity, irrespective of the different sintering atmospheres. This implies that the total porosity increases linearly with the M_3O_8 contents for all the different sintering atmospheres considered in this work. However, the data for the open and closed porosity provide different observations as shown in Fig. 2. While the open porosity for all the specimens sintered in the different sintering atmospheres increases as the amount of M_3O_8 increases, the closed porosity of the specimens with the CO_2/CO ratios of 1/1 and 1/10 shows a slight decrease but those for the pure CO_2 and 10/1 show, respectively, a slight increase and constant. This reveals that the contribution of an addition of M_3O_8 to the formation of the pores in the pellet specimens is different among the sintering atmospheres with the different oxygen potentials examined in this work. This difference was confirmed by a microscopic observation of the microstructure developed in the pellet specimens. U_3O_8 phase has an about 30% larger lattice volume than the cubic UO_2 phase and so a lot of pores are formed as the U_3O_8 phase converts to UO_2 during the reduction. Similarly, M_3O_8 makes larger pores in low oxygen potential atmosphere like CO_2/CO = 1/10 by rapid conversion to MO_2 during the sintering than CO_2 atmosphere, as shown in Fig. 3. It is very difficult
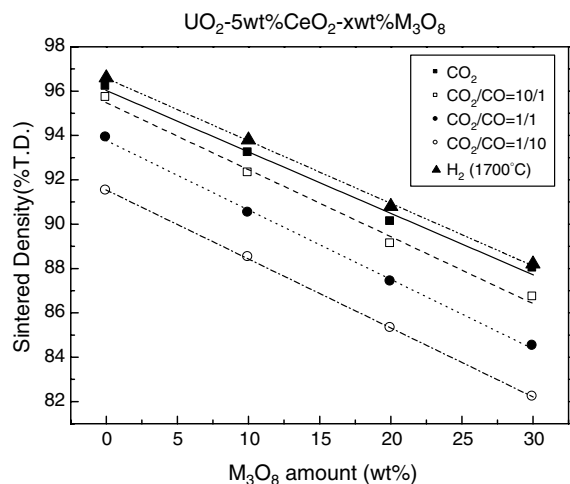

Fig. 1. Variation of the sintered density as a function of the amount of M_3O_8 addition for the sintering atmospheres with different gas mixtures.
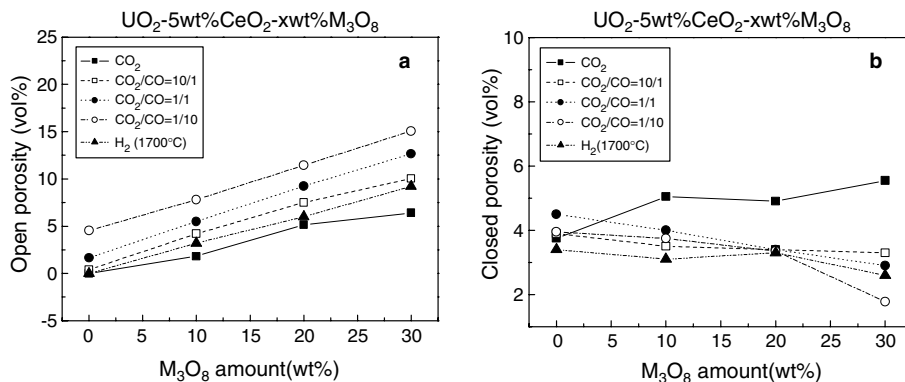
Fig. 2. Variation of the open and closed porosity as a function of the amount of M_3O_8 addition for the sintering atmospheres with different gas mixtures: (a) open porosity and (b) closed porosity.
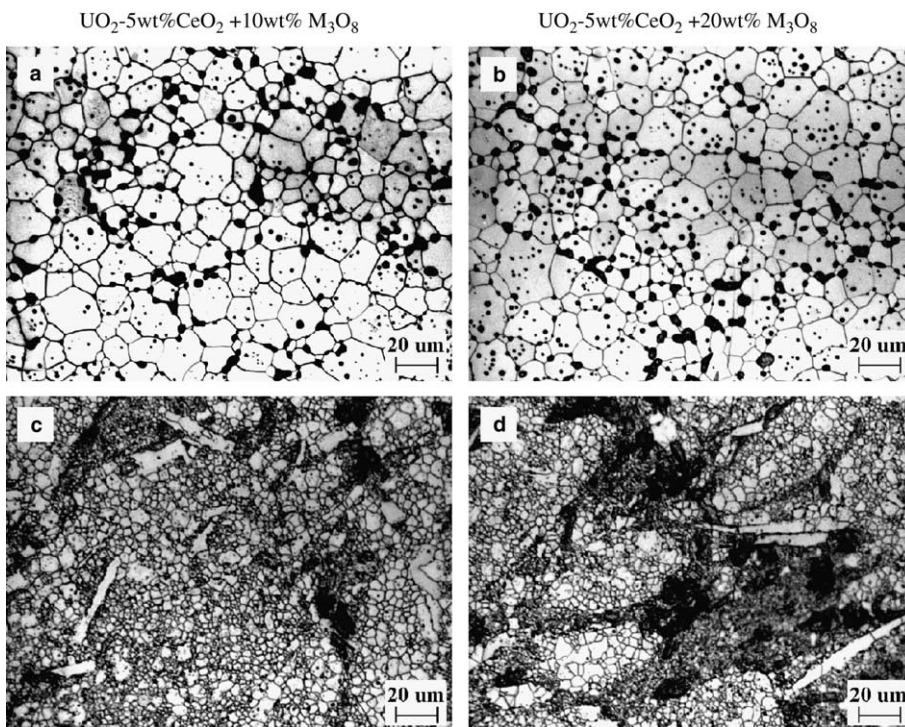

Fig. 3. Micrographs of the pellet specimens sintered in pure CO_2 and $CO_2/CO = 1/10$, and with 10 and 20 wt% of M_3O_8: (a) in pure CO_2 and 10 wt%, (b) in pure CO_2 and 20 wt%, (c) $CO_2/CO = 1/10$ and 10 wt% and (d) $CO_2/CO = 1/10$ and 20 wt%.

for these large pores to be annihilated during the sintering.

The microstructural examination permits the determination of the effect of the M_3O_8 addition on the evolution of the grain structure of the pellet specimens. Fig. 4 shows the variation of the average grain size of the pellet specimens with the M_3O_8 addition. Average grain size remains nearly constant irrespective of the amount of M_3O_8 addition at each sintering atmosphere except

H_2. In H_2 atmosphere, average grain size linearly decreases as the M_3O_8 contents increase. This is due to the oxygen potential of the sintering atmosphere and O/M ratios of the pellet specimens. That is to say, O/M ratio of the pellet specimens is nearly 2.00 at 1450 °C in $CO_2/CO = 10/1$, 1/1, 1/10 and H_2 even if reduction rate will be different between CO_2/CO and H_2 atmosphere but that of the pellet specimens in pure CO_2 is nearly 2.16. Matzke [5] proposed that the
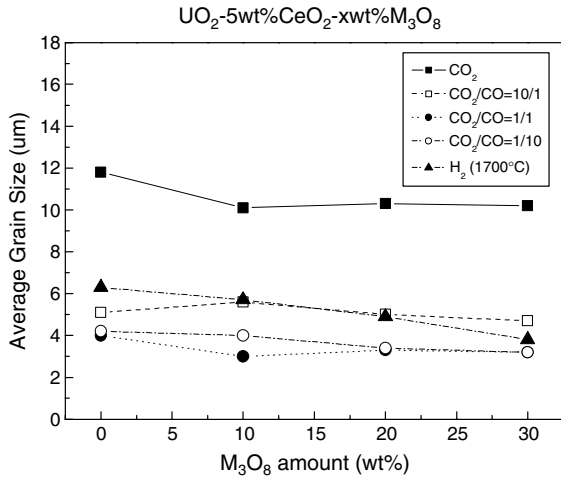
Fig. 4. Variation of the average grain size of the pellet specimens as a function of the M_3O_8 amount.

uranium self-diffusion coefficients increased approximately with x^2 in UO_{2+x}. Therefore, large grain growth occurred only in CO_2 atmosphere.

In order to investigate the role of the oxygen potential in such systems, thermogravimetry (TG) was used to elucidate the oxidation/reduction behavior of the specimens during sintering in different atmospheres. Fig. 5 shows the TG curves of the weight changes during sintering of the specimens with different amounts of M_3O_8 and with different CO_2/CO mixtures for the sintering atmospheres. It was revealed that, first of all, during a sintering for 4 h, with pure CO_2, the pellet specimens without M_3O_8 and with 10 wt% M_3O_8 are oxidized, while the pellet specimens with 20 and 30 wt% M_3O_8 are reduced to equilibrate with CO_2 atmosphere. This is due to the M_3O_8 introduced with different amounts and this means that the specimens with 20 and 30 wt% M_3O_8 have higher oxygen potentials than that of CO_2. However, it is to be noted, with $CO_2/CO = 10/1$, that the specimens are always slightly oxidized with a
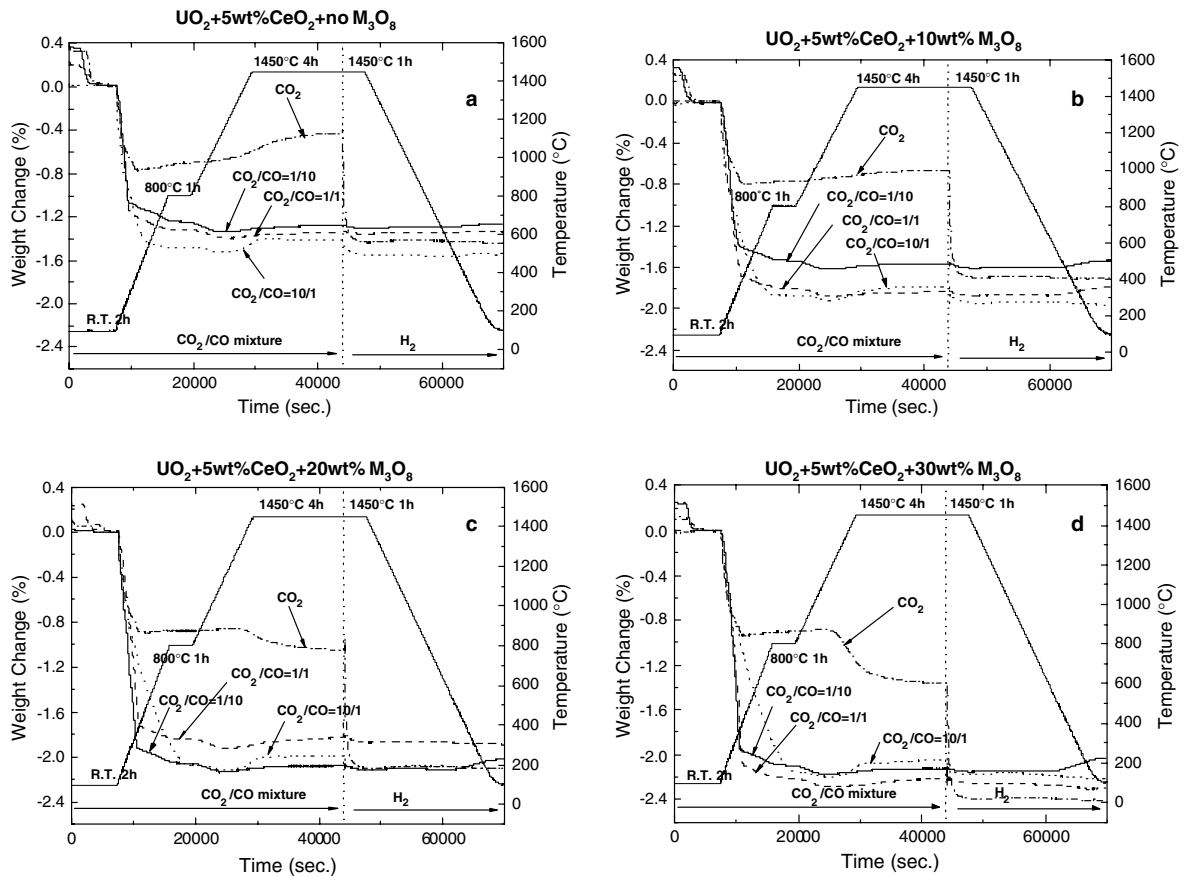

Fig. 5. TG curves of the weight changes during a sintering of the specimens with different amounts of M_3O_8 and with different CO_2/CO mixtures for the sintering atmospheres: (a) UO_2–5wt%CeO_2 without M_3O_8, (b) UO_2–5wt%CeO_2 with 10 wt% of M_3O_8, (c) UO_2–5wt%CeO_2 with 20 wt% of M_3O_8, (d) UO_2–5wt%CeO_2 with 30 wt% of M_3O_8.

different weight change rate during a sintering, irrespective of the amount of M_3O_8 addition. For reference, a calculation made of the oxygen potentials at 1450 °C with the HSC Chemistry® for these different gas mixtures gives about -135, -200, -265 and -330 kJ/mol for pure CO_2, $CO_2/CO = 10/1$, $CO_2/CO = 1/1$ and $CO_2/CO = 1/10$, respectively. For comparison, that of a pure H_2 sintering atmosphere(with a due point of -30 °C) at 1700 °C was calculated and gives about -520 kJ/mol [6]. By an observation of the weight change at the end of the sintering (4 h), the oxygen potential of the specimens increased with an increasing amount of M_3O_8 addition to the powder specimens. It is also interesting to note that, for the amount of 20 and 30 wt% of the M_3O_8 addition, the levels of the weight changed for a reduction change with different sintering atmospheres, and this means that the oxygen potentials vary dependently with the CO_2/CO ratios and the amount of M_3O_8.

4. Conclusions

In order to examine the role of the oxygen potentials in the sintering of a UO_2–5wt%CeO_2 powder mixture with different amount of M_3O_8 (M = U + Ce) powder and oxidizing atmospheres, the microstructure of the sintered pellet specimens in sintering atmospheres with different CO_2/CO gas mixtures (10/1, 1/1 and 1/10) as well as pure CO_2 and H_2 gas and an addition of 10, 20 and 30 wt% of M_3O_8 was evaluated by optical microscopy and the thermogravimetry on the behavior of the different powder mixtures. From the results obtained and discussed in terms of the variations of the sintered density, microstructural evolution and weight change during sintering, the following conclusions can be drawn.

(1) The sintered density of the UO_2–5wt%CeO_2 simulated MOX pellet decreases linearly with the amount of M_3O_8 addition in the oxidizing sintering atmosphere. When the density drop becomes large, the open porosity is very large.
(2) The contribution of an addition of M_3O_8 to the formation of the pores in the pellet specimens is

different for the sintering atmospheres with different oxygen potentials.
(3) The addition of M_3O_8 to the UO_2–5wt%CeO_2 powder mixture had no effect on the grain size when the powder mixture is sintered.
(4) The oxygen potential of the specimens increased with increasing the amount of M_3O_8 addition to the powder specimens.
(5) For the amount of 20 and 30 wt% of M_3O_8 addition, the levels of the weight changed for a reduction change with different sintering atmospheres. This means that the oxygen potentials vary dependently with the CO_2/CO ratios and the amount of M_3O_8.

It is also to be noted that a further detailed examination shall be required for an experimental in situ measurement of the oxygen potentials for a comparison with the results obtained in this work.

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