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Temperature dependences of the reduction kinetics and densification behavior of U_3O_8 pellets in Ar atmosphere

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Abstract

The reduction behavior of U_3O_8 during sintering in an Ar atmosphere has been investigated in the temperature range between 1200 and 1500 °C. The changes in stoichiometry (O/U ratio) and dimension of the U_3O_8 pellets were measured by TGA and TMA, respectively. During the reduction at 1400 and 1500 °C, the reduction rate was decreased abruptly at the O/U ratio below about 2.25 while a constant reduction rate was observed at 1200 and 1300 °C. The retardation was accompanied by a significant decrease of the activation energy for the reduction process, possibly due to the shift of the rate determining step. The sintered density, however, was similar irrespective of the sintering temperature. The microstructural observation by SEM demonstrated that the pores did not contribute to the densification due to their coalescence and entrapment in the grain boundaries, triple junctions, and inside the grains, resulting in the porous microstructures.

Keywords: Pyroprocessing; Reduction kinetics; Densification; U_3O_8 powder; UO_2 pellet

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1. Introduction

The head-end process in pyroprocessing converts a spent fuel assembly into a suitable feed material, which is supplied to the following electrolytic reduction and molten salt processes. Simultaneously, uranium and transuranic (TRU) elements are recovered from spent fuel material while fission products are removed during the head-end process. Among the various decladding methods, the oxidative decladding has the advantage of high recovery of the fuel material from rod-cuts [1]. During the oxidative decladding, the UO_2 fragment is oxidized to U_3O_8 powder, which can be used as a starting material for fabricating the feed material for the electrolytic reduction process. To improve the reduction efficiency while maintaining safety in electrolytic reduction, the feed material has to satisfy the following requirements: (1) a porous solid with a fine grain size for a rapid reduction, (2) a solid with a well-organized grain structure that has sufficient mechanical strength for safe handling, (3) a shape that can be closely packed, and (4) a solid structure that can minimize the salt carryover and contamination of the salt bath during the process. Taking into account these requirements, a pellet form of uranium oxides with a porous structure is being considered as a promising candidate for the feed material [2].

A porous pellet can be prepared from the U_3O_8 powder via ceramic processing such as pressing and sintering [3]. According to Westphal et al., a reducing atmosphere enhances the removal of fission products such as cesium and molybdenum [4]. Considering that the removal of fission products is one of the main purposes of the head-end process, the pelletized U_3O_8 material, therefore, needs to be reduced to UO_2 by thermal treatment in a reducing atmosphere. The reduction behavior of the U_3O_8 has been extensively studied in many investigations thus far [5–11]. Among these, many of the previous researches have been made in the hydrogen or hydrogen-containing gas atmospheres [6–9]. The reduction process would be quite different depending on whether or not the hydrogen

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participates in the reduction process [10]. Under inert gas atmospheres, uranium oxides undergo reduction by the loss oxygen during heat treatment. Therefore, the reduction process has to be studied under various reducing atmospheres in order to gain a comprehensive understanding about the reduction process. Yang et al. [10] studied the reduction kinetics and microstructural changes of U_3O_8 in various atmospheres: Ar, CO_2, and H_2. In their result, all samples showed abnormal columnar type grain structures after the reduction. They focused on examining the oxygen potential dependence of the reduction kinetics and the cause of the formation of the columnar grain structures during sintering under those atmospheres. On the other hand, the reduction kinetics and the densification behaviors of the U_3O_8 in an Ar atmosphere have not yet been studied in detail.

In the present investigation, the temperature dependence of the reduction kinetics and related microstructural variations such as grain growth and densification of U_3O_8 have been studied in the temperature range from 1200 °C to 1500 °C. For a comprehensive understanding, the changes in the O/U ratio and length changes of the samples were measured during the reduction heat treatment, and were analyzed with microstructural variations. From a technological viewpoint, the results of this investigation can be employed to the design of thermal pretreatment conditions for fabricating porous UO_2 pellets during pyroprocessing.

2. Experimental

As the starting material, U_3O_8 powder was prepared by oxidation of UO_2 pellets in a voloxidation chamber at 500 °C for 5 h in air with a rotating rate of 2 rpm. Green pellets were fabricated by compaction of the U_3O_8 powder under a pressure of 300 MPa using a small amount of Zn stearate as a lubricant. The compacts were sintered in the temperature range between 1200 °C and 1500 °C for 10 h in an Ar gas flow and then reduced for 2 h in a 4%H_2/Ar gas flow.

During sintering in an Ar gas flow, the weight changes of the U_3O_8 compacts were measured by thermo-gravimetric analysis (TGA, SETARAM TG92). For the measurement, the U_3O_8 compacts were placed on an alumina crucible and heated up to the temperature range of 1200–1500 °C at the rate of 5 °C/min. The flow rate of Ar gas (20 ml/min) was constantly maintained during the thermo-gravimetric measurement. Before each run, the blank test was initially carried out for the calibration of TGA results. From the calibrated TGA data, the variation of O/U ratio was determined and shown in Fig. 1. For the dilatometric analysis, the dimensional change of the U_3O_8 samples was measured using a thermo-mechanical analyzer (TMA, SETARAM SETSYS Evolution-1750 apparatus). In the sample chamber of TMA, the U_3O_8 compacts were heated up to the target temperatures (1200–1500 °C) in an Ar gas flow. After the isothermal heat treatment at the target temperatures for 10 h, all samples were reduced in a 4% H_2/Ar gas flow for 2 h to convert the samples to UO_2 and then cooled down to room temperature. Both the heating and cooling rates were 5 °C/min. The densities of sintered pellets were determined through the geometric dimension and a water immersion method as described in ASTM C830. The microstructures of the sintered samples were observed by scanning electron microscope (SEM, Philips XL-30) after thermal etching. The specific surface area of the UO_2 pellets was determined using TriStar 3000 V6.05 A BET equipment.

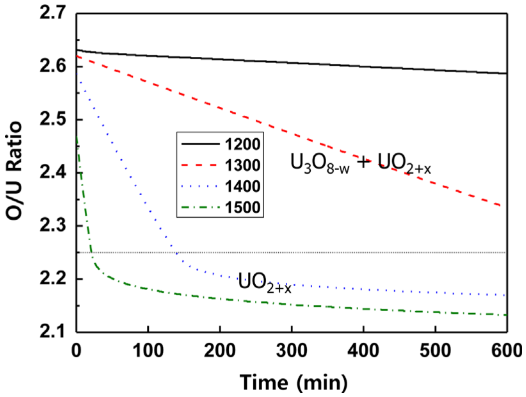

Fig. 1. Changes of O/U ratio with respect to sintering temperature and holding time.

3. Results and discussion

Fig. 1 shows the changes in average O/U ratio of U_3O_8 as a function of temperature and time during sintering in an Ar atmosphere. The equilibrium oxygen potential of the Ar gas, −149.2 kJ/mol [12], is lower than that of the $UO_{2.2}$ (−111.9 kJ/mol [11]), and thus the U_3O_8 has a tendency to be reduced during sintering in Ar. It was previously reported that the U_3O_8 converts into a mixed phase of U_3O_{8-w} and then UO_{2+x} during sintering in Ar [13]. In this study, it was also confirmed in Fig. 1 that the U_3O_8 converted to a mixed phase while the O/U ratio dropped by 2.25 (denoted by a horizontal dashed line in Fig. 1). When the O/U ratio dropped below 2.25 with a further reduction, it converted to UO_{2+x}. The reduction rate significantly increased with an increasing sintering temperature, indicating a thermally activated process. Therefore, the final O/U ratio of the samples was quite different with the sintering temperature despite the same periods of holding time (10 h): 2.59 at 1200 °C, 2.35 at 1300 °C, 2.17 at 1400 °C, and 2.14 at 1500 °C. Meanwhile, it is worth noting that the reduction kinetics was also different with sintering temperature. In the case of the samples sintered at both 1200 and 1300 °C, the O/U ratio was linearly decreased up to 10 h, suggesting a constant reduction rate. At 1400 and 1500 °C, however, the two-step kinetics was clearly observed during the reduction. At these temperatures, initially, the O/U ratio was dropped linearly by about 2.25, but the reduction rate was retarded soon after, showing much more gentle slopes at the O/U ratio below about 2.25. In other words, the reduction kinetics varied significantly, according to the O/U ratio. In a general chemical reaction process, the reaction rate is determined by the slowest step during the reaction, known as a rate determining process. The drastic retardation of reduction observed at the specific O/U ratio range can be resulted from