

Effect of continuous change of sintering atmosphere on the grain growth of Cr-doped UO₂ pellets

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1. Introduction

Cr-doped UO₂ pellet is one of the promising candidates for the high burn-up fuel in commercial LWRs. Major nuclear fuel vendors of such as AREVA or Westinghouse initiated the development of Cr-doped or Cr-containing additives doped UO₂ pellets since at the mid of 90's. Now, qualification programs are on-going to provide these pellets commercially.

The main characteristics of the Cr-doped pellets are large-grain and visco-plasticity. Large grain pellet can reduce the corrosive fission gas release at high burn up. Viscoplastic soft pellets can lower the pressure to a cladding caused by a thermal expansion of a pellet at an elevated temperature during transient operations. Those advantages can provide room for additional power uprates and high burnup limits. Especially, PCI resistance improvement can be achieved by enlarging the pellet grain size and enhancing the fuel deformation at an elevated temperature.

In this paper, to study the effect of oxygen partial pressure on grain growth in Cr-doped UO₂ pellets, Cr-doped UO₂ samples have been sintered with and without a step-wise change of sintering atmospheres. An introduction of a step-wise variation of oxygen partial pressure during the sintering enhances the grain growth of UO₂ pellets greatly. This step-wise sintering effect has been explained in terms of a continuous increase of Cr concentration along the grain boundary. The observed grain growth behavior under step-wisely changed sintering atmospheres demonstrates the possibility of reducing the amount of Cr₂O₃ to minimum via control of oxygen partial pressure while keeping the large grain size.

2. Experimental

Cr₂O₃ doped UO₂ powder mixtures were blended for 2h in a tumbling mixer. The contents of the additives were determined to be a 1500ppm in weight. The UO₂ powder used in this work was produced through the ADU (Ammonium Di-Uranate) process. The prepared Cr₂O₃ containing UO₂ powder mixtures were pressed into green pellets at 3 ton/cm². The green pellets were sintered at 1700 °C for 6h. In order to investigate the effect of oxygen potential change of sintering atmosphere on the grain structure of sintered pellets, three different kinds of sintering atmospheres

had been adopted. The first sintering condition was that the powder compacts were sintered at 1700 °C for 6 h in 1.6% of CO₂ containing H₂ gas. In the second condition, the powder compacts were heated to 1700 °C in H₂ gas and when the temperature reached at 1700 °C the sintering gas was changed to 1.6% of CO₂ containing H₂ gas. In the last condition, the green pellets were heated up to 1700 °C in H₂ gas and then hold for 1h. After then, the sintering gas was step-wisely changed to 0.5%CO₂+H₂, 1%CO₂+H₂ and 1.6%CO₂+H₂ in 2h interval. The compacts were dwelled in 1.6%CO₂+H₂ gas for 1h. From now, for a convenience, three different sintering conditions were denoted as A, B, and C, respectively.

The sintered density of the UO₂ pellets was measured by the water immersion method. The pellets were sectioned axially, ground and polished. The polished pellets were thermally etched at 1290 °C in carbon dioxide gas in order to examine their grain boundaries. The grain structures were examined by an optical microscope and the grain size was determined by the linear intercept method.

3. Results

Photographs in Fig. 1 show the grain structure evolution according to the sintering condition of the Cr₂O₃ doped UO₂ sintered pellets. The measured grain size A, B and C were 40, 62, and 130µm respectively. This grain size variation reveals that the grain growth of the pellets was deeply influenced by the oxygen potential change during the isothermal sintering even though the sintering temperature, sintering time and doping amount were identical to each other.

The effect of Cr₂O₃ doping on the grain growth of UO₂ was studied by various researchers [1-3]. Bourgeois et al. [3] illustrated that in a specific oxygen potential Cr-O system form the liquid eutectic phase at sintering temperature and that liquid phase activates the grain growth of UO₂. In the sintering process of A, the sintering was conducted in 1.6%CO₂ containing H₂. In this sintering atmosphere Cr₂O₃ can form a eutectic liquid phase. Grain growth in A was due to the liquid phase formation. There is a solubility limit of Cr₂O₃ in UO₂, namely around 0.07wt% in the 1500-1700 °C temperature range. So in the case of A, about a half portion of the doped- Cr₂O₃ could be dissolved in to

UO₂ lattice. Cr dissolution can be suppressed by heating the green pellet up to the sintering temperature in H₂ gas. Cr solubility decreases with decreasing of oxygen potential of atmosphere. In process B, a larger fraction of Cr-O liquid phase could be formed during the sintering than in process A. Therefore, grain size was enlarged in B.

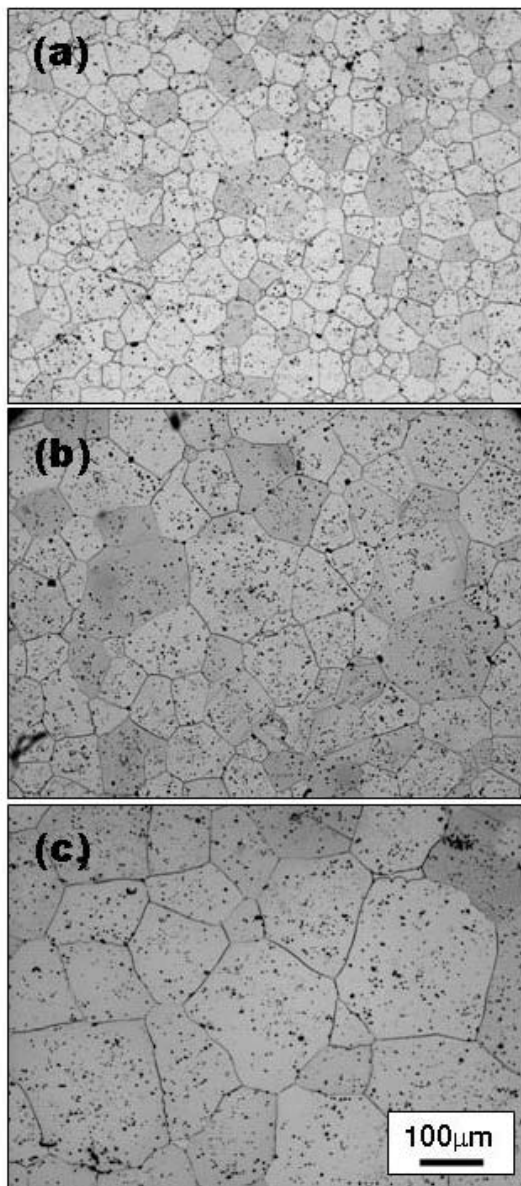


Fig. 1. Microstructure of 1500ppm Cr₂O₃ doped UO₂ pellets. (a) sintered via process A, (b) sintered via process B, and (c) sintered via process C.

The grain size of UO₂ pellet was dramatically increased in the pellet obtained by process C. In this process, the oxygen potential of sintering gas was stepwisely increased. This grain growth might be explained as follows. During the sintering at high temperature, Cr dissolved along the grain boundary and formed defects. Then the mass transport across the grain boundary was

enhanced. However, Cr in the grain boundary dissolved into the UO₂ lattice with time. Then the Cr concentration in the grain boundary or the Cr concentration gradient across the grain boundary was reduced with time. This can lead to the decrease of grain growth rate. In process C, the oxygen potential of sintering gas was continuously increased. Because the solubility of Cr increases with oxygen potential, the Cr concentration in the grain boundary could be maintained or increased by newly dissolving Cr. Then the Cr concentration gradient could be maintained at a certain level in whole sintering stage. This means that the driving force for the grain growth was not decreased in process C.

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REFERENCES

- [1] J.B. Ainscough, L.F.A. Raven, P.T. Sawbridge, Int. Symp. on water reactor fuel fabrication with special emphasis on its effect on fuel performance, Prague, Nov. 6-10 (1978) IAEA-SM233
- [2] J.C. Kileen, J. Nucl. Mater. 88(1980)177.
- [3] L. Bougeois, Ph. Dehaut, C. Lemaignan, A. Hammou, J. Nucl. Mater. 297(2001)313.