Liquid phase sintering of Cr$_2$O$_3$-doped UO$_2$

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1. Introduction

Recently, the Cr$_2$O$_3$ doped UO$_2$ pellet has been intensively investigated in terms of fuel fabrication and irradiation tests [1]. It is supposed that the Cr$_2$O$_3$ doped UO$_2$ fuel is more resistant to PCI failure. The Cr$_2$O$_3$ doped UO$_2$ pellet is known to have a large grain size, compared to undoped UO$_2$ pellet [2]. The grain growth mechanism in the Cr$_2$O$_3$ doped UO$_2$ is changed depending on the Cr$_2$O$_3$ content and sintering gas. The liquid phase sintering has been reported in the specific gas environment [2]. In this study, we have investigated the liquid phase sintering in the Cr$_2$O$_3$-doped UO$_2$ using detailed ceramography.

2. Experimental method

The UO$_2$ powder used in this work was produced through the IDR process. Mixture of IDR-UO$_2$ and Cr$_2$O$_3$ powder was wet ball-milled in order to homogeneously disperse the additive. The green pellets used for sintering experiments were obtained by pressing the milled powder under the pressure of 3 ton/cm$^2$.

Sintering was performed at 1700°C for 4h in mixed gas of CO$_2$ and to H$_2$. The ratio of CO$_2$ to H$_2$ in the mixing gas was 1.6%. The heating and cooling rate was 5K/min.

The microstructure of polished section of sintered pellets was observed with an optical microscope. The detailed morphological observations were made by scanning electron microscope. Identification of liquid phases was performed using energy dispersive X-ray analysis.

3. Results

Fig. 1 shows the equilibrium oxygen potential of CO$_2$/H$_2$ mixing gas with temperature together with equilibrium Cr-Cr$_2$O$_3$ reaction line [3]. In this figure, the $R$ denotes the volume ratio of CO$_2$/H$_2$ in %. The increase of $R$ extends the limit of the Cr$_2$O$_3$ phase stable region to higher temperature. In addition, when the $R$ is properly adjusted, Cr$_2$O$_3$ phase are reduced to Cr phase via CrO liquid phase as the temperature increases. The temperature where the liquid phase appears is very close to the conventional sintering temperature of UO$_2$. This fact makes the liquid phase sintering possible in the Cr$_2$O$_3$-doped UO$_2$ system.

Fig. 2 shows the microstructure of Cr-Cr$_2$O$_3$ obtained by annealing the Cr-Cr$_2$O$_3$ powder mixture at 1700°C for 4h in 1.6% CO$_2$/H$_2$ mixing gas. In this figure, the light color is the Cr-rich phase and dark color is Cr$_2$O$_3$-rich phase. It clearly confirmed that the Cr-Cr$_2$O$_3$ system is eutectic and melted at 1700°C in 1.7% CO$_2$ containing H$_2$ atmosphere.

Fig. 3 shows the microstructure of 3wt% Cr$_2$O$_3$ doped UO$_2$ pellet. Fig. 3(a) shows the typical grain structure in which the very large grain size of UO$_2$ is observed. Fig. 3(b) shows a more detailed structure. There are three kinds of phases in grain boundary. EDAX work reveals that white, gray, dark gray phase are UO$_2$, Cr-rich, and Cr$_2$O$_3$-rich phase, respectively. It implies that large grain growth of UO$_2$ phase is achieved by mass transport via the can be eutectic liquid phase of Cr-Cr$_2$O$_3$ in the sintering process.
Liquid phase sintering in Cr₂O₃-doped UO₂ pellet has been confirmed through detailed ceramography. The large grain growth of UO₂ in Cr₂O₃ doped UO₂ system corresponds to the existence of Cr-Cr₂O₃ eutectic liquid phase at the sintering stage.

**REFERENCES**


Fig. 3 SEM microstructure of 3wt%Cr₂O₃-doped UO₂ pellet obtained by sintering at 1700°C for 4h in 1.6% CO₂-H₂ mixing gas.

Fig. 4 shows SEM morphology of 0.5wt% Cr₂O₃-doped UO₂ pellet. The liquid phase is formed at along the grain corner of UO₂ phase.

4. Conclusion