Step-wise variation of sintering atmosphere during the isothermal sintering of Cr doped UO_2 pellets

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1. Introduction

The recent development of advanced UO_2 fuel pellet materials for water reactor fuel is mainly focused on the large grain pellet which can minimize corrosive fission gas release and deform easily at an elevated temperature. Among those, the technology regarding the doping of additives has been studied widely because this technology can increase the grain size significantly and is quite compatible with an industrial pellet fabrication process. Cr-doped UO_2 pellet is one of the promising candidate for PCI remedy.

In the sintering process of Cr- doped UO_2 pellet, it was known that tight adjusting of sintering atmosphere is most important to achieve large grain pellet. The relevant research revealed that the doped Cr_2O_3 became liquid phase in optimized oxygen potential and those liquid phase promoted the grain growth.

Although optimum composition and sintering process for Cr-doped UO_2 has been suggested by several researchers, developing a new sintering process which could minimize the doped amount of Cr_2O_3, while keeping the grain size and softness of UO_2 is still a challenge because doped Cr itself could reduce neutron economy and fission gas retention ability.

In this paper, to study the effect of oxygen partial pressure on grain growth in Cr-doped UO_2 pellets, Cr-doped UO_2 samples have been sintered with and without a step-wise change of sintering atmospheres. The microstructure evolution of sintered pellets were observed and compared. This step-wise sintering effect has been explained in terms of a continuous increase of local Cr concentration especially along the grain boundary.

2. Experimental

Cr_2O_3 and UO_2 powder mixtures were prepared by blending two powders for 12h in a tumbling mixer. The prepared Cr_2O_3 containing UO_2 powder mixtures were pressed into green pellets at 3 ton/cm_2. The green pellets were sintered at 1700℃ for 10h. The heating rate to sintering temperature was 300 K/h. The CO_2 and H_2 gas mixtures were used to control the oxygen potential during the sintering process. In the conventional sintering process, the composition of sintering atmosphere was fixed during the whole sintering process. In the step-wise-sintering process, the oxygen potential during the isothermal sintering had been varied by step wise manner to investigate the effect of oxygen potential change of the sintering atmosphere on the grain structure of sintered pellets. In step-wise sintering process, the green pellets were heated up to 1700℃ in H_2 gas and then held for 1h. Thereafter, the sintering gas was step-wisely changed from H_2+0.3vol% CO_2 to H_2 +1.5 vol % CO_2 via H_2+0.7vol% CO_2 and H_2+1vol% CO_2 in 2h interval. And then compacts were dwelled in H_2+1.7%CO_2 gas for 1h. The sintered pellets after each step were also acquired to examine the microstructure change.

The sintered density of the UO_2 pellets was measured by the water immersion method. The pellets were sectioned axially, ground and polished. The polished pellets were thermally etched at 1290℃ 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. Grain boundary structure of the sintered pellets were observed by using scanning electron microscopy (SEM). The elemental composition variation along the grain boundaries or around precipitates were measured by using energy dispersive X-ray spectroscopy (EDS) and standardless quantitative data were obtained by the ZAF correction algorithm of the EDAX Genesis X-ray microanalysis software.

3. Results

Fig. 1 shows the grain structures of Cr-doped UO_2 pellets. It is revealed that grain size was greatly enlarged by applying a step-wise sintering process.

Fig 2. show the grain size variation curves as a function of Cr contents and sintering atmospheres in Cr_2O_3 doped UO_2 pellets. The measured mean grain sizes revealed that the grain growth of the pellets was greatly influenced by the sintering atmosphere even though the sintering temperature, sintering time and doping amount were identical. The grain size curve for the pellets sintered in dry hydrogen declined slightly with increase of Cr contents. When the CO_2 ratio in the sintering gas was increased, the grain growth was occurred in doped pellets. However, the grain growth curves showed different shape to each other. The grain size started to increase at a lower Cr level in the pellet sintered in H_2-0.8vol%CO_2 than in the pellet sintered in H_2-1.8vol%CO_2. Whereas the slope of grain size curve

for the pellets in H_2-1.8vol%CO_2 was more steper. At high level of Cr doping, the grain size were more increased in the pellet sintered in H_2-1.8vol%CO_2. The grain size curve of the pellet sintered by step-wise sintering showed huge enlargement in grain size.

According to interpretation described by previous researchers [1-3], grain growth for pellets sintered in H_2-1.8vol%CO_2 might be due to the formation of eutectic liquid phase. When the Cr-dope UO_2 sintered in H_2-0.8vol%CO_2, dissolved Cr may play an important role because the formation of eutectic liquid phase is not expected when we consider the oxygen potential of sintering gas.

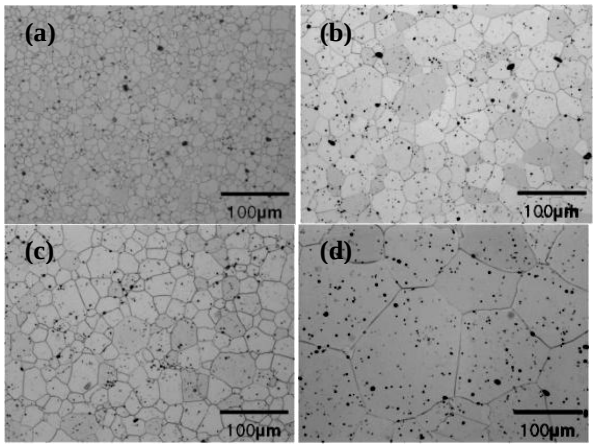

Fig .1 Grain structure of Cr_2O_3 doped UO_2 pellets (μg(Cr)/g(U)=1200) sintered in different atmospheres of (a) H_2 (b) H_2+0.8vol%CO_2 (c) H_2+1.8vol%CO_2 and (d) step-wise sintering.

Two assumptions have been made to interpret consistently the role of Cr grain growth in Cr- doped UO_2. First, there is a solubility limit of Cr in UO_2 and the limit increased with increase of oxygen potential. Second assumption is that the inhomogeneous distribution of Cr concentration along the grain boundary increases the driving force for grain growth

During the sintering at a high temperature, small amount of Cr may be dissolved along the grain boundary then the driving force for grain growth at that boundary is increased and grain can grow. However, due to the solubility limit, the Cr- concentration along the grain boundary is saturated with time and, consequently, driving force for grain growth was decreased gradually. However, when we increase the oxygen potential of sintering atmosphere, the solubility of Cr is increased further and the chemical in-homogeneity of Cr concentration along the grain boundary is appeared again. Then the driving force for grain growth increases and grain can grow again. Therefore, the great enhancement of grain size in the Cr-doped UO_2 pellets sintered by the step-wise sintering might be related with the Cr concentration variation along the grain boundary.

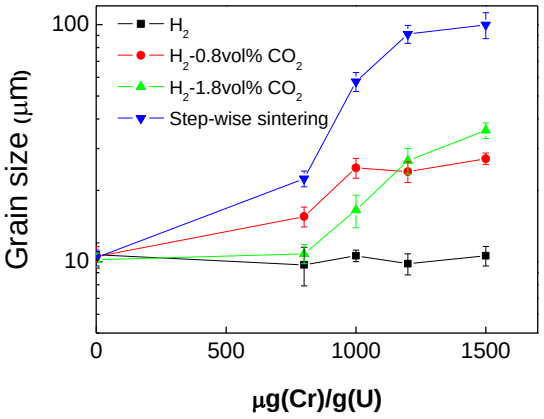

Fig. 2 Grain size evolution according to the sintering condition of the Cr_2O_3 doped UO_2 sintered pellets

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