Grain growth behavior of Cr dispersed UO_2 pellets according to change of oxygen potential during the isothermal sintering

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1. Introduction

Recent development of advanced UO_2 pellet materials for commercial reactors is mainly focused on the large grain pellet which can deform easily at an elevated temperature. Cr_2O_3-doped UO_2 pellet is one of the promising candidates. To increase the grain size effectively, it is important to control the additive content and sintering atmosphere. Relevant research on the Cr_2O_3 doped UO_2 system revealed that the doped Cr_2O_3 formed a liquid phase under optimized oxygen potential, and those liquid phases promoted the grain growth [1]. Recent work also showed that step-wise variation of sintering atmosphere during the isothermal annealing step significantly increased the grain size of Cr_2O_3 doped UO_2 pellet [2].

In this paper, we investigated effect of oxygen potential change at the beginning of isothermal sintering stage on the grain growth in metallic Cr dispersed UO_2 pellets. The study on the milling effect of powder mixture on the grain growth is also a part of this work.

2. Experimental

Two kinds of Cr_2O_3-doped UO_2 powder mixtures were prepared by turbula mixing and planetary milling, respectively. The contents of the Cr_2O_3 were determined to be 1500ppm in weight. 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^{o}C for 1h in pure H_2. After that, the sample pellets were further sintered at the same temperature for 5h under the changed atmospheres of 0.5%CO_2+H_2, 1%CO_2+H_2, 1.7%CO_2+H_2, 3.4%CO_2+H_2, 4.8%CO_2+H_2 and 7.4%CO_2+H_2, respectively. For a comparison, UO_2 pellets sintered in pure H_2 for 6h were also prepared.

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.

3. Results

Fig. 1 shows the variations of grain size as a function of changed sintering atmosphere in Cr-dispersed UO_2 pellets. The grain size curve increased until the CO_2 in H_2 reached at 1.7% and then saturated. The grain size was much largely increased in the powder mixture prepared by planetary mill.

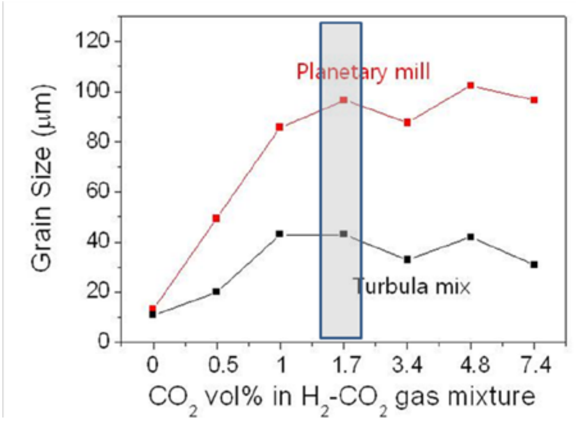

Fig. 1 Grain size variation as a function of isothermal sintering atmospheres.

Fig. 2 shows the microstructures of polished section of sintered pellets. Since the oxygen potential of H_2 gas at 1700 ^{o}C is low enough to reduce initially doped Cr_2O_3 and the solubility of metallic Cr in UO_2 is very low, the Cr particles were precipitated in the form of metal particles as shown in Figs. 2(a) and (b). The Cr particles in the pellets fabricated by using planetary milled powder were tinier and more homogeneously dispersed.

As the CO_2 ratio in H_2 was increased, the Cr particles were disappeared. It is known that Cr solubility in UO_2 increases with increase of oxygen potential of annealing atmosphere. Therefore, the disappearance of Cr particles means the dissolution of Cr into UO_2. Since the grain size was increased with increase of oxygen potential as shown in Fig. 1, dissolution of Cr is responsible for observed grain size enlargement of UO_2 pellets. Previous reports showed that, in H_2-1.7%CO_2, Cr-O could form a eutectic liquid phases and those liquid phases in grain boundary promoted the grain growth of UO_2. Hatched region in Fig.1 denoted the thermodynamically calculated gas composition in which Cr-O form eutectic liquid phase. Below the hatched region, metallic Cr is stable and above the region, Cr_2O_3 is a stable phase.

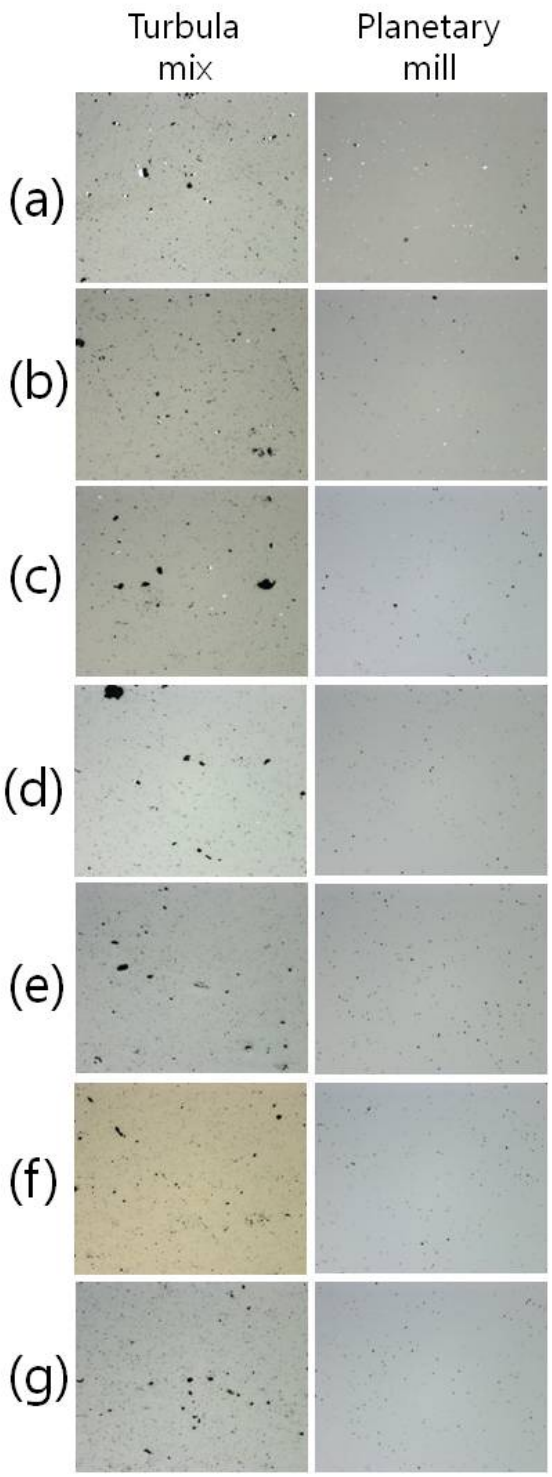

Fig. 2 Optical microstructures of Cr_2O_3-doped UO_2 pellets. Pellets were sintered at 1700 ^oC for 1h in H_2, and then further sintered for 5h in (b) H_2-05%CO_2, (c) H_2-1%CO_2, (d) H_2-1.7%CO_2, (e) H_2-3.4%CO_2, (f) H_2-4.8%CO_2 and (g) H_2-7.4%CO_2, respectively. For a comparison, (a) a pellet was sintered in H_2 for 6h at the same temperature

Fig. 1 indicated that dissolution of metallic Cr increase the grain size of Cr-dispersed UO_2 pellets effectively even though the solubility of Cr is limited. According to the previous work, Cr_2O_3 phase is not effective to increase the grain size of UO_2 pellet. Therefore, observed grain growth in the right part of Fig. 1 indicates that oxidation kinetics affect the grain growth behavior. That is, since the oxidation of Cr to Cr_2O_3 controlled by oxygen diffusion, eutectic liquid phase could be formed around the Cr particle during the oxidation and those liquid phases participate in the grain growth.

It is expected that oxidation of Cr is finished faster and thus sustainment time of eutectic liquid phase will be shortened when the oxygen potential is increased. Then the grain size of UO_2 is also expected to be decreased when the oxygen potential increased. However, grain size showed saturated value regardless of oxygen potential when the CO_2 ratio exceeded 1.7%. This result may imply that grains grow very fast when the liquid phase has been formed so that integral amount of liquid phase or its sustainment time does not affect the grain growth behavior.

It is obvious that Cr particles were dissolve faster in planetary milled case when we compare the two microstructures of Figs. 2(c). However, the Cr particles in turbula mixer case also completed disappeared when the oxygen potential was increased, as shown in Figs. 2(d)-(g). In spite of complete disappearance of Cr particles, the grain size difference between two mixtures was very large as shown in Fig.1. This result revealed that grain growth behavior was deeply affected by the initial size of Cr and its distribution in UO_2 matrix. Especially, initial amount of eutectic liquid and its distribution seem to be important factors governing the grain growth behaviors.

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