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Letter to the Editors

Density decrease of oxidatively sintered UO_2–5wt%CeO_2 pellets during resintering in H_2 atmosphere

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Abstract

Pellets admixed with zinc stearate showed density decrease of 3%T.D. during resintering in H_2 atmosphere, but density change was below 0.4%T.D. in the pellets admixed with Acrawax and stearic acid when all the powder compacts were sintered in CO_2 atmosphere. Experiments revealed that the density of the pellets doped with zinc compounds and sintered in CO_2 also displayed a density decrease of 3%T.D. after resintering. Therefore, it was considered that the major cause of the large swelling of the pellets sintered in CO_2 atmosphere after resintering was Zn residues. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Nuclear fuel is fabricated by the methods used conventionally in the area of powder metallurgy: namely, powder treatment, compacting and sintering. The addition of organo-metallic lubricants such as zinc stearate to metal or ceramic powders to facilitate compacting is a well-known practice and also these lubricants have an influence on the mechanical properties of the pellet [1–3]. The lubricants utilized up to now have a low melting point below 423 K and are decomposed almost completely below 773 K, irrespective of atmospheres [1]. Zinc stearate, among others, is perhaps the most commonly used lubricant in powder metallurgy areas including nuclear fuel manufacture.

Commercially, the sintering of UO_2 or UO_2–PuO_2 pellets is conducted in H_2 atmosphere at high temperatures of 1923–2023 K, which is usually determined by the sintered density of the pellets to be obtained. Several methods such as oxidative sintering and the addition of sintering aids have been attempted to obtain large-grained pellets for high burnup fuels [4–7]. The density decrease phenomena of UO_2 or UO_2–PuO_2 pellets sintered in CO_2 atmosphere during resintering in H_2 atmosphere are mentioned by several researchers [8,9]. Harada [8] and Kamath et al. [9] admixed zinc stearate and zinc behanate with UO_2 and UO_2–PuO_2 powder as a lubricant, respectively, and indicated that density change of the pellets after resintering in H_2 was observed up to about −5% T.D.

In this work, the density change of UO_2–5wt%CeO_2 pellets during resintering was studied using several lubricants to elucidate the cause of the large density decrease.

2. Experimental procedures

UO_2 powder used in this study was fabricated by British Nuclear Fuels public limited Co. (BNFL) and the O/U ratio and average particle size of the powder was 2.14 and 2 μm, respectively. The particle size and specific surface area of CeO_2 powder purchased from Aldrich Co. was 9 μm and 10 m^2/g, respectively. UO_2–5wt%CeO_2 powder was mixed in a Turbula mixer for 1–2 h and then milled by attrition mill for 1 h; the average particle size of the milled powder mixture was 0.2 μm. For pressing of the powder mixture, three different kinds

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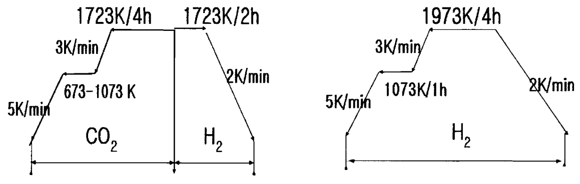

(a) oxidative sintering **(b) reducing sintering**

Fig. 1. Schematic diagram of sintering methods used in this study.

of lubricants were used; zinc stearate, stearic acid and Acrawax with a content of 0.22 wt% of the milled powder mixture. Zinc stearate is purchased from WITCO (zinc stearate USP). For the die-wall lubrication, zinc stearate suspended in benzene was used to coat the surface of the die wall. UO_2–5wt%CeO_2 milled powder was pressed with a compaction pressure of 3 ton/cm^2 and sintering was conducted both in oxidizing and in reducing atmospheres following the schedules as shown in Fig. 1. In the case of the oxidative sintering, the powder compact was sintered at 1723 K for 4 h in CO_2 atmosphere and then reduced at the same temperature for 2 h in H_2 atmosphere. The temperatures to evaporate the lubricants were set at 673–1073 K in order to observe the relation between the evaporation temperature and resintering behavior. The holding time for the evaporation was varied depending on the temperatures, for example, 6 h at 673 K and 1 h at 1073 K. In order to confirm the possible effect of Zn residue after evaporation of zinc stearate, Zn metal powder or ZnO powder was mixed with UO_2–5wt%CeO_2 powder and then milled for 1 h by attrition mill. Zn metal powder with 99.999% purity and ZnO with 99.9% purity was purchased from Alfa Aesar and Pioneer Chemical Co., respectively. The milled powders were pressed with a compaction pressure of 3 ton/cm^2 with a die-wall lubrication method to eliminate the lubricant admixing effects and the sintering method of Fig. 1(b) was used. In the reducing sintering, the powder compact was sintered at 1973 K for 4 h in H_2 atmosphere, and the evaporation temperature was set at only 1073 K. Oxidation and reduction experiment of Zn metal powder was performed using CO_2 and H_2 gas by TG (Cahn, TG171). All the sintered pellets were resintered at 1973 K for 24 h in H_2 atmosphere. Sintered density and resintered density was measured by the water immersion method.

3. Results and discussion

The properties of different lubricants used in this study are shown in Table 1 [1]. All the lubricants have a low melting point below 423 K and are mostly composed of C, H and O elements.

Table 1
The properties of lubricants used in this study

Lubricant	Density (g/ml)	Melting point (K)
Zinc stearate $Zn(C_{18}H_{35}O_2)_2$	1.1	403
Stearic acid $C_{18}H_{36}O_2$	0.97	326
Acrawax $C_{38}H_{76}N_2O_2$	0.98	413

Fig. 2 shows the density change of oxidatively sintered UO_2–5wt%CeO_2 pellets during resintering in H_2 atmosphere. Zinc stearate-admixed pellets and Acrawax-admixed pellets show the sintered density of 97.4 ± 0.3% T.D. and sintered density of stearic acid-admixed pellet and die wall-lubricated pellet is 97.5% T.D. and 96.8% T.D., respectively. Acrawax and stearic acid influenced the density change little during resintering, that is, the density change was −0.1% to −0.4% T.D. in the pellet admixed with Acrawax (indicated as A.W. admixing in Fig. 2) at the evaporation temperatures of 673–1073 K and −0.2% T.D. in the pellet admixed with stearic acid (indicated as S.A. admixing) at 1073 K. On the other hand, the density of the pellet admixed with zinc stearate (indicated as Z.S. admixing) was decreased to −2.6% to −3.3% T.D. during resintering. The evaporation temperatures of 673–1073 K did not largely influence the density decrease during resintering. The resintered density of the pellet pressed by the die wall lubrication (indicated as Z.S. die-wall) was increased to about 0.3% T.D. compared with the sintered density. If the cause of the large swelling of the oxidatively sintered pellet during resintering is trapped gases such as CO_2 and CO [8], both Acrawax admixed and stearic acid admixed pellets should also show the large density decrease after resintering because both the lubricants are composed of C–H–O mixtures, but density decrease during resintering was occurred only slightly in these

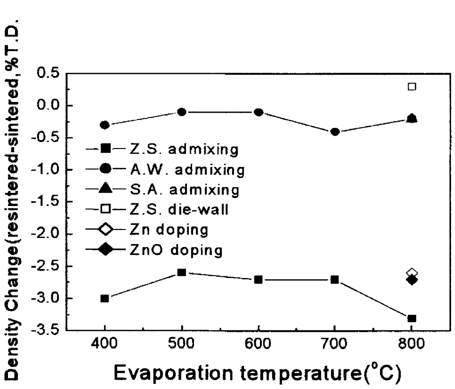

Fig. 2. Variation of the density depending on evaporation temperature, lubrication method and lubricant type in UO_2–5wt%CeO_2 sintered in CO_2 atmosphere.

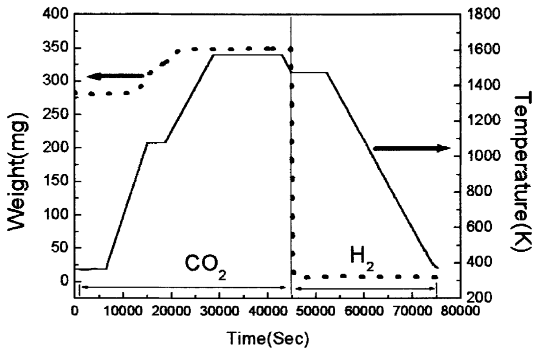

Fig. 3. Oxidation and reduction behaviors of Zn metal powder.

pellets. Therefore, it is considered that trapped CO_2 or CO gases within the pore may not be the main cause of the large swelling.

Fig. 3 shows the oxidation and reduction behaviors of Zn metal in flowing CO_2 and H_2 atmospheres, respectively. CO_2 gas with a flow rate of 30 ml/min. was used during the oxidation in the temperature range between room temperature and 1573 K with a holding step at 1073 K for 1 h, and was replaced by H_2 gas at 1473 K on cooling. Oxidation of Zn started at about 773 K and was completed at about 1233 K. Reduction of the oxidized product, ZnO, to Zn metal occurred immediately on changing the gas from CO_2 to H_2 and almost all the Zn metal was evaporated in 10 min at 1473 K.

When the powder compact admixed with zinc stearate was sintered in CO_2 atmosphere, decomposed Zn from zinc stearate may be oxidized to ZnO during heating. If the decomposed Zn metal is oxidized to ZnO by the reaction with the gaseous phase decomposed from CO_2 gas or excess oxygen from the powder or O_2 gas from the decomposed stearate, ZnO will never discharge out of the powder compact up to the sintering temperature of 1723 K because the melting point of ZnO is about 2223 K. But the ZnO can be reduced to Zn during the reduction at 1723 K in H_2 atmosphere. The reduced Zn may be in the gaseous state at the reducing temperature of 1723 K because the reducing temperature is above the boiling point of Zn metal, and this can not diffuse out of the UO_2–5wt%CeO_2 matrix, remaining in closed pores or grain boundaries. The pressure inside the pores containing Zn will be likely to become increasingly high, and thereby produce large stress in the pellet matrix at the resintering temperature and in the end, crack-like pores can form to release the stress.

In order to confirm the effect of the Zn stearate addition on the resintering behavior, UO_2–5wt%CeO_2 pellet specimens were prepared under the same condition except for the addition of Zn or ZnO of the same Zn impurity level as 0.22 wt% zinc stearate and by using die-wall lubrication to avoid any other Zn introduction in the pellet specimens. Sintered density of zinc-doped pellet and zinc oxide-doped pellet is 97.7% T.D. and 98.7% T.D., respectively. The density change by resintering of these specimens was about −2.7% T.D. with both Zn and ZnO additions as shown in Fig. 2. These results reveal that the Zn contained in UO_2–5wt%CeO_2 would be oxidized to ZnO during CO_2 sintering.

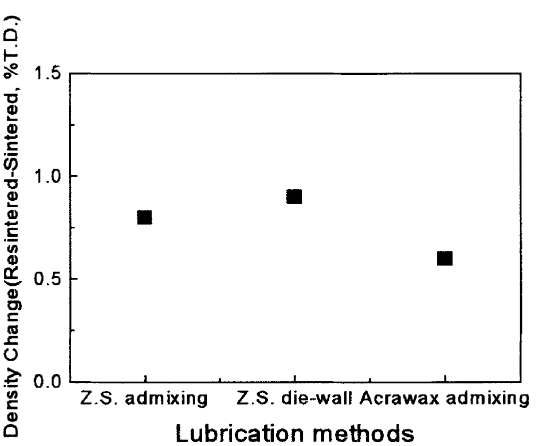

Fig. 4. Variation of the density depending on lubrication method and lubricant type UO_2–5wt%CeO_2 sintered in H_2 atmosphere.

Fig. 4 shows the differences between the sintered and resintered density in the pellet sintered in H_2 atmosphere. Sintered density of zinc stearate-admixed pellet and Acrawax-admixed pellet is the same as 98% T.D. and die wall-lubricated pellet shows the sintered density of 98.5% T.D. All the pellets sintered in H_2 atmosphere displayed density increase of 0.6–0.8% T.D. after resintering. In the case of the zinc stearate admixed pellet, the zinc stearate contained in the powder compact will starts its decomposition to Zn, C, CO_2 and CO at about 403 K. The melting and boiling point of Zn metal is about 688 K and 1188 K, respectively and therefore almost all of the decomposed Zn from the zinc stearate will be discharged to the outside of the the powder compact below 1273 K because the pellet shrinkage does not occur up to this temperature in H_2 atmosphere [10].

Table 2 shows the results of the chemical analyses of Zn and C in UO_2–5wt%CeO_2 pellet compacted with a Zn stearate admixing and sintered in oxidizing and reducing atmospheres. The UO_2–5wt%CeO_2 pellet sintered in H_2 atmosphere contains little Zn, but that sintered in CO_2 atmosphere has about 200 wppm Zn even though both powder compacts contained the same amount of zinc stearate. On the other hand, there was little zinc in the UO_2–5wt%CeO_2 pellet die-wall lubricated with zinc stearate even though it was sintered in oxidizing atmosphere. Therefore, it can be concluded that large density decrease during resintering was to a large extent related to zinc residues contained in the UO_2–5wt%CeO_2 pellet.

Table 2
Zn and C contents in UO_2–5wt%CeO_2 sintered in CO_2 and H_2 atmospheres

	Zn (wppm)	C (wppm)
Zinc stearate die-wall (CO_2 atm.)	9.7	20
Zinc stearate admixing (CO_2 atm.)	233	20
Zinc stearate admixing (H_2 atm.)	3	10

The microstructures of the sintered and resintered pellets are shown in Fig. 5. All of the pellets were sintered oxidatively as indicated in Fig. 1(a). All the pellets shown in Fig. 5 have crack-like pores along the grain boundary after resintering except the pellets pressed by die-wall lubrication. The crack-like pores did not connect to the pellet surface and also have particular directions, for example, a vertical direction in the cylindrical surface and a horizontal direction in top and bottom surface of the pellet. It is considered that the large swelling toward the four sides occurred in the pellet during resintering, thus causing plastic deformation to release the stress.

4. Conclusions

1. The pellets sintered in H_2 showed density increase of 0.5–0.8% T.D. after resintering.

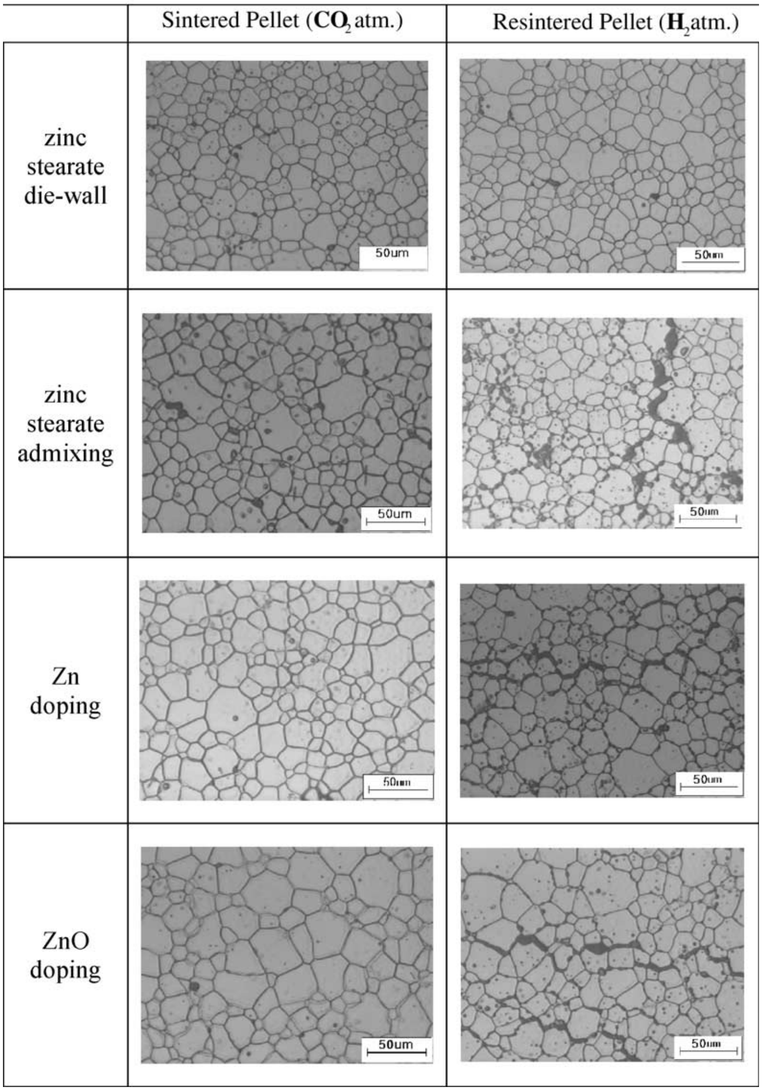

Fig. 5. The microstructures of UO_2–5wt%CeO_2 pellets sintered in CO_2 atmosphere.

2. When the powder compacts pressed by die wall lubrication were sintered in CO_2 atmosphere, the density decrease with resintering did not occur. However, the density of the zinc stearate admixed UO_2–5wt%CeO_2 was largely decreased and a number of crack-like pores were formed in the pellet during resintering and about 200 wppm Zn residue remained in this pellet.
3. Oxidatively sintered UO_2–5wt%CeO_2 pellets, doped with Zn or ZnO, also displayed the large density decrease due to crack-like pores formed during resintering. Therefore, it can be concluded that the major cause of the large swelling of the oxidatively sintered pellets after resintering was Zn residues rather than CO_2 or CO gas trapping in closed pores.

Acknowledgements

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