

Effects of the Decomposition Residue of Compound Additive on Resintering Behavior

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Abstract

Various types of compounds were tested with the aspects of decomposition and formation of residue in a CO_2 or $7\text{H}_2+93\text{N}_2$ atmosphere. The evaporation temperature range of each compound was determined from thermogravimetric curve. Decomposition of dicarbon amide, stearic acid, acrowax and zinc stearate was studied by thermogravimetry in CO_2 or in $7\text{H}_2+93\text{N}_2$ atmosphere. All compounds were decomposed in CO_2 atmosphere at lower than 400°C , but the residue, ZnO remained for zinc stearate. ZnO did not decompose in CO_2 atmosphere up to 1300°C , but reduced into Zn metal and disappeared in the temperature range of 600°C to 1200°C in $7\text{H}_2+93\text{N}_2$ atmosphere. The effect of residue, which trapped in closed pores of sintered pellet, on the thermal stability was studied using the resintering test at 1700°C in $7\text{H}_2+93\text{N}_2$ atmosphere. In the case of oxidative sintered pellet with admixing zinc stearate, the cavity formation accompanied with a density drop after resintering is due to the pressure of the Zn gases trapped in the isolated pores.

Key Words : fuel pellet, oxidative sintering process, shrinkage, lubricant, pore former, resintering, solarization

1. Introduction

The addition of compound to oxide powder, to lubricate compacting tools or to control sintered density as pore formers is well known in the fabrication process of oxide fuels [1-3]. Thermal stability of a fuel pellet, which is strongly related to the irradiation performance, depends on the fine porosity content and grain size of the pellet [4, 5]. The irradiation-stable pellet is possibly fabricated

by the minimizing of the fine pores. The use of pore former with a highly sinterable UO_2 powder improves the irradiation stability by reducing the level of fine pores. Many kinds of compounds were used in the fuel pellet fabrication process as a lubricant and/or a pore former [3].

For the MOX pellet process, powder compaction with die wall lubrication is not adapted in general, because of the process characteristics and radiation dose of workers, so that

0.2~0.5wt% of the compound is admixed to oxide powders as a lubricant or pore former [3-5].

Zinc stearate is one of the typical ionic surfactants of metal soaps, and is used as a lubricant and/or pore former in ceramic powder processes. Other compounds such as dicarbon amide, stearic acid and acrowax are also used as a lubricant or a pore former [3]. However, their effects on the pellet properties depend on their particle size distributions, decomposition temperatures and the doping methods employed.

In the case of MOX pellet compacted with the admixing of zinc stearate and sintered in CO₂, the density decreased about 3~5% T.D. after resintering at 1700°C in 8H₂+92N₂ for 24h [6]. Harada[7] prepared zinc stearate admixed compacts and sintered them by three different processes, a normal process in wet H₂, a two-stage process, and a three-stage process, respectively. He observed that only the pellet sintered by the two-stage process, first in CO₂ and second in H₂, swelled to a large extent after a thermal resintering test in wet H₂ at 1700°C. Kamath et al.[8] observed that the MOX pellets sintered in CO₂ at 1200°C with 0.5~1.0wt% of zinc behenate had a tendency of swelling during the resintering test. Amato et al. [9] observed this phenomenon in the UO₂ pellet sintered at a temperature below 1400°C in steam and explained the phenomenon as solarization. Joung et al. [10] explained the causes for the solarization of U_{1-y}Ce_yO₂ pellet after resintering could be due to

the loss of weight and the increase of lattice parameter by the reduction of pellet to hypostoichiometric U_{1-y}Ce_yO_{2-x} during resintering in reducing atmosphere.

From the studies on the solarization [9-12], several different aspects, such as pore growth, reduction of pellet to hypostoichiometry, use of compound additives as lubricants, excessively high density of green pellet and plasticity of the pellet matrix at the resintering temperature, are considered as the causes of density drop and swelling during resintering.

The present study was performed to better understand the resintering behavior of mixed oxide pellet produced by the oxidative sintering process. Various types of compounds were tested in the aspects of decomposition and formation of residues in CO₂ and 7H₂+93N₂ atmospheres to assess their effect on the density and thermal behavior of the pellets. The effect of the residues, which remained in closed pores of sintered pellets, on the thermal stability was studied using a resintering test.

2. Experimental Procedures

2.1. Thermal Decomposition

Four kinds of compound additives, such as zinc stearate, stearic acid, dicarbon amide and acrowax, were used as a lubricant or a pore former. Their physical properties are listed in Table 1.

Table 1. Compound Additives and Their Properties

Compound name	Chemical formula	Particle size (μm)	Purity (%)	Melting point (°C)	Density (g/cm ³)
Zinc stearate	[CH ₃ (CH ₂) ₁₆ CO ₂] ₂ Zn	<10	>90	128~130	1.1
Stearic acid	CH ₃ (CH ₂) ₁₆ CO ₂ H	<50	98	67~69	0.97
Dicarbon amide	C ₂ H ₄ N ₂ O ₂	6	97	155~157	-
Acro wax	C ₃₈ H ₇₆ N ₂ O ₂	10	>90	140	0.98

Thermal decomposition of each compound was studied by using thermogravimetry with a ramping rate of 5°C/min in CO₂ or in 7H₂+93N₂ up to 1300°C. The residue remained after the decomposition of zinc stearate in CO₂ was heated in 7H₂+93N₂ up to 1300°C. The decomposition temperature and the evaporation temperature range of each compound were determined from thermogravimetric curves.

X-ray analysis of the residue was carried out using Cu K α radiation (step; 0.020°, scanning speed; 4°/min).

2.2. Powder Treatment and Sintering

UO₂ powder used in this study was produced by Integrated Dry Route [13] and has the O/U ratio of 2.11, the average particle size of 2.2 μ m, and the specific surface area of 2.36m²/g. CeO₂ powder as a surrogate of PuO₂ has an average particle size of 6.7 μ m and a specific surface area of 9.46m²/g.

UO₂+ 5wt% CeO₂ powder was blended in a Turbula mixer for 2h then milled by using a continuous type attrition mill described elsewhere [3]. In order to control the pore structure, 0.5wt% of compound was added to the milled powder and mixed in a Turbula mixer for 2h.

The powder mixture was pressed into cylindrical compacts of a diameter of 10.00mm and a height of about 8.5mm using a double-acting hydraulic press at 370MPa. These compacts were sintered at 1450°C in CO₂ for 5h, and then reduced at 1450°C in 7H₂+93N₂ for 1h. Shrinkage of the compact was measured in CO₂ up to 1500°C for each kind of compound using a TMA(Thermo-Mechanical Analysis system, TMA92, Setaram). Some compacts were sintered at 1700°C in 7H₂+93N₂ for 5h to compare their thermal stability with that of the pellets sintered in oxidizing atmosphere. The thermal stability was

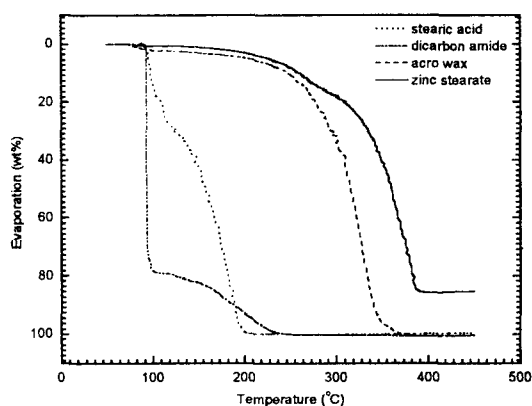


Fig. 1. Weight Changes of Compounds with Evaporation Temperature in CO₂ Atmosphere

evaluated by resintering of the pellet at 1700°C in 7H₂+93N₂ for 24h.

3. Results and Discussion

Thermal decomposition was studied with the addition of each compound alone in CO₂ atmosphere, and Fig. 1 shows the weight % of compound evaporation according to ramping temperature. Dicarbon amide, which decomposed by two steps, and stearic acid evaporated in a relatively lower temperature range. Evaporation of both dicarbon amide and stearic acid was completed at a lower temperature than 250°C. Acrowax was decomposed and fully evaporated in the temperature range of 250°C to 360°C. Zinc stearate was evaporated at a little higher temperature compared with the other compounds. Zinc stearate has a lower melting point than those of dicarbon amide and acrowax as shown in Table 1. The case is quite different from the evaporation behavior. This may be caused by the ionic groups, which play the role of anchor and stabilize the alkyl chains [14]. Zinc stearate only leaves a residue of about 14wt% of the initial weight in

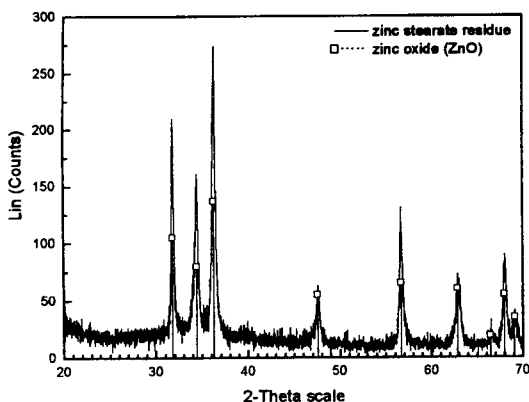


Fig. 2. X-ray Diffraction Pattern of the Residue and the Search/Match Results; Square Symbols Show the Matched Peaks of ZnO

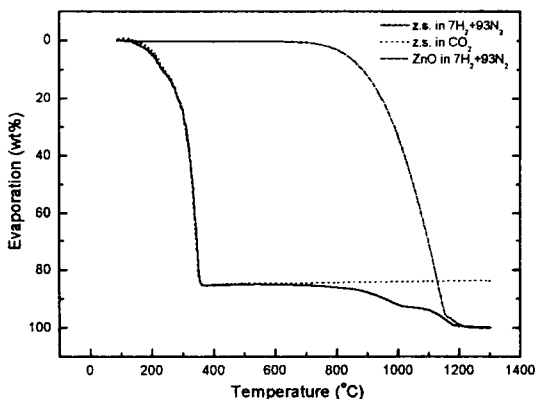


Fig. 3. Evaporation Curves for Zinc Stearate and Zinc Oxide

CO₂, even at a higher temperature than 400°C.

The residue was analyzed by a x-ray diffraction. Fig 2 shows that the reflection peaks of the residue completely correspond with those of ZnO.

Zinc stearate was evaporated with a linear ramp rate of 5°C/min up to 1300°C and the weight % of evaporation loss was shown in Fig. 3. The figure shows that zinc stearate was completely evaporated during heating up to 1300°C in 7H₂+93N₂ atmosphere. However, it remains the residue in CO₂ atmosphere, which constantly exists through the heating schedule. Zinc stearate

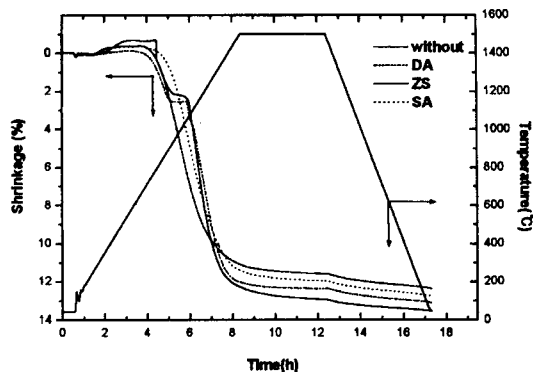


Fig. 4. Axial Shrinkage of Compound-admixed UO₂+5wt%CeO₂ Compact in CO₂

could be decomposed into Zn and CH_n in CO₂, and the residue was formed by oxidation of metal Zn at lower temperature than 360°C. Zinc oxide did not decompose in oxidizing atmosphere up to 1300°C, but reduced into Zn metal in 7H₂+93N₂. Zinc oxide started to evaporate at about 600°C and fully disappeared at 1200°C in 7H₂+93N₂. The evaporation curve for zinc stearate and ZnO met each other above 1200°C. Both of zinc stearate and zinc oxide can be completely evaporated in 7H₂+93N₂ during heating up when the temperature reaches 1200°C with the rate of 5°C/min.

Fig. 4 shows shrinkage curves of pellets according to the oxidative sintering process in CO₂. Both curves for a UO₂+5wt%CeO₂ without compound and for a dicarbon amide-admixed UO₂+5wt% CeO₂ show very similar shrink behavior, and a step exists in both curves at the temperature range of 900~1050°C. The step is relative to thermal processes such as phase transformation or formation of solid solution [8]. The formation of a solid solution between UO₂ and CeO₂ causes the step to form in this case. Both zinc stearate-admixed and stearic acid-admixed UO₂+5wt%CeO₂ compacts shrank continuously without any steps and their final

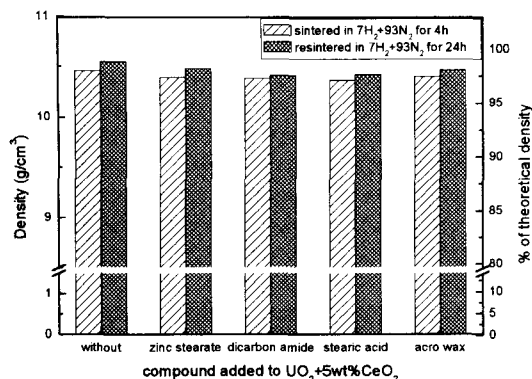


Fig. 5. Density Change of (U, Ce)O₂ Pellet After Resintering for Each Compound

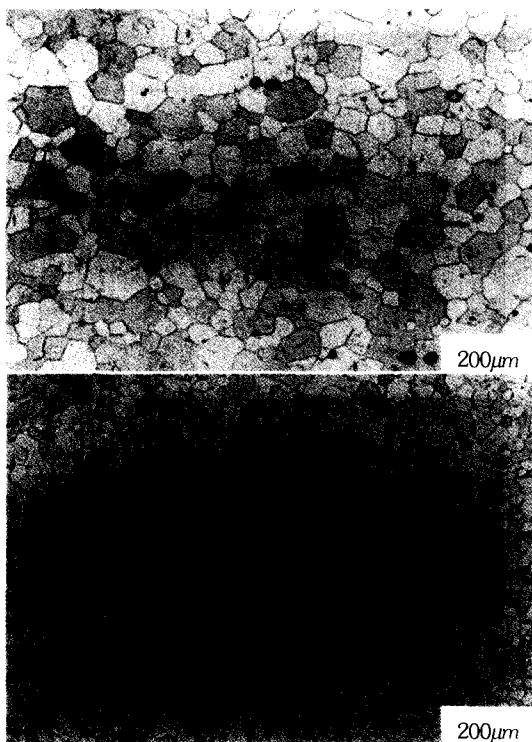


Fig. 6. Microstructures of Zinc Stearate-admixed UO₂+5wt%CeO₂ Pellets: (a) as Sintered by the Routine Process; 7μm , (b) After Resintering; 10 μm

shrinkages are less than those of the others. This result means the step on the shrinkage curve is also relative to the evaporation process of the

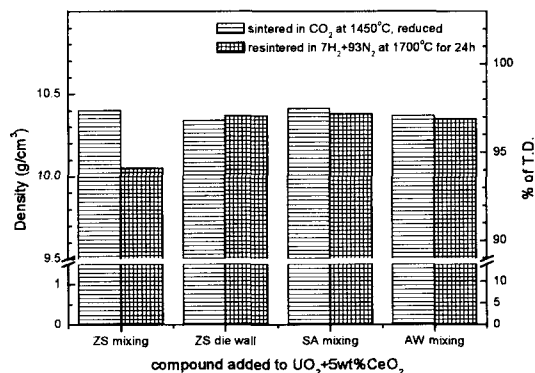


Fig. 7. Density Changes of the Oxidative Sintered Pellets After Resintering, ZS; Zinc Stearate, SA; Stearic Acid, AW; Acrowax

compound additives from the pellets.

In the shrinkage curve of zinc stearate admixed compact, densification was saturated around 1200°C in CO₂. The shrinkage of UO₂ compact begins to occur at about 700°C and saturates at about 1100 °C in CO₂ [15, 16]. Pore channels have been closed in the stage when the densification is to be saturated so that the residue can't be removed from the closed pores for the oxidative sintering process.

The pellets sintered in reducing atmosphere were resintered for 24h at 1700°C in 7H₂+93N₂, and the sintered density was compared with the resintered density for each compound in Fig. 5. Compound-admixed pellets are generally lower than that of the pellet pressed without compound, i.e. pressed with die wall lubrication. The resintered density increased 0.6~0.8% of theoretical density, compared with the sintered density. The results in Fig.1 and Fig. 5 show that every kind of compound can be removed from the MOX pellets before closing pore channels for the routine sintering process.

The grain structure of sintered pellet was compared with that of resintered one in Fig. 6, typically for the zinc stearate. Grain size of the

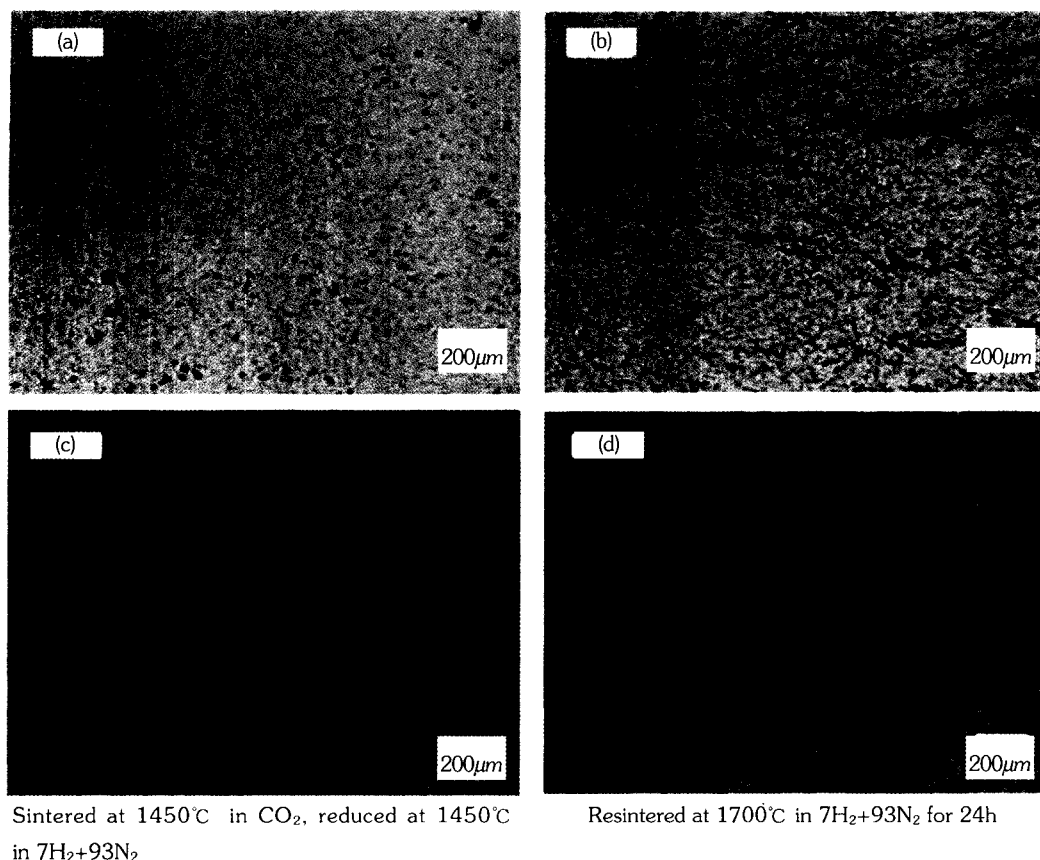


Fig. 8. Pore and Grain Structures of Zinc Stearate-admixed UO₂+5wt% CeO₂ Pellets

pellet increased during resintering, from 7 μ m to 10 μ m, for the routine sintering process. There were not any differences in microstructures between the compounds. Grain growth occurred during resintering though, pore growth or solarization wasn't observed in the pellet.

Fig. 7 shows the sintered density decreased after resintering in the case of the oxidative sintering process, contrary to the case of the routine sintering. The resintered density for the zinc stearate-admixed UO₂+5wt%CeO₂ decreased about 3.3% of theoretical density (0.35g/cm³) compared with the sintered density, and swelling and cracks were observed in appearance. This density drop is not acceptable for the thermal

stability requirement of fuel specification. However, the density decrease was only 0.28% T.D.(0.03g/cm³) for stearic acid or acrowax admixed UO₂+5wt%CeO₂. The tiny decrease in the resintered density could be due to the reduction of sintered pellet from near stoichiometry to hypostoichiometry during resintering [10]. When stearic acid or acrowax was used as a lubricant even for the oxidative sintering, the pellet was sound after resintering, because both compounds completely evaporated in CO₂,

Fig. 8 shows the microstructures of zinc stearate-admixed UO₂+5wt%CeO₂ pellets. The pore structure of sintered pellet in Fig. 8(a) shows a homogeneous distribution of spherical pores.

The grain structure of sintered pellet in Fig. 8(c) is also a typical microstructure of fuel pellet in terms of size distribution and shape. After resintering of the sintered pellet, the pore structure Fig. 8(a) transformed into Fig. 8(b). Fig. 8(b) shows the pores are aligned largely in a transverse direction of the pellet, forming intergranular networks and macroscopic cavities. Grain structure of Fig. 8(d) shows the cavity was formed with intergranular mode.

Amato et al. [9] defined the term solarization as the decrease of density in sintered bodies that takes place with the increase of the soaking time or temperature. Normally solarization is accompanied with the pore growth by the transport of fine pores to coarse pores with the grain boundary movement. The pressure p of a gas trapped within a closed pore is given by $p=2\gamma/r$, where γ is the surface energy and r is the radius of a spherical pore. Thus, the gas transported from a small into a large pore expands because the equilibrium pressure in the large pore is lower therefore the density of the body decreases.

In the case of zinc stearate-admixed $\text{UO}_2+5\text{wt}\%\text{CeO}_2$ pellets, grain did not grow during resintering, compared Fig. 8(c) with Fig. 8(d). Pores are aligned along grain boundaries, and form a kind of cavity or crack. Cavities in the resintered MOX pellet are possibly due to the pressure of the Zn gases trapped in the isolated pores, which are unable to diffuse through the (U, Ce) O_2 matrix, causes to swell some of the pores by hoop stress. If the stress is such that creep may take place and pores are close enough in the matrix at resintering temperature, the pores must grow larger and the cavity itself will expand. This phenomenon was observed only for the zinc stearate admixed pellet that sintered in oxidizing atmosphere. It is clear that the residue of zinc stearate has adverse effects on the thermal stability of the pellet. Therefore, in order to remove the

zinc stearate from MOX pellets, a de-waxing step in a reducing atmosphere must be adopted in the oxidative sintering process.

4. Conclusions

Dicarbon amide, stearic acid and acrowax were completely evaporated at a lower temperature than 360°C in CO_2 . Zinc stearate were decomposed and evaporated at the temperature range of 250°C to 390°C in CO_2 , but remained a residue of 14wt% of the initial weight. XRD analysis found that the residue was ZnO .

Zinc oxide remained intact in CO_2 during heating up to 1300°C , but it was decomposed into gaseous components by heating up in $7\text{H}_2+93\text{N}_2$, completely evaporated at the temperature range of 600°C to 1200°C .

In the case of MOX pellets sintered by the routine process, the solarization didn't occur after resintering for all compounds. Swelling and cavities were observed only for the zinc stearate-admixed pellet that sintered in oxidizing atmosphere. The zinc oxide remained in the pores caused the pellet to swell during resintering.

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