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Developments in the fabrication technology of low density MOX pellets for fast breeder reactor fuel

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Abstract

The fabrication technology of low density MOX pellets was studied using some organic compounds as pore formers. The pore former, K3 showed the best performance among five organic compounds in the 7.5 kg-UOX runs, but K3 lost this in the 36 kg-MOX run, possibly because plutonium decay heat affected its performance. Comparison of thermal stability between K3 and a newly introduced pore former, Avicel, of high softening temperature, showed that K3 lost its spherical particle shape and consequently, its pore forming ability at 70 °C which was below its reported melting point (84–88 °C) while Avicel could maintain its spherical particle shape up to 150 °C. The pore forming performance of Avicel was also confirmed in the 36 kg-MOX run which is the same scale as for mass production of MOX fuel pellets.

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1. Introduction

A significant extension of mixed oxide (MOX) fuel pin life is critically important for fast breeder reactors (FBRs) to economically compete against light water reactors. When the MOX fuel is irradiated up to a high burn up beyond 100 GWd/t, the fission gas release fraction and swelling rate become large, affecting the integrity and consequently, the fuel pin life. The use of low density or annular pellets is a powerful solution to these problems. Both of these pellet types can increase the free volume and improve the storage capacity of fission gas and mitigation ability towards swelling in the fuel matrix. Annular pellets moderate the temperature in the central region, but their fabrication technique is complicated, because the diameter of FBR fuel pellets is so small. Thus, the fabrication technology of low density pellets was studied here.

A number of papers have described developments in fabrication of low density pellets [1–5]. One of the most important properties in low density pellets is their dimensional stability during the initial stage of irradiation. Low density pellets containing large diameter pores have to be fabricated to prevent irradiation-induced densification. Up to now, two methods have been tried to fabricate these pellets. The first one uses less active raw powder

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[1–3] and the second one uses mixed organic additives as pore formers with the MOX powder [4,5].

In this study, the fabrication process of low density pellets was investigated, based on the addition of pore former to raw MOX powder. Twenty organic compounds were surveyed, and from their decomposition temperature, ease of granulation and green pellets stability, six pore formers were selected as candidates for process development study. UO_2 (UOX) and MOX runs were carried out using six pore formers and the fabrication process of low density MOX fuel pellets was established.

2. Experimental

2.1. Pore former and pellet fabrication test

Table 1 shows the properties of the six candidate pore formers. Nos. 1–5 had melting points below 150 °C. Nos. 4 and 5 were the same material, but differently processed. No. 4 was processed as hollow spherical particles and No. 5 was processed as powder.

Their performance as pore formers was examined in two pellet fabrication tests, UOX runs on a 7.5 kg batch scale (7.5 kg-UOX runs) and MOX runs on a 36 kg batch scale (36 kg-MOX runs). The 36 kg-MOX runs correspond to conditions used for the practical mass production of MOX fuel pellets. Fig. 1 shows the process flow sheet applied to fabrication of low density pellets in this study.

2.2. Preparation of feed powders

In the 7.5 kg-UOX runs, natural UOX powder prepared by the ADU (ammonium diuranate) process was used as a feed powder after ball milling for 6 h. In the 36 kg-MOX runs, MOX powder, ADU UOX powder and recycled MOX powder were weighed and mixed in the ball mill for 6 h, and this mixed powder was utilized as a feed MOX powder. The properties of these feed powders are shown in Table 2.

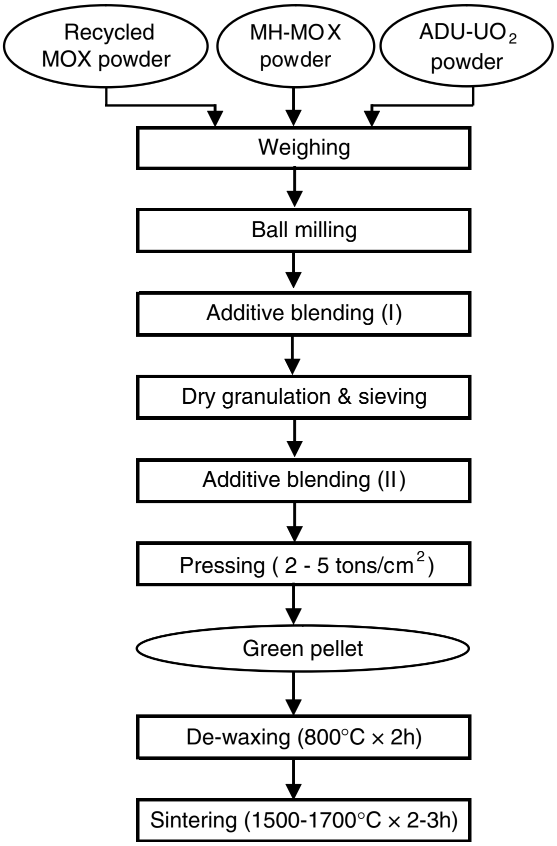


Fig. 1. Process flow used in UOX and MOX pellet fabrication runs.

2.3. 7.5 kg-UOX runs

The stability of dry granulation was checked by a fabrication test of low density pellets using natural

Table 1
Properties of candidate pore formers

No.	Poreformer		Molecular formula	Molecular mass	Melting point (°C)	Bulk density (g/cm^3)
	Product name	Chemical name				
1	Benzoic acid	Benzenecarboxylic acid	C_6H_5COOH	122.1	122–126	0.48
2	Stearic acid	Octadecanoic acid	$CH_3(CH_2)_{16}COOH$	284.5	69–72	0.48
3	Alflow-H-50S	1,2-Bis(octadecanamido)ethane	$C_{17}H_{35}CONHCH_2CH_2NHOCOC_{17}H_{35}$	593	135–146	0.61
4	Alflow-H-50T					0.37
5	K3	Glycerin trihydroxystearate	$CH_2COOR–CHCOOR–CH_2COOR$, $R = (CH_2)_{10}–CH(OH)–(CH_2)_5–CH_3$	938	84–88	0.93
6	Avicel	Crystal cellulose	$C_6H_{10}O_5$	162	350–400[a]	0.33

[a] Decomposition temperature.

Table 2
Properties of feed powders used in UOX and MOX runs

Test type	Plutonium content (wt%)	Uranium content (wt%)	O/M ratio	B.E.T. specific surface area (m^2/g)	Average particle size (μm ϕ)	Bulk density (g/cm^3)	Tap density (g/cm^3)
7.5 kg-UOX runs	–	87.70	2.07	4.90	1.2[a]	2.30	3.40
36 kg-MOX runs	18.39–18.67	69.73–69.77	–	3.85–4.20	0.42–0.51[b]	2.57–2.69	3.08–3.85
Supplementary MOX runs	18.86	69.60	–	3.21	0.51[b]	2.87	4.04

[a] Measured by sub-sieve sizer.

[b] Measured by laser scattering method.

UOX powder. In the additive blending (I) step (Fig. 1), 37 g of zinc stearate as binder and 110 g of each candidate pore former were added to the 7.5 kg of UOX feed powder, and then blended for 15 min in the V blender. This blended powder was compacted by roll pressing at a pre-determined pressure, then crushed and sieved through a set of meshes. Powders of particle sizes ranging from 0.85 to 0.125 mm ϕ were collected, and then supplied to the following step. The crushing and sieving were repeated for the powder particles larger than 0.85 mm ϕ, while the powder particles under 0.125 mm ϕ were sent back to the roll press again. The fluctuation of roll pressure from the pre-determined pressure during pressing and the ratio of collected granulated powders to the feed-blended powder were measured to evaluate dry granulation performance with each candidate pore former.

The powder thus obtained was mixed with 14.8 g of zinc stearate as lubricant in the V blender for 15 min, and then pressed into green pellets at pressures ranging from 2 to 4.5 tons/cm^2. The final concentrations of zinc stearate and each of the candidate pore formers were 0.7 and 1.5 wt%, respectively. The green pellets were heated to 800 °C at a heating rate of 200 °C/h, and then kept at this temperature for 2 h in the de-waxing step (Fig. 1). This was followed by cooling to room temperature at the same rate under $N_2 + 5\%H_2$ mixed gas atmosphere to remove all three additives before the next sintering step. These de-waxed pellets were heated from room temperature to 1650 °C at a heating rate of 400 °C/h and kept at this temperature for 2 h under $N_2 + 5\%H_2$ mixed gas atmosphere.

The geometrical densities of sintered pellets were measured and their circumferential surfaces were visually observed after they were ground by center-less grinding. Next, a sintered pellet was impregnated with epoxy resin. After cutting this specimen to a thickness of few millimeters, its transverse section was finally mirror-polished. The cracks and pore distribution were also examined on this transverse section with an optical microscope.

In an attempt to investigate the dependence of sintering temperature on the density, green pellets containing 0.5, 1.5, 2.0 and 2.5 wt% of K3 were sintered at 1500, 1600 and 1700 °C, after de-waxing by the same procedure as described above.

2.4. 36 kg-MOX run

In the additive blending (I) step (Fig. 1), 175 g of binder were mixed with 36 kg of MOX powder in the V blender for about 20 min. After the dry granulation, this powder was mixed with 701 g of the pore former K3 or Avicel and 70 g of lubricant in the V blender for about 20 min. In the intermediate steps between powder treatments, 36 kg of MOX powder were divided into two portions of 18 kg MOX powder and stored in transfer containers (Fig. 2). These MOX powder portions were pressed into green pellets at a pressure of about 5 tons/cm^2.

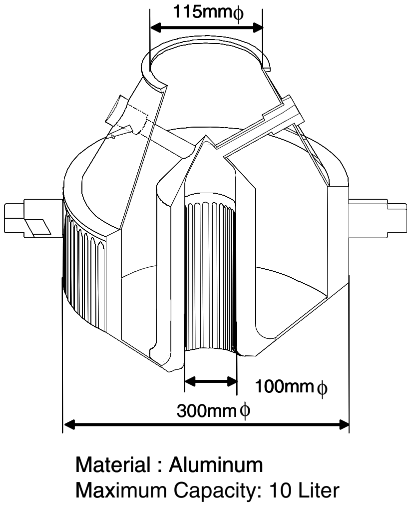


Fig. 2. Cutaway view of transfer container for MOX powder.

The green pellets doped with K3 were de-waxed and sintered by the same procedures as for the UOX runs. The green pellets doped with Avicel were de-waxed and sintered under the same heating conditions for the UOX runs under the Ar + 5%H_2 mixed gas atmosphere. The geometrical densities of sintered pellets were measured, and the cracks and pore distribution were ceramographically observed on the transverse sections of sintered pellets with the optical microscope. Nitrogen and carbon contents in the sintered pellets were measured by the fusing-thermal conductivity method and infrared spectroscopy, respectively.

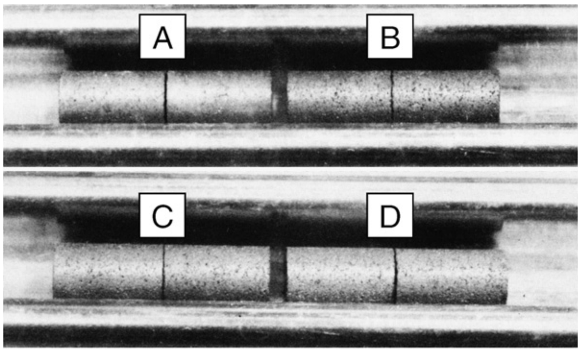
3. Results

3.1. 7.5 kg-UOX runs

UOX powders mixed with 2 wt% of Nos. 1–5 pore formers were granulated at roll pressures of 0.7 and 1.5 tons/cm^2, and then pressed into green pellets at the pressures ranging from 2.0 to 4.5 tons/cm^2. These green pellets were, subsequently, sintered at 1650 °C for 2 h after de-waxing at 800 °C for 2 h. Results on the fluctuations of roll pressure and stabilities of green pellets are summarized in Table 3, together with visual observation results on the circumferential surfaces and ceramographic examination results on the transverse sections of sintered pellets. The scattering ranges of roll pressures at 0.7 and 1.5 tons are the smallest in the MOX powder blended with K3, although the pellets fabricated with the four other pore formers (benzoic acid, stearic acid, Alflow-H-50S and Alflow-H-50T) have sufficient stabilities to allow their handling. Regarding cracks on the circumferential surfaces of ground pellets, many are seen for the pellets fabricated with benzoic acid, while none are seen for the pellets fabricated with K3 (Fig. 3) and a few are seen for the pellets fabricated with stearic acid, Alflow-H-50S and Alflow–H -50T.

The sintered densities of UOX pellets fabricated with Nos. 1–5 pore formers are shown in Fig. 4 as functions of rolling and pelletizing pressures. The sintered densities of pellets fabricated with benzoic and stearic acids are much higher than the targeted density of 85%T.D. In addition, the sintered densities of pellets with the two types of Alflow-H-50S (hollow sphere type) and Alflow-H-50T (powder type) are widely scattered, although some near the targeted density.

It is concluded that K3 shows the best performance among the five pore formers. Moreover, from the ceramographic examinations on the transverse sections, it is seen that pores are distributed homogeneously without any cracks in the sintered pellets with K3, while pores are distributed inhomogeneously or slightly inhomogeneously in the



	K3 content	Pelletizing pressure (tons/cm^2)
A	0.5 wt%	4.5
B	1.5 wt%	3.5
C	1.5 wt%	4.5
D	2.5 wt%	3.5

Fig. 3. Circumferential surfaces of ground UOX pellets fabricated with K3.

Table 3
Results of 7.5 kg-UOX runs

No.	Pore former	Scattering range of roll pressure from pre-determined value during granulation		Stability of green pellet after pressing	Cracks on the circumferential surface of ground pellet	Observation of transverse section of sintered pellet	
		Roll pressure at 0.7 tons	Roll pressure at 1.5 tons			Cracks	Distribution of pores
1	Benzoic acid	±0.9 tons	±0.5 tons	Good	Many	Many	Slightly inhomogeneous
2	Stearic acid	±0.7 tons	±0.4 tons	Good	Few	None	Slightly inhomogeneous
3	Alflow-H-50S	±0.5 tons	±0.2 tons	Good	Few	None	Slightly inhomogeneous
4	Alflow-H-50T	±0.4 tons	±0.2 tons	Good	Few	Few	Inhomogeneous
5	K3	±0.2 tons	±0.2 tons	Good	None	None	Homogeneous

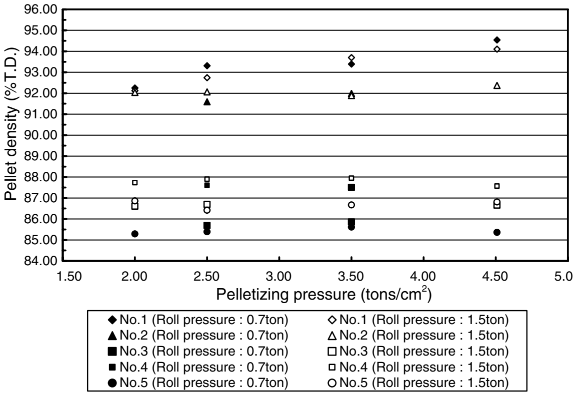


Fig. 4. Dependence of sintered pellet densities on the rolling and pelletizing pressures.

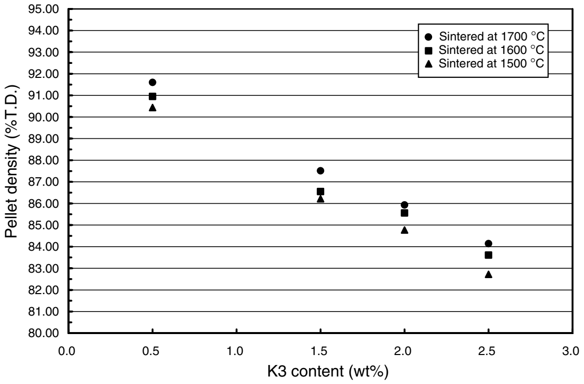


Fig. 5. Reproducibility of fabrication of low density in UOX pellets using K3.

sintered pellets fabricated with the other four pore formers. Fig. 5 shows the sintered densities of pellets as functions of sintering temperature and K3 content. It is suggested from this figure that about 2 wt% K3 content is the best to obtain the targeted density of 85%T.D. when sintered at 1650 °C for 2 h. A histogram of the sintered densities of about 300 pellets taken from the 7.5 kg-UOX fabrication run using 2 wt% K3 is shown in Fig. 6(A). The average and standard deviation are 84.66% and 0.53%T.D., respectively. It can be estimated from these results that all sintered pellets fabricated in this run using K3 have densities within 85.0 ± 2.0%T.D.

3.2. 36 kg-MOX runs using K3

Based on the results in the 7.5 kg-UOX runs described above, three 36 kg-MOX runs were conducted to confirm the pore former performance of K3 on the same scale as for the practical mass production of MOX fuel pellets. The average and standard deviation of sintered densities of about 300 pellets taken from each of three runs are shown in Table 4, together with other results on the green densities of pellets and impurity analyses. The average sintered densities of pellets obtained in the three runs are in the range from 86.29% to 88.03%T.D., higher than the targeted density. The histogram of sintered densities of about 300 pellets taken from No.3 run is shown in Fig. 6(B). The average and standard deviation are 86.28% and 1.36%T.D., respectively. It can be estimated from these results that a considerable percentage of sintered pellets fabricated in this run have densities outside the

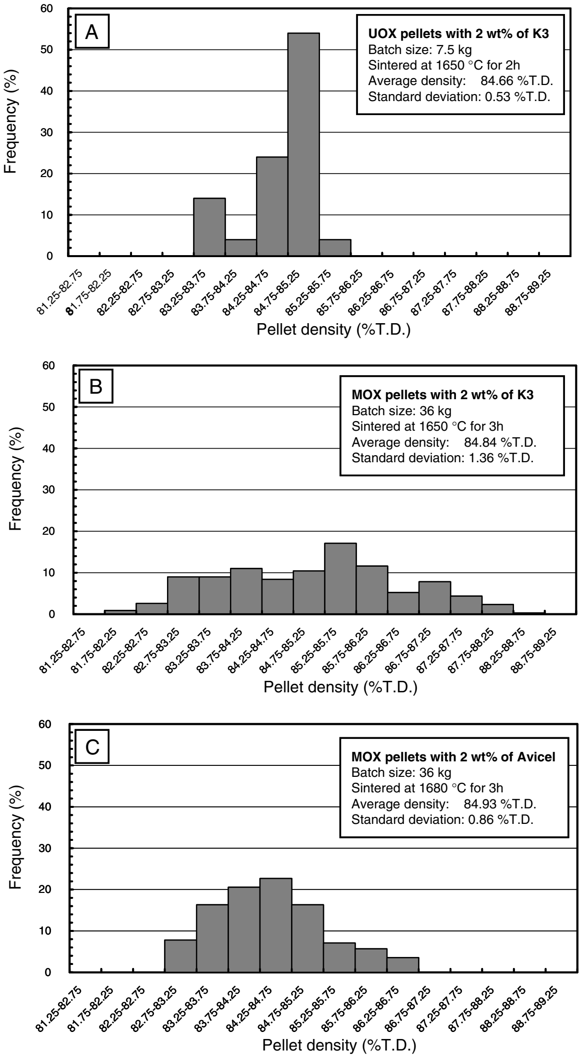


Fig. 6. Density histograms of sintered pellets taken from UOX and MOX runs.

Table 4
Results of 36 kg-MOX runs using K3

Run no.	K3 content (wt%)	Green pellet density (%T.D.)		Sintered pellet density (%T.D.)		Impurity content after de-waxing (ppm)		Impurity content after sintering (ppm)	
		Average	Standard deviation	Average	Standard deviation	Nitrogen	Carbon	Nitrogen	Carbon
1	2.0	51.53	1.02	88.03	2.09	190	3800	3300	<30[a]
2		51.25	0.54	87.03	1.63	90	3000	2800	<30
3		51.36	0.61	86.28	1.36	140	3500	5800	65

[a] Detection limit.

range of 85.0 ± 2.0%T.D. resulting in lower pellet fabrication yield.

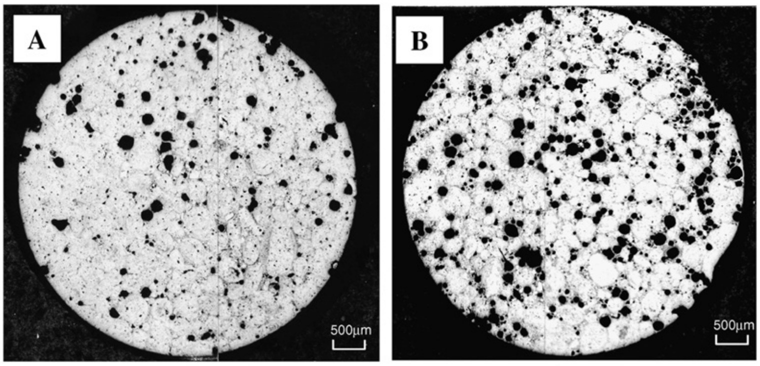
Fig. 7(A) and (B) shows two ceramographs obtained on the transverse sections of two sintered pellets with densities of 89.44%T.D. and 84.15%T.D. taken from No. 1 run, respectively. The number of pores is smaller in the high density pellet (Fig. 7(A)) than in the low density one (Fig. 7(B)).

Although K3 shows good results as the pore former in 7.5 kg-UOX runs, it does not show the same results in the 36 kg-MOX runs. The difference between UOX and MOX runs might be attributable to the following reason. Since the half lives of α-decay half-lives in plutonium nuclides are shorter than in uranium nuclides, the temperature in 18 kg MOX powder stored in the transfer container increased, resulting in the significant decrease in the function of K3 as the pore former. In the experiment, the temperatures ranged from room temperature to 90 °C in the MOX powder during its storage in the transfer containers.

Thus, supplementary MOX runs were carried out on a small scale to investigate the effect of plutonium decay heat on the thermal stabilities of K3 and new pore former, which has a softening temperature sufficiently higher than the maximum temperature in 18 kg MOX powder. As a result of the second survey for an organic compound with high softening temperature, Avicel, which has a decomposition temperature above 350 °C (Table 1), was selected as the new pore former for supplementary MOX runs.

3.3. Supplementary MOX runs

Two kinds of green pellets doped with several particle sizes of K3 and Avicel were prepared and were kept in the air at temperatures from 48 to 150 °C for 6 or 12 h. The properties of feed powder used in the supplementary MOX runs are also shown in Table 2. The plutonium content, B.E.T. specific surface area, average particle size and bulk density of this feed MOX powder are similar to



Pellet density : 89.44 %T.D.
Sintered at 1650°C for 3 h
K3 content : 2 wt%
K3 particle size : 150-250 µmϕ

Pellet density : 84.15 %T.D.
Sintered at 1650°C for 3 h
K3 content : 2 wt%
K3 particle size : 150-250 µmϕ

Fig. 7. Ceramographs of transverse sections of sintered pellets from 36 kg-MOX runs using K3.

those of feed MOX powder used in 36 kg-MOX runs.

The content and particle size of K3 and Avicel and the heat treatment conditions are shown in Table 5. After heat treatment, the green pellets were de-waxed and sintered by the same procedures as in 36 kg-MOX runs using K3, except that the atmospheric gas was changed from $N_2 + 5\%H_2$ to $Ar + 5\%H_2$ to reduce nitrogen content in the sintered pellets.

Fig. 8 shows the sintered densities of pellets as a function of heat treatment temperature for green pellets before de-waxing. It can be seen in this figure that the sintered densities of pellets using K3 increase with increasing heat treatment temperature, and their total increments in density reach 6%T.D. On the other hand, the sintered densities of pellets using Avicel do not depend on the heat treatment temperature. Table 6 shows the density measurement results of sintered pellets, together with results of impurity analyses of sintered pellets fabricated in the supplementary MOX runs.

Table 5
Particle sizes of K3 and Avicel, and heat treatment conditions

Pore former	Content (wt%)	Particle size (μm ϕ)	Heat treatment temperature (°C)	Holding time (h)
K3	1.5	70–125	52	12
			57	
			70	
		212–250	52	
			57	
			70	
Avicel		100–150	48	
			54	
			65	
			80	6
			100	
			150	

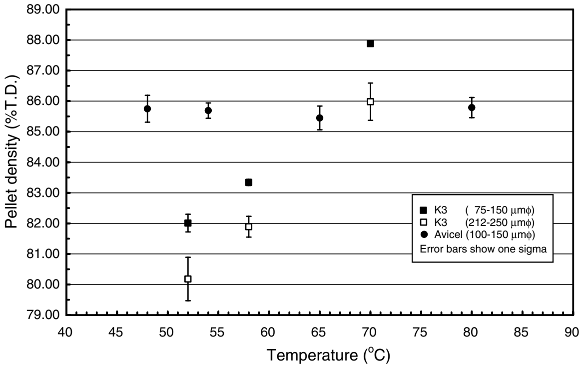


Fig. 8. Densities of sintered pellets after heat treatment for green pellets.

Fig. 9(A)–(C) shows ceramographs obtained on the transverse sections of sintered pellets after heat treatment for green pellets doped with K3 of particle sizes ranging from 75 to 125 μm ϕ at 52, 57 and 70 °C, respectively. A considerable number of pores can be seen after heat treatment at 52 °C (Fig. 9(A)), but only a few pores can be observed after heat treatment at 70 °C (Fig. 9(C)). These tendencies of pore distribution are similar for K3 of large particle sizes (212–250 μm ϕ) as shown in Fig. 9(D)–(F).

Fig. 10(A)–(C) shows ceramographs obtained on the transverse sections of sintered pellets after heat treatment for green pellets doped with Avicel at 80, 100 and 150 °C, respectively. Comparison of them with the results when using K3 shows no remarkable difference in pore distribution for the different temperatures.

In order to investigate the reproducibility of low density pellet fabrication with Avicel, several MOX pellet fabrication runs were done while changing the content of Avicel and particle size as shown in Table 7. Fig. 11 shows the sintered densities of pellets as functions of Avicel content and particle size. It is suggested from this figure that 2 wt% of Avicel content with particle sizes ranging from 100 to 150 μm ϕ or 150 to 200 μm ϕ is the best to obtain the targeted density of 85%T.D.

To summarize the above results, K3 completely lost its ability to function as a pore former by the heat treatment at 70 °C for the green pellets, while Avicel maintained its ability up to 150 °C. It is concluded that the Avicel is a good pore former for the large scale MOX pellet fabrication.

3.4. 36 kg-MOX runs using Avicel

Two 36 kg-MOX runs were carried out in order to confirm the results of supplementary MOX runs. 2 wt% of Avicel was added to 36 kg of MOX powder with 0.5 wt% of binder and MOX pellets were fabricated by the same procedures as in the 36 kg-MOX runs using K3 under $Ar + 5\%H_2$ mixed gas atmosphere.

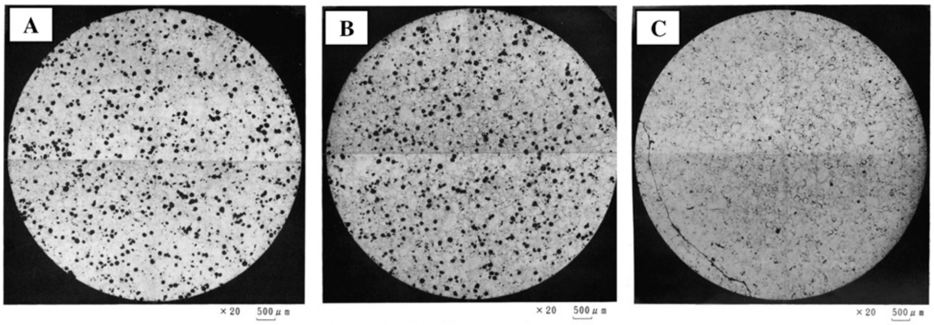
Fig. 6(C) shows the histogram of the sintered densities of about 300 pellets taken from a 36 kg-MOX run using 2 wt% of Avicel. The average and standard deviation are 84.93% and 0.86%T.D., respectively. It can be estimated from these results that more than 90% of sintered pellets fabricated in this run have densities in the range of 85.0 ± 2.0%T.D. Fig. 12

Table 6
Results of density measurement and impurity analysis of sintered MOX pellets in the supplementary MOX runs

Pore former	Pore former content (wt%)	Pore former particle size (μm ϕ)	Heating treatment temperature (°C)	Sintered pellet density (%T.D.)		Impurity content (ppm)	
				Average	Standard deviation	N (≦30)[a]	C (≦200)[a]
K3	1.5	75–125	52	82.01	0.29	120	<30[b]
			58	83.32	0.10	120	<30
			70	87.88	0.07	120	<30
		212–250	52	80.18	0.71	140	<30
			58	81.99	0.34	120	<30
			70	85.98	0.61	140	<30
Avicel		100–150	48	85.75	0.44	<50[b]	<30
			54	85.69	0.25	<50	<30
			65	85.45	0.39	<50	<30
			80	85.79	0.33	<50	<30
			100	85.27	0.39	<50	<30
			150	83.38	0.48	<50	<30

[a] Specification limit.

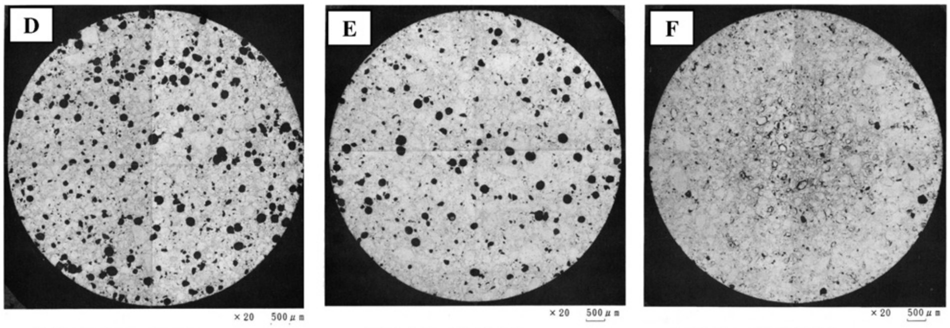
[b] Detection limit.



K3 content : 1.5 wt%
K3 particle size : 75-125 μmϕ
Heat treatment at 52 °C
Sintered at 1650 °C

K3 content : 1.5 wt%
K3 particle size : 75-125 μmϕ
Heat treatment at 58 °C
Sintered at 1650 °C

K3 content : 1.5 wt%
K3 particle size : 75-125 μmϕ
Heat treatment at 70 °C
Sintered at 1650 °C



K3 content : 1.5 wt%
K3 particle size : 212-250 μmϕ
Heat treatment at 52 °C
Sintered at 1650 °C

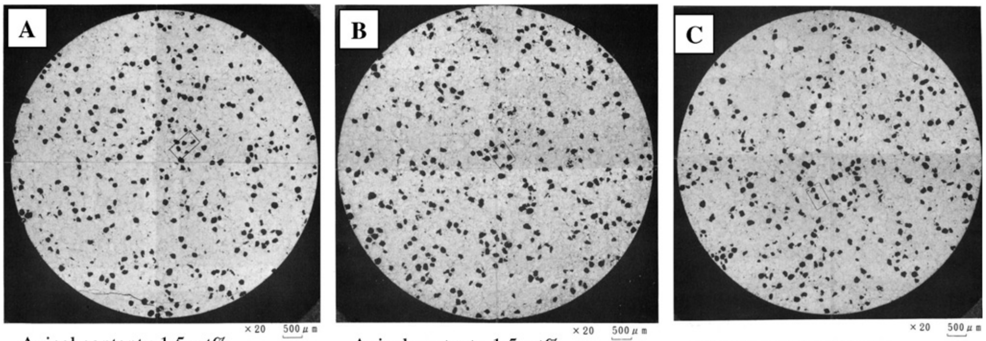
K3 content : 1.5 wt%
K3 particle size : 212-250 μmϕ
Heat treatment at 58 °C
Sintered at 1650 °C

K3 content : 1.5 wt%
K3 particle size : 212-250 μmϕ
Heat treatment at 70 °C
Sintered at 1650 °C

Fig. 9. Ceramographs of the transverse sections of sintered pellets from supplementary MOX runs examined with K3.

shows a ceramograph of a transverse section of a sintered pellet fabricated in this run. Homogeneous distribution of pores is obtained.

Table 8 shows the density measurement results of green and sintered pellets, together with results of impurity analyses of sintered pellets fabricated in



Avicel content : 1.5 wt%
Avicel particle size:100-150 μmϕ
Heat treatment at 80 °C
Sintered at 1650 °C

Avicel content : 1.5 wt%
Avicel particle size:100-150 μmϕ
Heat treatment at 100 °C
Sintered at 1650 °C

Avicel content : 1.5 wt%
Avicel particle size:100-150 μmϕ
Heat treatment at 150 °C
Sintered at 1650 °C

Fig. 10. Ceramographs of the transverse sections of sintered pellets from supplementary MOX runs using Avicel.

Table 7
Avicel content and particle size

Avicel content (wt%)	Avicel particle size (μm ϕ)
1.0	100–150
	150–200
	200–250
1.5	100–150
	150–200
	200–250
2.0	100–150
	150–200
	200–250

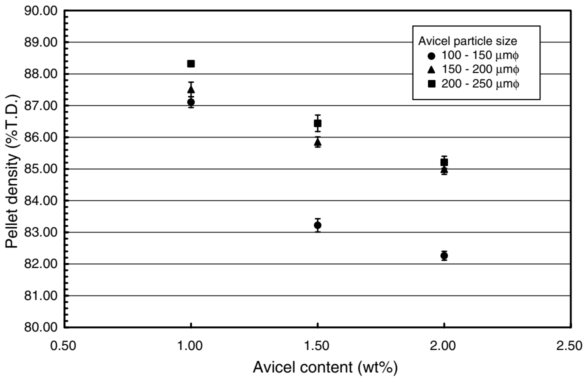
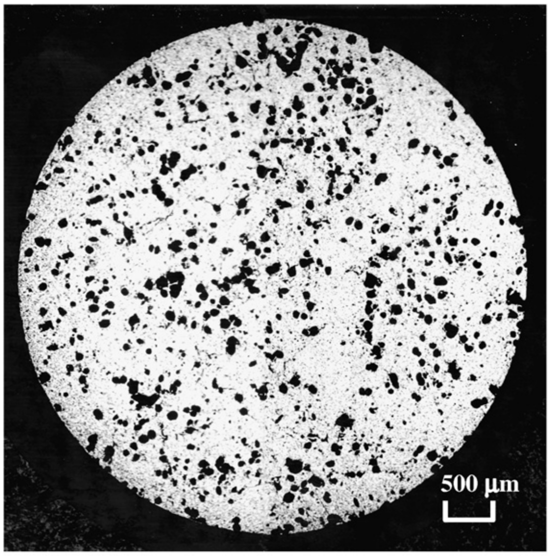


Fig. 11. Dependence of the sintered pellet densities on the content and particle size of Avicel.



Avicel content : 2 wt%
Average density : 84.93 %T.D.
Standard deviation : 0.86 %T.D.
Sintered at 1680 °C

Fig. 12. Ceramograph of a transverse section of sintered pellet from a 36 kg-MOX run using Avicel.

these two runs. The averages and standard deviations of green and sintered densities of pellets show good results for mass production. Nitrogen and carbon contents are less than the detection limits, similar to the results of supplementary MOX runs as shown in Table 6.

4. Discussion

4.1. Thermal stability of pore former

Radford and Pope [6] investigated the performances of many kinds of volatile additive pore

Table 8
Results of 36 kg-MOX runs using Avicel

Run no.	Avicel content (wt%)	Green pellet density (%T.D.)		Sintered pellet density (%T.D.)		Impurity content (ppm)	
		Average	Standard deviation	Average	Standard deviation	Nitrogen	Carbon
1	2.0	58.04	0.84	84.93	0.86	<50[a]	<30[a]
2		58.16	0.88	84.86	0.76	<50	<30

[a] Detection limit.

formers to control the sintered density of UO_2 fuel. As the pore formers, they used volatile ammonium compounds and some partially volatile uranium bearing compounds, because they are easily prepared without residues other than UO_2 and they do not affect the pelletizing and sintering operations. However, these results can not be applied to large scale MOX fuel fabrication because thermal stabilities of pore formers are affected by decay heat of plutonium during processing for MOX pellet fabrication as described above. The required thermal stability of pore formers depends largely on batch size, specified plutonium concentration in the MOX fuel pellets and plutonium isotopic composition used for MOX fuel fabrication.

The vender's reported melting point of K3 is 84–88 °C (Table 1), but K3 had already lost its ability to function as the pore former after heat treating green pellets at 70 °C (Fig. 8), which is below its reported melting point. It is, therefore, considered that the particles of K3 soften below the melting point and consequently lose their spherical particle shape in the green pellet matrix after the heat treatment at 70 °C for 12 h. It can be understood from this fact why few pores are observed on the transverse sections of sintered pellets (Fig. 9(C) and (F)). Based on the sintered densities of pellets after heat treatment for green pellets (Fig. 8) and ceramograph observations of the supplementary MOX runs (Fig. 9), it can be concluded that K3 starts to soften at temperatures over 50 °C.

In order to introduce stable pores into the sintered pellets, it is, therefore, important to select pore formers with a higher softening temperature than the maximum temperature reached in MOX powder during pellet fabrication. The thermal stability of Avicel was examined in a temperature rising test, using a high temperature microscope, and it was not deformed by temperatures up to 250 °C. It is, therefore, reasonable that no remarkable difference in the pore distribution can be observed on the transverse sections of sintered pellets heat treated for green pellets at 80, 100 and 150 °C (Fig. 10(A)–(C)).

4.2. Pellets densities in low density MOX pellet fabrication

Fig. 6(A)–(C) shows the histograms of sintered densities of about 300 pellets taken from 7.5-kg UOX run using K3 and 36 kg-MOX runs using K3 and Avicel, respectively. Average and standard deviation are also shown. From Fig. 6(A), the standard deviation of sintered densities is 0.53%T.D and this value is sufficient for mass production of low density pellets because the value of 0.53%T.D. is small enough for almost 100% of the sintered densities of pellets to distribute within 85.0 ± 2.0 %T.D.

In the plutonium fuel fabrication facility (operated by one of predecessors of JAEA) which started its operation in 1972, high density MOX pellets with 1.84 and 2.27 wt% of plutonium fissile content had been fabricated without any pore former for the Advanced Thermal Reactor, 'FUGEN'. Because the plutonium content is less than 3 wt% in MOX pellets for 'FUGEN', it is, reasonable, to consider that these MOX pellets show almost the same sintering behavior as UOX pellets. Okita et al. [7] reported that the average standard deviation of sintered densities of pellets in 30 MOX pellet fabrication runs on a 30 kg scale for 'FUGEN' was 0.17%T.D. This standard deviation is much smaller than that of the UOX run using K3.

For the low density pellet fabrication in the UOX run using K3, no effect of decay heat of plutonium was observed. The bulk density of UOX powder is about three times larger than that of K3 (Tables 1 and 3). In general, it is not easy to mix two materials with a big difference in bulk density homogeneously. It is, reasonable, to consider that the difference in standard deviation of sintered densities of pellets between the UOX run using K3 and MOX runs for 'FUGEN' without any pore former is caused by the somewhat poor homogeneous distribution of pore former K3 in the UOX powder.

The standard deviation of sintered densities of about 300 pellets taken from each of three 36 kg-MOX runs using K3 are from 1.36 to 2.09%T.D.

(Table 8), and they are larger than that of the UOX run using K3. From the results of supplementary MOX runs shown in Fig. 8, the function of K3 as the pore former was degraded with the increase of heat treatment temperature. As Asakura and Ohtani [8] reported, the temperatures of MOX powder blended with K3 are widely distributed from room temperature to about 90 °C depending upon the location in the MOX powder during fabrication. In addition, K3 started to soften at temperatures over 50 °C in the supplementary MOX runs as described above. It is, therefore, considered that sintered pellets fabricated from the powder kept at a temperature above about 50 °C, estimated softening temperature of K3, show higher densities than the targeted one, while sintered pellets fabricated from the powder kept below about 50 °C show densities close to the targeted one as shown in Fig. 7(A) and (B). It can therefore be understood that the standard deviation of sintered densities of pellets increases with the wide distribution of powder temperature in 36 kg-MOX runs using K3, while the decay heat has no effect on the softening of K3 in the 7.5 kg-UOX runs.

In 36 kg-MOX runs using Avicel, the standard deviation of sintered densities of about 300 pellets taken from each of No.1 and No.2 runs are 0.76 and 0.86%T.D., respectively. These values are slightly larger than the result of the UOX run using K3. As shown in Table 1, the bulk density of Avicel is one third of that of K3. It is, therefore, most likely that the degree of homogeneity of Avicel in the blended MOX powder is degraded compared to K3 and consequently the standard deviation of sintered pellets densities slightly increases because of this enlarged difference in bulk density between pore former and feed powder.

4.3. Nitrogen content

It was observed that the nitrogen contents higher than the specification limit remained in the pellets de-waxed and sintered under N_2–5%H_2 mixed gas atmosphere as shown in Table 4. Pautasso et al. [9] used thermogravimetric techniques to investigated the formation kinetics of uranium and plutonium nitride pellets by a carbothermic reduction of uranium and plutonium oxides under atmospheres of flowing N_2 gas. They reported that the direct synthesis of nitrides occurred by carboreduction at 1400–1600 °C under flowing N_2 or N_2–8%H_2 gas. Muromura and Tagawa [10] also reported that the carbothermic conversion reaction of uranium dioxide under an atmosphere of N_2 gas occurred at >1350 °C. The additives doped in low density MOX pellets such as the binder, lubricant and pore former are decomposed during de-waxing, but certain amounts of carbon still remain in the pellet matrix after de-waxing [11]. It is, therefore, considered that the carbon remains in the de-waxed pellets, and then almost all the carbon remaining in the pellet matrix is converted to the nitride by the following reactions under the N_2–5%H_2 mixed gas atmosphere.

$$MO_{2+x} + C + 1/2N_2 \rightarrow MO_{2-x} + MN + CO \qquad (1)$$

or

$$MO_{2+x} + C + 1/2N_2 \rightarrow MO_{2-x} + MN_xC_{1-x} + xCO, \qquad (2)$$

where $M = U$ or (U, Pu).

From the results shown in Table 4, it can be considered that the above reactions are caused in the pellets during sintering under the N_2–5%H_2 mixed gas atmosphere. It is, therefore, important to utilize Ar–5%H_2 without nitrogen as the sintering atmospheric gas.

5. Conclusion

Six organic additives were examined as pore formers in fabrication of low density MOX pellets for fast breeder reactors. First in 7.5 kg-UOX runs, 2 wt% of five pore formers were mixed with UOX powder, and their performances were evaluated from the results of fluctuations of rolling pressures, stabilities of green pellets and sintering behaviors. K3 showed the best results, but when the results for the 7.5 kg UOX run using K3 were compared to the results for the 36 kg MOX runs, K3 was unacceptable for the large size run because the plutonium decay heat possibly affected its performance. Supplemental MOX runs on the small scale were conducted to investigate the effect of plutonium decay heat on the thermal stabilities of K3 and a newly introduced candidate, Avicel which has a high softening temperature, as the pore formers. It could be understood from these results that K3 lost its spherical particle shape and consequently lost its ability to function as the pore former at 70 °C which was below its reported melting point, 84–88 °C, while Avicel could maintain its spherical particle shape up to 150 °C. Low density MOX pellets were successfully fabricated in 36 kg MOX runs on the same scale as in practical mass production of MOX pellets. In addition, it was important for the reduction of nitrogen content in the sintered MOX pellets to utilize Ar + H_2 gas instead of N_2–5%H_2 gas as the sintering atmospheric gas.

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