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Wet precipitate method for mixing magnesium and uranium in preparation of $Mg_yU_{1-y}O_{2+x}$ solid solution

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Abstract

A wet method was studied to mix magnesium and uranium finely for fabricating homogeneous solid solution $Mg_yU_{1-y}O_{2+x}$ ($x \geq 0$ or $x < 0$). The method consists of precipitate formation of ammonium diuranate (ADU) from dilute HNO_3 solution containing calculated concentrations of uranyl nitrate, NH_4NO_3 and $Mg(NO_3)_2 \cdot 6H_2O$. Since a small portion of the solution containing Mg is held in the cream-like precipitate of ADU, subsequent heating after careful drying of the precipitate leads to form homogeneous solid solutions. NH_4NO_3 prevents the solution from precipitating $Mg(OH)_2$ on ammonia addition. The concentration relation of the chemical species was examined for 10 ml of 0.21 M uranyl nitrate solution in 0.014 M HNO_3. It was found that $Mg(OH)_2$ did not precipitate with the addition of 2 g NH_4NO_3. The 5 ml addition of 25 wt% ammonia water was sufficient for ADU formation. The concentration of Mg in the solid was proportional to the amount of $Mg(NO_3)_2 \cdot 6H_2O$ under the relevant condition. From the vacuum dried ADU precipitate (method (4)), homogeneous $Mg_yU_{1-y}O_{2+x}$ solid solutions were prepared. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

A number of metal oxides react with UO_2 forming solid solutions in which the metals substitute for U atoms in the fluorite type $(Fm\bar{3}m)$ UO_2 crystal. Studies to clarify the formation and physico-chemical properties of these solid solutions have made a large contribution to the development of oxide fuels. It was found that the addition of a low concentration of the oxides of metals such as Ti [1–5], Nb [3,6–8], V [3,9], Cr [10,11], La [6], Mg [1,11,12] and Ca–Ti [13,14] causes a significant increase in grain size which is expected to lower the FP gas release during irradiation. The Gd burnable poison fuel [15,16] and the uranium–plutonium mixed oxides (MOX) [17–19] are well known solid solution fuels.

For preparing solid solutions, the importance of the process to mix the object metal oxide with uranium oxide before heating does not need to be mentioned. It is difficult to obtain homogeneous solid solutions without sufficient mixing. The foreign metal oxide agglomerates in an inhomogeneous solid solution has been pointed out to have the possibility of inducing undesirable secondary effects on fuel burnup performance. The plutonium spots in MOX fuel are probably responsible for the enhancement of the FP gas release [20].

In efforts to fabricate homogeneous MOX fuel adopting easier mixing process than the mechanical mixing process [21], various techniques have been developed. High temperature resistance heating or arc-melting of UO_2–PuO_2 mixtures facilitates chemical diffusion of Pu resulting in formation of satisfactorily homogeneous solid solutions [22]. Coprecipitation of hydroxides from UO_2^{2+}–Pu^{4+} nitrate solution or that of carbonates, i.e. UO_2CO_3 and Pu_2CO_3 or $(NH_4)_4UO_2(CO_3)_3$ and $(NH_4)_4PuO_2(CO_3)_3$, has often been adopted [23,24]. The method which consists of drying-up of the solution and subsequent thermal

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decomposition of nitrates by microwave heating gave a satisfactory result in fabrication of the MOX fuels of various Pu contents [25]. The sol–gel microsphere pelletization followed by sintering in H_2 is another route to yield MOX fuel avoiding completely dust hazard of powder metallurgy [26].

Mg solid solution, $Mg_yU_{1-y}O_{2+x}$, has a stable range of solid solution for both $x \geq 0$ and $x < 0$ sides. At $x < 0$, i.e. O/(Mg + U) < 2, its oxygen potential is low, and the dominant defect of the solid solution in the anion sublattice is the oxygen vacancy in which the FP gases of Xe and Kr are expected to be trapped [27,28]. The formation reaction of this solid solution from MgO (or $MgUO_4$) and UO_2 proceeds, however, rather slowly on heating at high temperatures, where the mixing was made by grinding the above oxides in an agate mortar [29]. Such a mixing method is not suited for large scale production of the solid solution. However, the usual coprecipitation method is hardly applied for this solid solution because the stability constant of hydroxide (or carbonate) of Mg^{2+} is largely differed from that of uranyl ions [30] resulting in partial precipitation of either $Mg(OH)_2$ (or $MgCO_3$).

This work was undertaken to have a simple wet method of mixing for the formation of Mg solid solution which is comparable with the coprecipitation method for the MOX fabrication process. The method presented here consists of filtration of ammonium diuranate (ADU) precipitate which is moist with a small amount of Mg^{2+} containing solution. The homogeneity of Mg and U by this mixing method was studied using X-ray diffraction analysis of the formed $Mg_yU_{1-y}O_{2+x}$ solid solution.

2. Description of the wet precipitate method

To the solution in which uranyl nitrate, NH_4NO_3 and $Mg(NO_3)_2 \cdot 6H_2O$ are dissolved, add 25 wt% ammonia water. The cream-like precipitate of so-called ADU is formed, which is subsequently filtrated by suction using glass filter after decantation. In this viscous precipitate, a small volume of the Mg nitrate solution is held, which yields a homogeneous solid solution, $Mg_yU_{1-y}O_{2+x}$, on heating at high temperature under suitably low oxygen partial pressure.

To discuss about the possibility of this method, the condition for precipitate formation is necessary to be fixed. The essential point is to precipitate ADU completely with no partial precipitation of $Mg(OH)_2$ in the presence of common ion of nitrate from NH_4NO_3 added. The item includes the concentrations of NH_4NO_3 and $Mg(NO_3)_2 \cdot 6H_2O$ in the solution and the volume of added NH_4OH solution. Higher concentration of NH_4NO_3 gives a higher saturation concentration of magnesium, $[Mg^{2+}]$, in the solution.

There have been a number of studies on the solubility of $Mg(OH)_2$ in aqueous solutions. However, agreement of these data is not so good because the solubility is low and difficulties are encountered in the measurements. Also, the solubility changes with temperature, i.e. it decreases with increasing temperature up to 100°C [31]. With the addition of electrolytes, the solubility product (298 K) of $Mg(OH)_2$ is reported to increase ($K_{sp} = 4.17 \times 10^{-10}$, 1.0 M $NaNO_3$ [32]) or decrease ($K_{sp} = 1.38 \times 10^{-12}$, 3.0 M $NaClO_4$ [33]). The solubility product of $Mg(OH)_2$ for ionic strength = 0 according to Ref. [31,34] is

$$K_{sp} = [Mg^{2+}][OH^-]^2 = 7.08 \times 10^{-12}. \quad (1)$$

The dissociation constant of NH_4OH [35] is

$$K = \frac{[NH_4^+][OH^-]}{[NH_4OH]} = 1.81 \times 10^{-5}. \quad (2)$$

Then, if the concentration of ammonium ion, $[NH_4^+]$, is kept high by the addition of NH_4NO_3 solution, the hydroxide ion concentration, $[OH^-]$, is low according to Eq. (2), which leads to yield a considerably high saturation concentration of Mg^{2+} in the solution added with NH_4OH. Higher concentration of Mg^{2+} ion should yield high concentation of Mg in the dried ADU precipitate but its relation with the y value in $Mg_yU_{1-y}O_{2+x}$ is to be determined experimentally since the volume of the solution held in the precipitate cannot be obtained by calculation. Another subject of this work is to fix the way to dry the precipitate for the formation of homogeneous solid mixture of Mg and U oxides.

3. Experimental

3.1. Materials

Uranyl nitrate hexahydrate, $UO_2(NO_3)_2 \cdot 6H_2O$, was purchased from Wako Pure Chemicals Industries. Its 105.5 g was dissolved into distilled water to the 1 l solution of 0.21 M uranyl nitrate. The solution was weakly acidified by adding 1 ml conc. HNO_3 beforehand in order to prevent the uranyl nitrate from hydrolysis.

Analytical grade NH_4NO_3, $Mg(NO_3)_2 \cdot 6H_2O$ and 25 wt% ammonia water were obtained from Wako Pure Chemicals Industries. To the 10 ml portions of the uranyl nitrate solution, NH_4NO_3 and $Mg(NO_3)_2 \cdot 6H_2O$ were dissolved. The amounts of NH_4NO_3 dissolved were 2.0, 3.0, 6.0 9.0 and 11.8 g, and those of $Mg(NO_3)_2 \cdot 6H_2O$ were 0.04, 0.2, 0.5, 0.8, 1.0, 3.0, 5.0, 7.0, 9.0, 11.0 and 13.0 g. The volume change of the solution by the addition of the solids was measured with a measuring cylinder.

3.2. Preparation of ADU containing Mg

The solution of uranyl nitrate, $Mg(NO_3)_2 \cdot 6H_2O$ and NH_4NO_3 was boiled for 5 min to remove CO_2. Ammonia water (1.0, 5.0, 10.0, 15.0, 20.0, 30.0, 40.0 and 50.0 ml each) was added to the solution with stirring, giving rise to a precipitate of ADU. The precipitate was filtrated while suction using the G4 glass filter (Sibata, 1GP16.1307–116). The obtained solid was dried in either air bath (ambient pressure, 120°C) or vacuum at room temperature.

3.3. Preparation of solid solution

The dried Mg–ADU precipitate was changed to the homogeneous mixture of MgU_3O_{10} and UO_3, as ascertained by the X-ray diffraction analysis, by heating at 500°C in air for a period longer than 24 h. The mixture solid of about 0.5 g was pressed into a pellet of 10 mm diameter in a one axial die with a pressure of 50 MPa, which was then heated to form the solid solution in a horizontal SiC tube furnace at 1250°C for 72 h. This reaction was carried out in a stream of CO_2/H_2 gas mixture by controlling the mixing ratio of CO_2/H_2 to give 10^{-10} Pa O_2 using mass-flow controllers (Kofloc, Type-3510 1/4SW-500SCCM and 1/4-10SCCM).

3.4. X-ray diffraction analysis

X-ray powder diffractometry was performed with a Rigaku RAD-IC diffractometer using $CuK\alpha_1$ ($\lambda = 1.54056$ Å) radiation (40 kV, 20 mA) monochromatized with curved pyrolytic graphite. The slit system was 1°–0.15 mm–1°–0.3 mm. Measurements were made in a 2θ range of 10–140° with a scanning rate of 1° min^{-1}. The cubic lattice parameter of the solid solution was calculated by least-squares method using the LCR2 program [36]. The precipitation of MgO phase from the solid solution phase was checked by step-scanning the X-ray intensities over the range $2\theta = 43 \pm 2°$, in which the strongest reflection of MgO is expected to appear, with 0.004° interval.

3.5. Determination of Mg

About 10 mg of the 500°C heated U oxide containing Mg, in which U is supposed to be in a hexavalent state, was precisely weighed out, and dissolved into 1 ml of 2 M HNO_3. The solution was then diluted to 10 ml by distilled water. The Mg concentration in this solution was determined by measuring the absorption at $\lambda = 285.2$ Å with a Seiko SAS-760 type atomic absorption analyzer. The hollow cathode lamp of Ca–Mg (L233 type) purchased from Hamamatsu Photonics was used. The standard solution of Mg used was a nitrate solution of 0.995 mg Mg ml^{-1} (20°C) obtained from Kanto Chemicals. The calibration curve was prepared by diluting the standard solution to the solutions of 2, 4, 6, 8, 10, 20, 50 and 100 ppm concentrations, but for the samples of which the Mg concentration exceeded 50 ppm, determination was made by diluting the sample solution to the 1/10 concentration. The error of the determination is estimated to be ±0.4 ppm Mg.

3.6. Determination of oxygen nonstoichiometry

The oxygen nonstoichiometry of solid solution, viz. the x value in $Mg_yU_{1-y}O_{2+x}$, was determined for the samples of known y value by means of Ce back-titration method [37,38]. 10–20 mg of the solid solution powder was weighed to an accuracy of ±10 μg and dissolved in 5 ml of Ce(IV) sulfate solution in 1.5 M H_2SO_4. Titration was carried out using Fe(II) ammonium sulfate solution in 1.5 M H_2SO_4 using ferroin indicator. The estimated standard deviation in the titrated x values by this method is ±0.005.

4. Results and discussion

4.1. Concentration of chemical species in solutions

The volume increase of the 0.21 M uranyl nitrate solution caused by the addition of NH_4NO_3 and $Mg(NO_3)_2 \cdot 6H_2O$ solids was measured for the solution of 10 ml initial volume in a measuring cylinder. Table 1 shows the mol concentrations $[NH_4^+]$, $[Mg^{2+}]$ and $[NH_4OH]$ obtained from the measured volume increase of the solution. The above concentrations are those estimated for the solutions after ADU was precipitated by the addition of ammonia water, where the additivity was assumed to hold for the volumes of the solution and ammonia water. The volume of ADU precipitate in the solution was not taken into account. It was found that the volume increase by the addition of NH_4NO_3 and $Mg(NO_3)_2 \cdot 6H_2O$ in Table 1 well follows the equation

$$\Delta V[\mathrm{ml}] = 0.64407 \cdot W(NH_4NO_3) + 0.61231 \cdot W(Mg(NO_3)_2 \cdot 6H_2O), \quad (3)$$

where $W(NH_4NO_3)$ and $W(Mg(NO_3)_2 \cdot 6H_2O)$ are the weights of NH_4NO_3 and $Mg(NO_3)_2 \cdot 6H_2O$ in g, respectively. Eq. (3) shows that there are no significant interactions causing anomalies in volume change between the NH_4^+ and Mg^{2+} ions.

The theoretical Mg^{2+} concentration of saturated solution can be obtained from Eqs. (1) and (2). These values were, however, not listed in Table 1 since the solubility product in Eq. (1) was not known as a function of concentration of the electrolytes although it was assumed to change with a factor larger than 10 [31,34]. The second reason is that the activity coefficients of the related chemical species were not known. However, a rough estimation for $[Mg^{2+}]_{sat}$, which stands for the saturated Mg^{2+} ion concentration, shows that $[Mg^{2+}]_{sat}$ is much higher than $[Mg^{2+}]$, which indicates the Mg^{2+} ion concentration in the solution, when the addition volume of NH_4OH is 1 ml. The latter is calculated from the added $Mg(NO_3)_2 \cdot 6H_2O$ amount. Meanwhile, $[Mg^{2+}]_{sat}$ becomes of the order of the same magnitude as $[Mg^{2+}]$ in the case of 5 ml addition of NH_4OH. When the addition volume is as large as >10 ml, $[Mg^{2+}]_{sat}$ is calculated as lower than $[Mg^{2+}]$. This result is estimated to be not changed by the NH_4NO_3 amount added.

4.2. Drying method of precipitate

It is required that the solid solutions are homogeneous with the Mg concentrations of several at.%. As the drying method of the filtrated ADU precipitate, two methods were first tested: (1) The precipitate in the glass filter was dried in situ in an air-bath of 120°C. (2) After the precipitate was transferred from the glass filter to a porcelain crucible, it was dried in the air-bath of 120°C. The materials dried in the crucible were found to be somewhat moist still after 72 h standing in the air-bath. The powder free from inhomogeneous dew-like precipitates was not obtained.

The above two methods are compared in Fig. 1 by plotting the at.% of Mg against the weight of $Mg(NO_3)_2 \cdot 6H_2O$ added. In Fig. 1, the weight of NH_4NO_3 was 11.8 g, and the volume of ammonia water added was 1 ml for both the drying methods. The figure shows that the Mg content in ADU for method (1) is much lower (by about a factor of 0.1) than that for method (2). This discrepancy was ascribed to the melting of $Mg(NO_3)_2 \cdot 6H_2O$ (mp = 89°C) in the ADU precipitate. The low Mg content in ADU dried in glass filter is thought to be because the $Mg(NO_3)_2 \cdot 6H_2O$ melt flowed down through the glass filter during warming the precipitate in air-bath. The homogeneity of Mg was good in the ADU dried in glass filter but not good in the ADU dried in crucible due to inhomogeneous solidification of the $Mg(NO_3)_2 \cdot 6H_2O$ melt. It was possible to dry the precipitate in the air-bath at temperatures lower than the melting point of $Mg(NO_3)_2 \cdot 6H_2O$. This experiment was, however, not carried out because too long heating time was supposed to be necessary to dry. Instead, the ADU precipitate was dried in a vacuum of rotary pump after it was transferred to the porcelain crucible. The remark of C,V(3h) (method (3)) in Table 1 means that the precipitate in crucible was vacuum dried for 3 h followed by heating at 120°C in air-bath at ambient pressure. The C,V(24h) process (method (4)) shows that the precipitate was dried by evaporation in vacuum for 24 h at room temperature. The loss of Mg could not occur for the C,V processes (methods (3) and (4)). The best result to yield homogeneous fine powder was obtained by method (4). The G and C marks in the remark of Table 1 indicate methods (1) and (2), respectively.

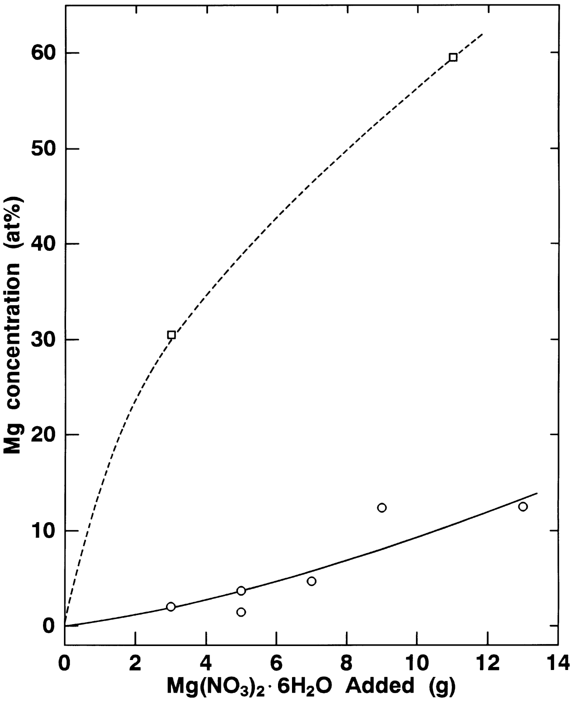

Fig. 1. Plot of Mg concentration vs. $Mg(NO_3)_2 \cdot 6H_2O$ weight showing the effect of drying method. ○, ——: Drying at 120°C in air in glass filter; □, - - -: Drying at 120°C in air in crucible; NH_4NO_3: 11.8 g; 25 wt% ammonia water: 1.0 ml.

4.3. Effect of ammonia water added

The addition of ammonia water is necessary to precipitate ADU from the uranyl nitrate weakly acidified solution. However, on addition of too much volume of ammonia water, there may be the case of precipitate formation of $Mg(OH)_2$, since the increase of $[NH_4OH]$ results in an increase in the OH^- concentration, $[OH^-]$, by Eq. (2), which lowers the saturation concentration of Mg according to Eq. (1).

To the 10.0 ml solution of 0.21 M uranyl nitrate in 0.015 M HNO_3, 11.8 g NH_4NO_3 and 1.0 g $Mg(NO_3)_2 \cdot 6H_2O$ were added. The volume of the solution became 18.23 ml (Table 1, No. 5–8). To this solution, 25 wt% ammonia solution was added. Fig. 2 shows the change of Mg concentration with the volume of ammonia water added. It is seen from the solid curve of this figure that the Mg concentration first rapidly increases with increasing volume of NH_4OH until ∼3 ml, but exceeding that volume the Mg concentration turns into a rapid decrease on further increase of the addition volume.

Table 1
Calculated concentrations of chemical species and measured Mg at.% in ADU as related with the drying methods

No.	NH_4NO_3 added (g)	$Mg(NO_3)_2 \cdot 6H_2O$ added (g)	Solution (ml)	NH_4OH added (ml)	$[NH_4^+]$ (M)	$[Mg^{2+}]$ (M)	$[NH_4OH]$ (M)	Mg in ADU (at.%)	Remark
1	0	0	10.0	5.0	2.9×10^{-1}	0	4.0	0.44	
2	11.8	0.2	17.74	1.0	8.1	4.2×10^{-1}	3.8×10^{-1}	4.83	C,V(3h)
3	11.8	0.5	17.96	1.0	8.0	1.0×10^{-1}	3.7×10^{-1}	10.3	C,V(3h)
4	11.8	0.8	18.14	1.0	7.9	1.6×10^{-1}	3.7×10^{-1}	14.1	C,V(3h)
5	11.8	1.0	18.23	1.0	7.9	2.0×10^{-1}	3.7×10^{-1}	17.1	C,V(3h)
6	11.8	1.0	18.23	5.0	6.5	1.7×10^{-1}	2.6	19.9	C,V(3h)
7	11.8	1.0	18.23	10.0	5.4	1.4×10^{-1}	4.5	14.5	C,V(3h)
8	11.8	1.0	18.23	20.0	4.0	1.0×10^{-1}	6.8	10.7	C,V(3h)
9	11.8	3.0	19.44	1.0	7.4	5.7×10^{-1}	3.5×10^{-1}	2.04	G
10	11.8	3.0	19.44	1.0	7.4	5.7×10^{-1}	3.5×10^{-1}	30.5	C
11	11.8	3.0	19.44	5.0	6.2	4.8×10^{-1}	2.5	3.12	G
12	11.8	3.0	19.44	10.0	5.2	4.0×10^{-1}	4.3	36.2	C
13	11.8	3.0	19.44	15.0	4.4	3.4×10^{-1}	5.6	2.26	G
14	11.8	3.0	19.44	20.0	3.9	3.0×10^{-1}	6.6	25.3	C
15	11.8	3.0	19.44	30.0	3.1	2.4×10^{-1}	8.0	20.3	C
16	11.8	3.0	19.44	40.0	2.6	2.0×10^{-1}	8.9	16.1	C
17	11.8	3.0	19.44	50.0	2.2	1.7×10^{-1}	9.5	11.1	G
18	11.8	5.0	20.64	1.0	7.0	9.0×10^{-1}	3.3×10^{-1}	1.48	G
19	11.8	5.0	20.64	1.0	7.0	9.0×10^{-1}	3.3×10^{-1}	3.70	G
20	11.8	7.0	21.9	1.0	6.6	1.2	3.1×10^{-1}	4.70	G
21	11.8	9.0	23.16	1.0	6.3	1.5	2.9×10^{-1}	12.4	G
22	11.8	11.0	24.3	1.0	6.0	1.7	2.8×10^{-1}	59.5	C
23	11.8	13.0	25.56	1.0	5.7	1.9	2.7×10^{-1}	12.5	G
24	0	1.0	10.6	5.0	2.8×10^{-1}	2.5×10^{-1}	3.9	66.0	C,V(24h)
25	3.0	1.0	12.56	5.0	2.4	2.2×10^{-1}	3.5	20.3	C,V(3h)
26	6.0	1.0	14.46	5.0	4.1	2.0×10^{-1}	3.1	18.7	C,V(3h)
27	9.0	1.0	16.44	5.0	5.5	1.8×10^{-1}	2.8	17.5	C,V(3h)
28	2.0	0.04	11.34	5.0	1.8	9.6×10^{-3}	3.7	1.13	C,V(24h)
29	2.0	0.2	11.4	5.0	1.8	4.8×10^{-2}	3.7	3.30	C,V(24h)
30	2.0	0.5	11.66	5.0	1.8	1.2×10^{-2}	3.7	8.07	C,V(24h)

In Fig. 3, the weight of NH_4NO_3 was the same as the experiment of Fig. 2 (i.e. 11.8 g), but the $Mg(NO_3)_2 \cdot 6H_2O$ amount was increased to 3.0 g. The shape of the solid curve of Fig. 3 is seen to be very similar to that of Fig. 2. The volume of 25 wt% ammonia water which gave the maximum Mg concentration in ADU was 3–4 ml. This volume is essentially the same as Fig. 2. Since the precipitate was dried by methods (3) and (2) for Figs. 2 and 3, respectively, there is no loss of Mg from ADU during drying, which enables us to discuss about the concentration of Mg in ADU. The maximum Mg concentrations are 21 and 39 at.% as shown by the solid curves of Figs. 2 and 3, respectively. This ratio 0.54 is roughly in line with the ratio 0.35 of the calculated Mg^{2+} ion concentrations in the aqueous solutions when 3 ml ammonia water was added, i.e. 1.84×10^{-1} and 5.21×10^{-1} M, for the experimental conditions of Figs. 2 and 3, respectively. Obviously, the amount of ammonia is insufficient in the region of the first steep increase of Mg concentration in Figs. 2 and 3. The decrease after attaining the maximum is explained by the decrease of $[Mg^{2+}]$ due to volume increase by the addition of excess ammonia water. The precipitate of $Mg(OH)_2$ does not seem to be formed in this region by the excess ammonia, since otherwise the Mg concentration would not straightforwardly decrease with increasing volume of ammonia water added. This experimental result does not match well with the calculated $[Mg^{2+}]_{sat}$ which is lower than $[Mg^{2+}]$ when the volume of ammonia water exceeds ~10 ml. This difference may be due to the high concentrations of electrolytes in the solution.

The dash–dotted curve in Fig. 2 depicts the change of the calculated Mg concentration in ADU with the volume of ammonia water added. This value was obtained by assuming the linearlity between the Mg concentration in ADU and $[Mg^{2+}]$ in aqueous solution. The proportionality constant was figured out by fitting the calculated Mg concentration to the observed one (19.9 at.%) at 5 ml ammonia water. The curve is in fairly good agreement with the observed solid curve of Fig. 2 up to 20 ml ammonia water, showing that the above assumption that the decrease of the Mg concentration is caused by the decrease of $[Mg^{2+}]$ due to the volume increase is basically correct. It is seen that $Mg(OH)_2$ does not precipitate still with 20 ml ammonia water.

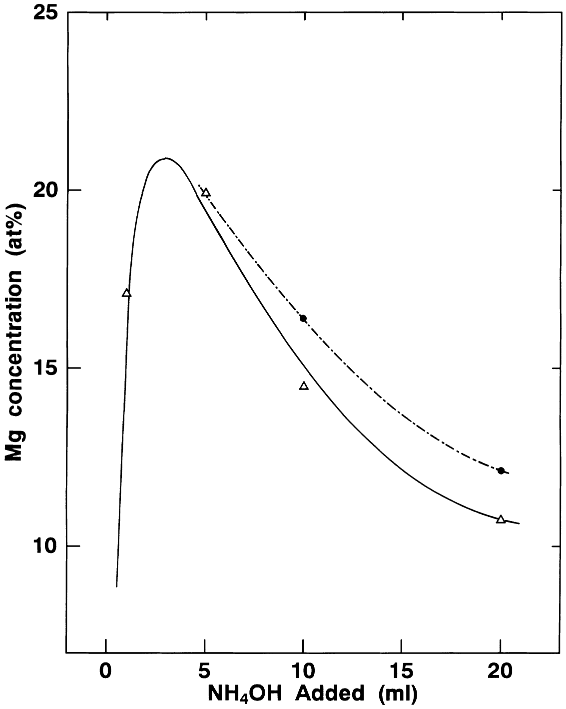

Fig. 2. Mg concentration (at.%) as a function of the volume of ammonia water added. △, ––: Observed curve; –·–·–: Calculated curve based on the assumption of proportionality between the Mg concentration in ADU and [Mg^{2+}] in solution normalized to the observed point at 5 ml ammonia water; NH_4NO_3: 11.8 g; $Mg(NO_3)_2 \cdot 6H_2O$: 1.0 g; Drying by method (3).

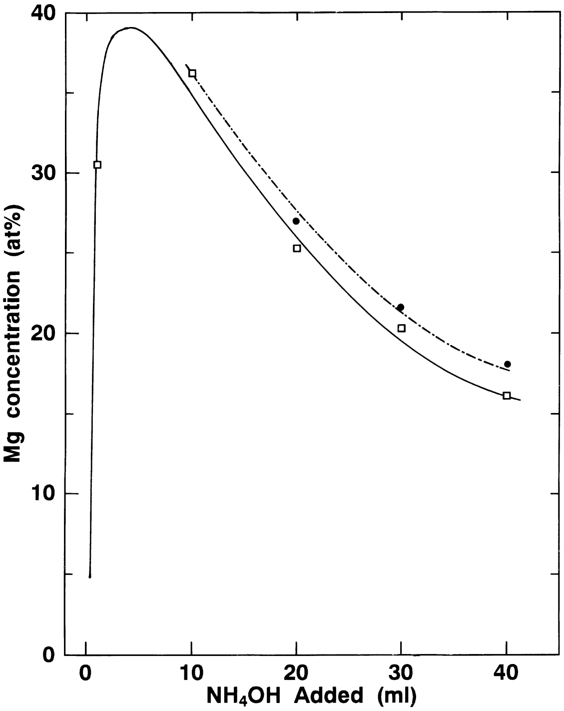

Fig. 3. Mg concentration (at.%) as a function of the volume of ammonia water added. □, ––: Observed curve; –·–·–: Calculated curve based on the assumption of proportionality between the Mg concentration in ADU and [Mg^{2+}] in solution normalized to the observed point at 10 ml ammonia water; NH_4NO_3: 11.8 g; $Mg(NO_3)_2 \cdot 6H_2O$: 3.0 g; Drying by method (2).

The dash–dotted curve in Fig. 3 was obtained in the same manner as Fig. 2 by fitting to the observed Mg concentration (36.2 at.%) at 10 ml ammonia water. Agreement of this curve with the observed curve (solid line) in Fig. 3 is rather better, which confirms the correctness of the above assumption. The precipitation of $Mg(OH)_2$ does not occur until 40 ml addition of ammonia water for 11.8 g NH_4NO_3 and 3.0 g $Mg(NO_3)_2 \cdot 6H_2O$. Figs. 2 and 3 show that the volume of ammonia water to be added for the present purpose is relatively small. The sedimentation rate of precipitate was high when the addition volume of ammonia water was sufficient (5 ml).

4.4. Effect of the $Mg(NO_3)_2 \cdot 6H_2O$ amount added

In order to have ADU containing Mg in an intended concentration, the quantitative relation between the Mg concentration in ADU and the added $Mg(NO_3)_2 \cdot 6H_2O$ amount should be known. Fig. 4 shows a plot for the solution containing 11.8 g NH_4NO_3 and 1 ml ammonia water. Even with this insufficient small volume of ammonia water, the Mg concentration increases with the amount of $Mg(NO_3)_2 \cdot 6H_2O$ showing a slight bend. The Mg concentration as high as 60 at.% was obtained with 11 g $Mg(NO_3)_2 \cdot 6H_2O$. The y value in $Mg_yU_{1-y}O_{2+x}$ is given by the equation $y = (\text{Mg at.\%})/100$.

Next, the relation was measured for a smaller amount of NH_4NO_3 and a larger volume of ammonia water, i.e. 2.0 g NH_4NO_3 and 5 ml of 25 wt% ammonia water. The weight of $Mg(NO_3)_2 \cdot 6H_2O$ was changed from 0.04 to 0.5 g. As shown in Fig. 5, the Mg concentration in ADU here increases linearly with increasing amount of $Mg(NO_3)_2 \cdot 6H_2O$ added. The Mg concentration attained 8.07 at.% at 0.5 g $Mg(NO_3)_2 \cdot 6H_2O$. As will be seen in the next section, the addition of 2 g NH_4NO_3 is the least sufficient amount to prevent the solution from producing $Mg(OH)_2$ precipitate when 5 ml of 25 wt% ammonia water is added.

4.5. Effect of the NH_4NO_3 amount added

If the concentration of ammonium ion, [NH_4^+], is high, [OH^-] becomes low according to Eq. (2), which leads to give a high [Mg^{2+}]$_{sat}$ by the relation of Eq. (1).

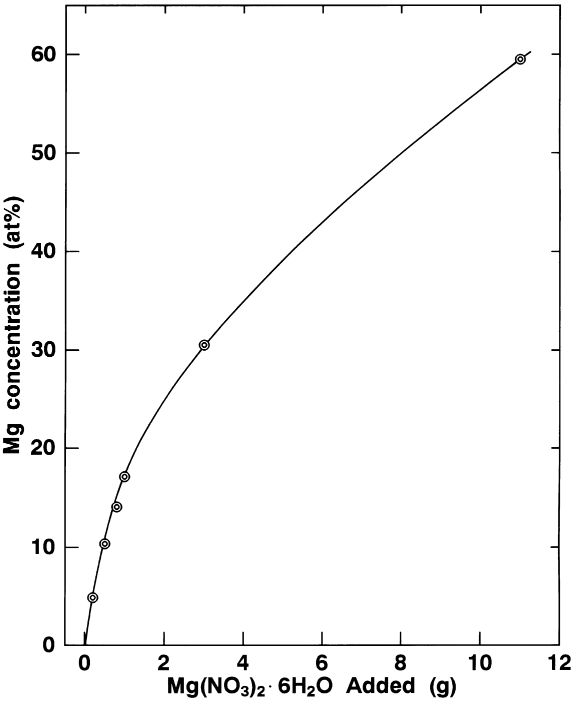

Fig. 4. Mg concentration (at.%) as a function of the $Mg(NO)_3)_2 \cdot 6H_2O$ amount added. NH_4NO_3: 11.8 g; 25 wt% ammonia water: 1.0 ml.

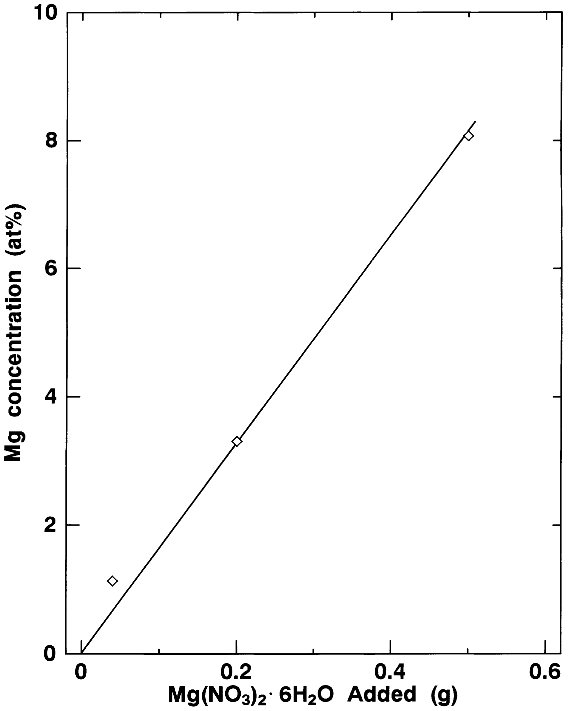

Fig. 5. Mg concentration (at.%) as a function of the $Mg(NO)_3)_2 \cdot 6H_2O$ amount added. NH_4NO_3: 2.0 g; 25 wt% ammonia water: 5.0 ml.

Fig. 6 shows the change of the Mg concentration in ADU as a function of the NH_4NO_3 weight added. In this experiment, the amount of $Mg(NO_3)_2 \cdot 6H_2O$ was 1.0 g and that of ammonia water 5.0 ml. It is seen from the figure that the Mg concentration is as high as 66 at.% if no NH_4NO_3 was added. This behavior is considered to show the formation of $Mg(OH)_2$ precipitate in ADU without addition of NH_4NO_3. The quality and homogeneity of the solid solution are thought to be lowered if the $Mg(OH)_2$ precipitate is contained in ADU, although quantitative study has not been made. The formation of the $Mg(OH)_2$ precipitate is also clearly undesirable since under such a condition the Mg concentration could not be controlled by the $Mg(NO_3)_2 \cdot 6H_2O$ amount added. Namely, the linear relation between the Mg concentration and the $Mg(NO_3)_2 \cdot 6H_2O$ weight would not hold.

The Mg concentration in Fig. 6 remains almost unchanged around 20 at.% when the added amount of NH_4NO_3 was larger than ~2 g, showing that the formation of the $Mg(OH)_2$ precipitate can be prevented with this amount for 5 ml of ammonia water and at least up to 1.0 g of $Mg(NO_3)_2 \cdot 6H_2O$. The y value of $Mg_yU_{1-y}O_{2+x}$ becomes 0.131 when 1.0 g $Mg(NO_3)_2 \cdot 6H_2O$ is added according to the linear relationship in Fig. 5.

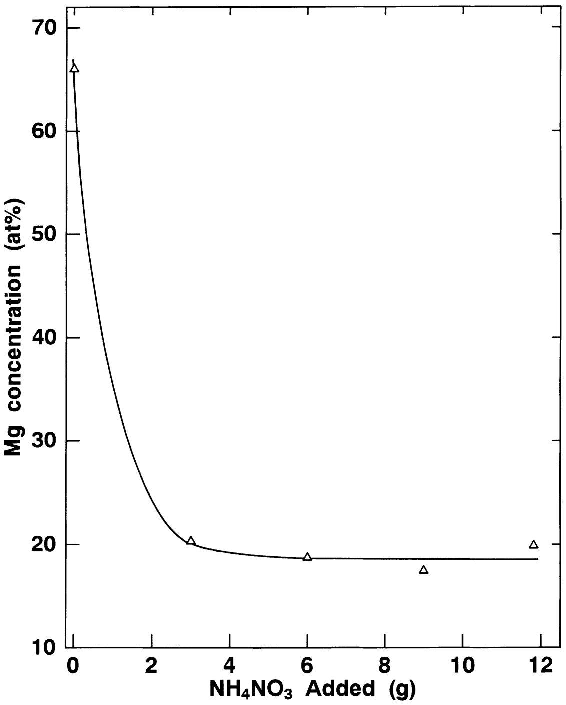

Fig. 6. Change of the Mg concentration with NH_4NO_3 amount added, showing the effect of NH_4^+ ion to prevent the $Mg(OH)_2$ precipitation. $Mg(NO_3)_2 \cdot 6H_2O$: 1.0 g; 25 wt% ammonia water: 5.0 ml.

Table 2
Lattice parameter and x and y values of solid solution $Mg_yU_{1-y}O_{2+x}$

No.	x value	y value	Uranium valency	Lattice parameter (Å)
28	0.011	0.0131	4.048	5.4522 ± 0.0002
29	−0.005	0.0330	4.058	5.4478 ± 0.0005
30	−0.061	0.0807	4.043	5.4496 ± 0.0004

4.6. Preparation of $Mg_yU_{1-y}O_{2+x}$ solid solution

The dried ADU precipitate containing Mg was heated in air at 500°C for >24 h. X-ray powder diffraction analysis of the products revealed that they consist of MgU_3O_{10} [39] and β-UO_3 [40] without the migration of MgO. However, for No. 24 sample (Table 1), in which $Mg(OH)_2$ is supposed to have precipitated because NH_4NO_3 was not added, MgU_3O_{10} was not present and the strongest X-ray diffraction peak of MgO was observed at $2\theta = 42.9°$ instead.

The preparation of solid solution was carried out for the sample Nos. 28, 29 and 30 of which the y values in $Mg_yU_{1-y}O_{2+x}$ become 0.0131, 0.0330 and 0.0807, respectively, if the solid solutions are formed completely. The mixture powder was pelletized, and then heated in a stream of CO_2/H_2 mixed gas at 1250°C for 72 h. The mixing ratio of CO_2/H_2 was 450 of which the oxygen pressure was 10^{-10} Pa at 1250°C. After the reaction, the system was evacuated followed by cooling on standing. The X-ray diffraction patterns of the products showed the formation of the fluorite-type $Mg_yU_{1-y}O_{2+x}$ solid solutions in a single phase. The diffraction peak of MgO was not detected in the step-scanning data over $2\theta = 41$–$45°$. The oxygen non-stoichiometry (x value) and the lattice parameter of the solid solutions obtained are given in Table 2. It can be concluded from the above results that the present mixing method well yields satisfactorily homogeneous magnesium solid solutions, $Mg_yU_{1-y}O_{2+x}$.

5. Conclusions

A wet precipitate method was studied to form ADU which contains Mg homogeneously. The method consists of addition of ammonia water to the solution in which uranyl nitrate, NH_4NO_3 and $Mg(NO_3)_2 \cdot 6H_2O$ are dissolved. In the ADU precipitate taken by filtration, a small volume of Mg nitrate solution is held. The precipitate was subsequently dried. The relevant condition was obtained for 10 ml solution of 0.21 M uranyl nitrate in 0.014 M HNO_3.

1. The increase of the volume of the uranyl nitrate solution by the addition of NH_4NO_3 and $Mg(NO_3)_2 \cdot 6H_2O$ was measured. The inequality relations between $[Mg^{2+}]_{sat}$ and $[Mg^{2+}]$ were calculated.
2. In situ drying of ADU in glass filter in air-bath of 120°C (method (1)) resulted in formation of solids with much lower Mg concentrations, which is due to melting of $Mg(NO_3)_2 \cdot 6H_2O$ at 89°C. The best result to yield homogeneous fine powder was obtained by method (4) which comprises drying of ADU in a rotary-pump vacuum for 24 h at room temperature.
3. The maximum Mg concentration in ADU was obtained at 3–4 ml addition of 25 wt% ammonia water, which is the least sufficient volume, for 11.8 g NH_4NO_3 and 1–3 g $Mg(NO_3)_2 \cdot 6H_2O$. Further addition of ammonia water caused a decrease of Mg concentration in ADU on account of dilution of Mg concentration in the solution. Precipitation of $Mg(OH)_2$ did not occur until 40 ml addition of ammonia water.
4. The concentration of Mg in ADU was proportional to the weight of $Mg(NO_3)_2 \cdot 6H_2O$ added for the solution with 2 g NH_4NO_3 and 5 ml of 25 wt% ammonia water. With 0.5 g $Mg(NO_3)_2 \cdot 6H_2O$, the Mg concentration in ADU was 8.07 at.% ($y = 0.0807$).
5. The addition of about 2 g NH_4NO_3 was found to prevent effectively the solution from precipitating $Mg(OH)_2$ at 5 ml of 25 wt% ammonia water up to 1 g $Mg(NO_3)_2 \cdot 6H_2O$.
6. Homogeneous $Mg_yU_{1-y}O_{2+x}$ solid solutions with $y = 0.0131$, 0.0330 and 0.0807 were obtained in a single phase by heating the present ADU containing Mg.

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