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Phase equilibria in the ternary URu_3–URh_3–UPd_3 system

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Abstract

In order to clarify the behavior of platinum metal fission products in the nitride fuel, the reactions of $UN+3(Ru_x+Rh_y+Pd_{1-x-y})$ $[0 \le (x,y) \le 1]$ in the pseudo-ternary and quaternary systems at 1673 K under vacuum ($\sim 10^{-2}$ Pa) were examined. The reactions of $UN+3(Ru_x+Rh_y)(x+y=1)$ and the reactions of $UN+3(Rh_y+Pd_{1-y})$ $(0.25 \le y \le 1)$ produced a Cu_3Au type compound. However two Cu_3Au type compounds were obtained from the reactions of $UN+3(Ru_x+Pd_{1-x})$ $(0.25 \le X \le 0.75)$. In the reactions of $UN+3(Ru_x+Rh_y+Pd_{1-x-y})$ with a lower Pd ratio, a Cu_3Au type compound was formed, but the increase in Pd ratio, $(x+y \le 0.33)$, caused the formation of two Cu_3Au type compounds. Although UPd_3 is crystallized to a hexagonal $TiNi_3$ type structure, the Cu_3Au type UPd_3 phase was formed in these reactions. © 1998 Elsevier Science S.A.

Keywords: Nitride fuel; Fission product; Platinum metals; Intermetallic compound

1. Introduction

Uranium mononitride (UN) has potential as an advanced fast breeder reactor fuel [1]. Its many favorable properties such as high melting point, high fissile material density and high thermal conductivity would lead to possible economy in the fuel cycle. If the nitride is used as the nuclear fuel in the future, it is necessary to know the behavior of the fission products because it may heavily influence the physical and chemical properties of the fuel.

In the nitride fuel, it is considered that most platinum metal fission products react with UN and form the UMe_3 type intermetallic compounds where Me are Ru, Rh and Pd [2]. Although several studies on the reaction behavior of uranium metal and Me have been made [3,4], the reaction behavior between UN and Me has been scarcely reported. Therefore, in order to understand the behavior of Me in the nitride fuel, a series of reactions involving UN and Me have been investigated.

In the pseudo-binary system at temperatures from 873 K to 1673 K and at nitrogen pressures from vacuum ($\sim 10^{-2}$ Pa) to 1 atm, the reactions between UN and Ru and between UN and Rh with the molar ratio of 1:3 produced URu_3 (Cu_3Au type) and URh_3 (Cu_3Au type) as intermetallic compounds, respectively. In the reaction between UN and Pd, UPd_4 phase (U:18~20 at.%, Cu_3Au type) was formed in addition to UPd_3 ($TiNi_3$ type) [5].

In the present study, to understand the reaction behavior of UN and platinum metal fission products in the pseudo-ternary and quaternary systems, the reactions of $UN+3(Ru_x+Rh_y+Pd_{1-x-y})$, $[0 \le (x,y) \le 1]$ were examined. In order to form the UMe_3 type intermetallic compounds as easy as possible, the experimental conditions, temperature and N_2 pressure, were determined to be 1673 K and vacuum ($\sim 10^{-2}$ Pa).

2. Experimental

UN powder was prepared from the metal by a hydride–dehydride–nitride procedure according to the work of Evans and Davies [6]. Ru and Pd powder with purities of more than 99.9% were obtained from Nakarai Tesque Co. Ltd. The molar ratio of UN and total Me was fixed at 1:3 because the UMe_3 type intermetallic compound, except for UPd_4, was detected in a previous study of pseudo-binary systems [5]. The starting materials containing UN, Ru, Rh and Pd with the desired molar ratios were pressed into pellets and heated in an electric furnace at 1673 K under vacuum ($\sim 10^{-2}$ Pa). The reaction products were identified by X-ray diffraction method and electron probe micro-

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Table 1
Compositions of the starting materials

Run No.	Reaction	x	y
①	$UN+3(Ru_x+Rh_y)$	0.25	0.75
②		0.50	0.50
③		0.75	0.25
④	$UN+3(Rh_y+Pd_{1-y})$	–	0.25
⑤		–	0.50
⑥		–	0.75
⑦	$UN+3(Ru_x+Pd_{1-x})$	0.25	–
⑧		0.50	–
⑨		0.75	–
⑩	$UN+3(Ru_x+Rh_y+Pd_{1-x-y})$	0.33	0.33
⑪		0.66	0.17
⑫		0.17	0.66
⑬		0.17	0.17

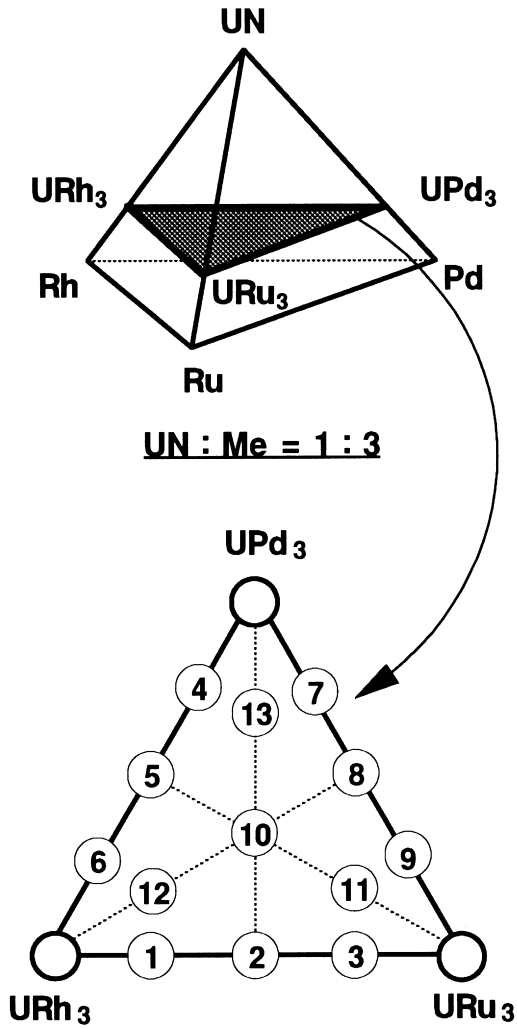

Fig. 1. Compositions of the starting materials.

analysis (EPMA). The composition of the starting materials is shown in Table 1 and Fig. 1.

3. Results and discussions

In the reactions between UN and (Ru, Rh) [$UN+3(Ru_x+Rh_y)$, $(x+y=1,\ x=0.25,\ 0.50,\ 0.75)$] at 1673 K under vacuum, Cu_3Au type compounds were observed as the reaction products. From the SEM and EPMA for these reaction products, U, Ru and Rh coexisted homogeneously. Therefore, it is considered that a continuous series of solid solution was formed between URu_3 (Cu_3Au type) and URh_3 (Cu_3Au type) in the reactions of UN and (Ru, Rh).

Though UPd_3 crystallizes to a hexagonal $TiNi_3$ type structure [7], the reactions between UN and (Rh, Pd) in any molar ratios produced a Cu_3Au type compound. From the SEM and EPMA for these products, it was observed that U, Rh and Pd coexist homogeneously. So it is also considered that U, Rh and Pd formed one phase Cu_3Au type intermetallic compound.

In the X-ray diffraction patterns for the reaction products between UN and (Ru, Pd) [$UN+3(Ru_x+Pd_{1-x})$, $(x=0.25,\ 0.50,\ 0.75)$] at 1673 K under vacuum shown in Fig. 2, two Cu_3Au type compounds are observed. SEM and EPMA for the product of the reaction of $UN+3(Ru_{0.5}+Pd_{0.5})$ are shown in Fig. 3. This figure indicates the two distinctive areas, in one area U and Ru coexist and

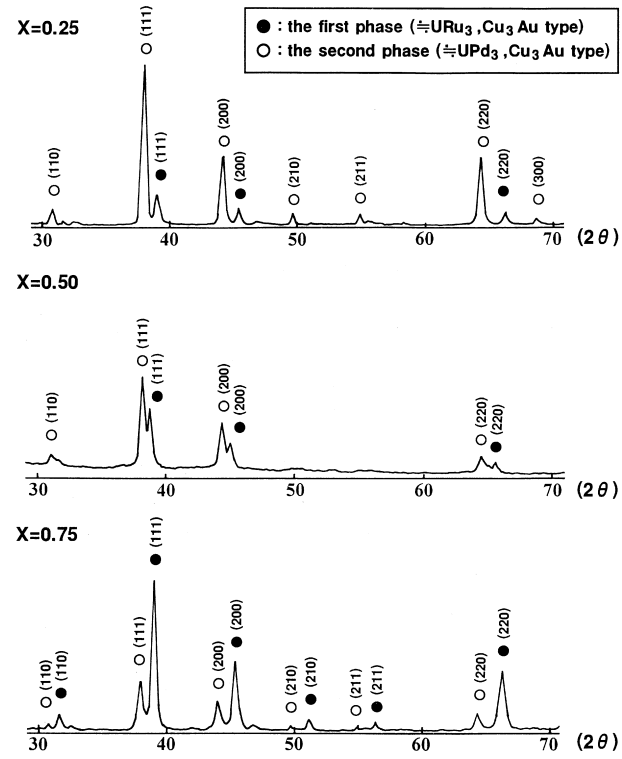

Fig. 2. X-ray diffraction patterns for the reaction products of $UN+3(Ru_x+Pd_{1-x})$, $(x=0.25,\ 0.50,\ 0.75)$ at 1673 K under vacuum.

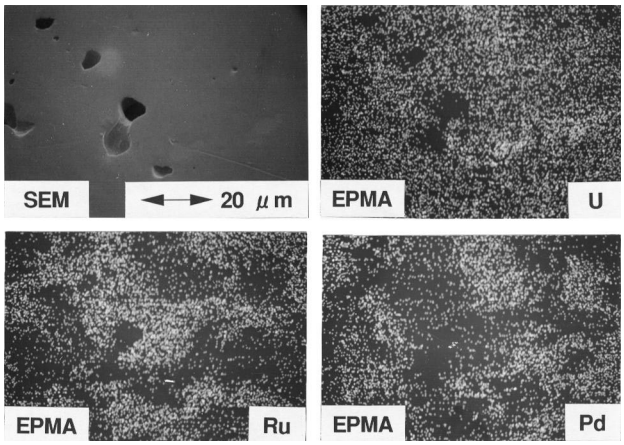

Fig. 3. The representation of SEM and EPMA for the reaction product of $UN+3(Ru_{0.5}+Pd_{0.5})$ at 1673 K under vacuum.

in the other area U and Pd coexist. In consequence, it is assumed that the two Cu_3Au type compounds obtained from the reactions of $UN+3(Ru_x+Pd_{1-x})$ are considered to be the intermetallic compound between U and Ru and between U and Pd, respectively.

The compositions of the starting mixtures, the observed phases and the lattice parameter of the produced intermetallic compounds are summarized in Table 2. It is seen that the lattice parameters of both the first phase, which has the smaller lattice constant, and the second phase, which has the larger lattice constant, are nearly constant. Therefore it is suggested that the compositions of the first and the second phase are constant irrespective of the compositions of the starting materials.

The first phase may be the URu_3 phase because the lattice parameter of this phase ($\fallingdotseq$3.98 Å) nearly equals that of pure URu_3. So the molar ratio of U and Pd in the second phase is assumed to be close to 1:3. Therefore it can be considered that the URu_3 phase (Cu_3Au type) dissolving a small amount of Pd and the UPd_3 phase (Cu_3Au type, $a\fallingdotseq$4.1 Å) dissolving a small amount of Ru were obtained in the reactions between UN and (Ru, Pd) at 1673 K under vacuum. Although the structure of UPd_3 is hexagonal $TiNi_3$ type [7], the Cu_3Au type UPd_3 phase

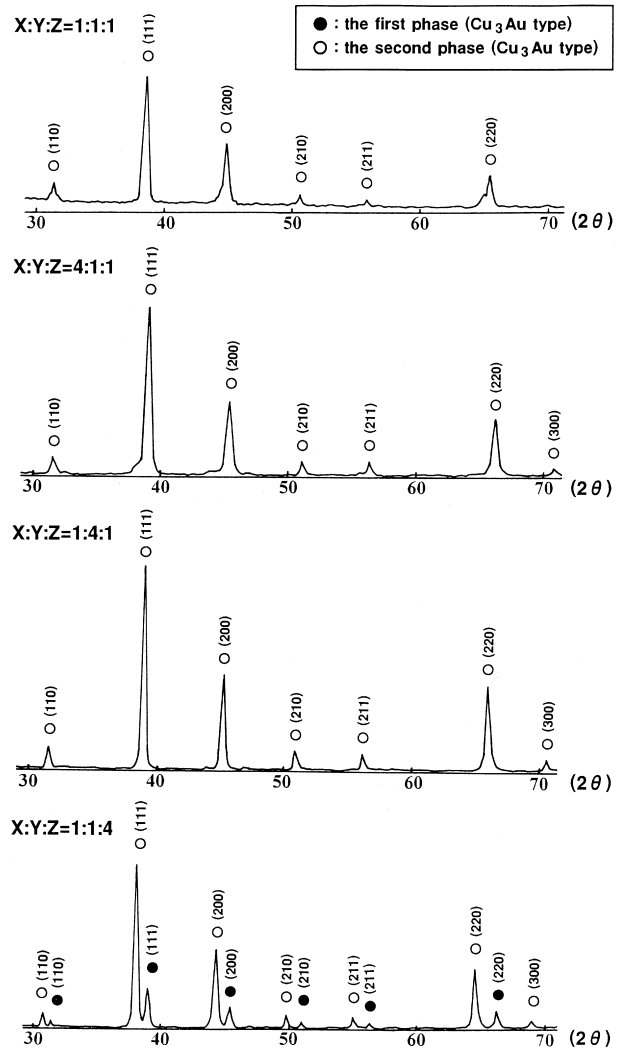

Fig. 4. X-ray diffraction patterns for the reaction products of $UN+3(Ru_x+Rh_y+Pd_{1-x-y})$ at 1673 K under vacuum.

may have been obtained in this study. The UPd_3 phase which crystallizes to a Cu_3Au type structure with dissolving a small amount of Ru has not been reported until now. The formation of only a Cu_3Au type UPd_3 phase, its

Table 2
The observed phases and the lattice parameters for the reaction products of UN and (Ru, Pd) at 1673 K under vacuum

Run No.	(UN:Me=1:3) Ru:Pd	Lattice parameters (Å)		Observed phases of the reaction products
(UPd_3)	0:1	($a_0=5.757$ $c_0=9.621$ [7])		$TiNi_3$ type
(UPd_4 phase) (U:18~20 at.%)	0:1	($a_0=4.06$~4.07 [5])		Cu_3Au type
		First phase	Second phase	
⑦	1:3	$a_0=3.98$	$a_0=4.09$	
⑧	1:1	–	$a_0=4.09$	Cu_3Au type
⑨	3:1	$a_0=3.98$	$a_0=4.08$	
(URu_3)	1:0	($a_0=3.980$ [7])		Cu_3Au type

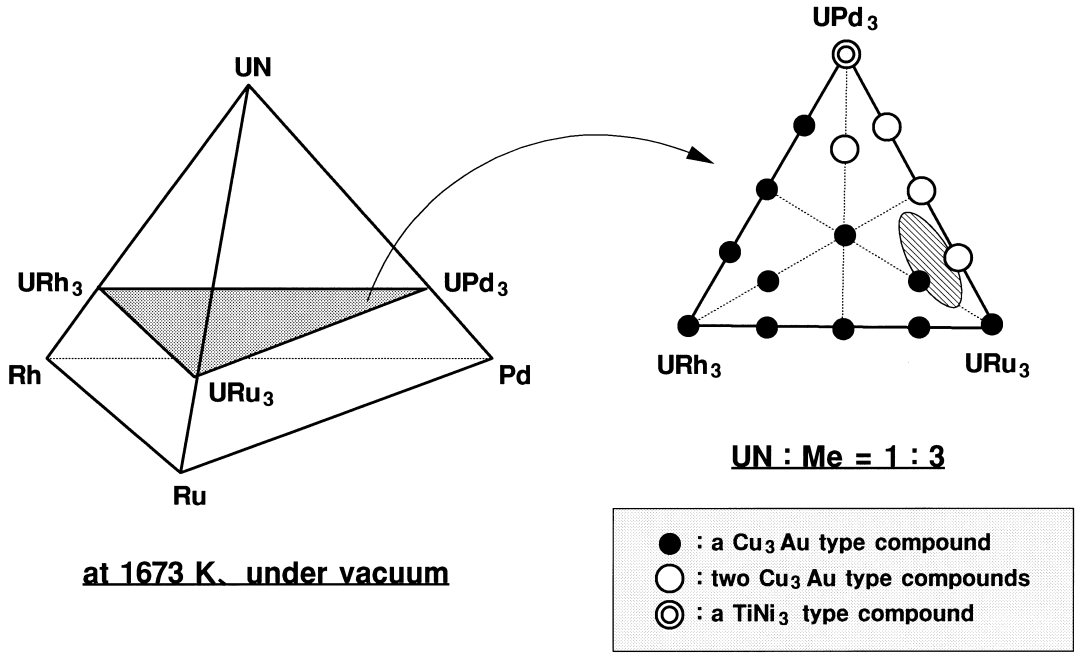

Fig. 5. The results of the reactions of UN+3(Ru, Rh, Pd) at 1673 K under vacuum.

composition and its transformation behavior will be discussed soon.

The X-ray diffraction patterns for the products of the reactions between UN and (Ru, Rh, Pd) [UN+3 ($Ru_x+Rh_y+Pd_{1-x-y}$), $(x,y)=(\frac{1}{3},\frac{1}{3})$, $(\frac{2}{3},\frac{1}{6})$, $(\frac{1}{6},\frac{2}{3})$, $(\frac{1}{6},\frac{1}{6})$] at 1673 K under vacuum are shown in Fig. 4. A Cu_3Au type compound is observed when the Pd content is less than 0.66, but two Cu_3Au type compounds are observed in the case of the Pd content more than 0.66. From the SEM and EPMA, it is observed that the reaction products consist of two coexisting areas, one is the U, Ru and Rh region and the other is the U and Pd region. So it is considered that the Cu_3Au type $U(Ru,Rh)_3$ phase dissolving a small amount of Pd and the Cu_3Au type UPd_3 phase dissolving a small amount of Ru and Rh were obtained in the reactions of $UN+3(Ru_x+Rh_y+Pd_{1-x-y})$ when the Pd ratio was more than 0.66 ($x+y\leq\frac{1}{3}$).

The results of the X-ray diffraction and EPMA analyses for all reaction products are summarized in Fig. 5. The shaded area in this figure shows the general chemical composition of UMe_3 type intermetallic compounds in the actual reactor fuel [8].

4. Conclusions

The reactions of $UN+3(Ru_x+Rh_y+Pd_{1-x-y})$, $[0\leq(x,y)\leq 1]$ in the pseudo-ternary and quaternary systems at 1673 K under vacuum ($\sim 10^{-2}$ Pa) were carried out. The products were identified by X-ray diffraction and EPMA.

From the reactions between UN and (Ru, Rh) ($x+y=1$) and between UN and (Rh, Pd) ($x=0$, $0.25\leq y\leq 1$), a Cu_3Au type compound was produced. However two Cu_3Au type compounds were obtained in the reactions between UN and (Ru, Pd) ($0.25\leq X\leq 0.75$, $y=0$). In the reactions between UN and (Ru, Rh, Pd) with Pd ratio less than 0.66 ($x+y>\frac{1}{3}$), a Cu_3Au type compound was formed, but the increase in Pd ratio, ($x+y\leq\frac{1}{3}$), resulted in the formation of two Cu_3Au type compounds. Although the structure of UPd_3 is a hexagonal $TiNi_3$ type, it was found that the Cu_3Au type UPd_3 phase with a slight amount of Ru or Rh was obtained in the reactions between UN and (Ru, Pd) at any Pd ratio and between UN and (Ru, Rh, Pd) at a greater Pd ratio (≥ 0.66).

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