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Reactions of uranium nitride with platinum-family metals

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Abstract

The reaction behavior of uranium nitrides with Ru, Rh, Pd at temperatures from 873 to 1673 K at nitrogen pressures from vacuum ($\sim 10^{-2}$ Pa) to 1 atm was examined by X-ray diffraction method and SEM, EDXA analysis. The reactions between UN and Ru and between UN and Rh with the molar ratio of 1:3 produced URu_3 and URh_3 as intermetallic compounds, respectively. In the reaction between UN and Pd, an unidentified product was formed in addition to UPd_3. The pure unidentified compound was obtained when the mixtures of UPd_3 and Pd containing U from 18 to 20 at.% were heated at 1273 K in vacuum. Therefore it can be concluded that the UPd_4 phase with Cu_3Au type structure is formed in addition to UPd_3 during the reaction of UN with Pd. © 1997 Elsevier Science B.V.

1. Introduction

Uranium mononitride (UN) is a potential advanced reactor fuel because of its many desirable properties, e.g., high melting point, high fuel density, and high thermal conductivity in comparison with uranium dioxide. In order to utilize UN as the nuclear fuel, it is necessary to know the behavior of the fission products during the irradiation because it may give large influences on physical and chemical properties of the fuel.

The platinum-family metal fission products have high fission yields, and are reactive and form solid solutions and intermetallic compounds with other fission products, fuel and cladding components. In the oxide fuel, platinum-family metals form mainly intermetallic compounds with Mo or Tc as the white metallic inclusion. However, in the nitride fuel, platinum-family metals react with UN and form intermetallic compounds of the type UMe_3 (where Me = Ru, Rh, Pd) in accordance with the following equations [1]:

$$UN + 3Me \rightarrow UMe_3 + \tfrac{1}{2}N_2, \quad (1)$$

$$3UN + 3Me \rightarrow UMe_3 + U_2N_3, \quad (2)$$

where Eq. (1) takes place in the hot central region of the fuel ($T = 1800$ K, $PN_2 = 10^{-2}$ atm), whereas Eq. (2) occurs in the colder outer part of the fuel ($T = 1200$ K, $PN_2 = 10^{-2}$ atm). Such intermetallic compounds may melt in the fuel and react with cladding materials [2].

Several studies on the reaction behavior of uranium metal and platinum-family metals, e.g., on the Gibbs free energy of formation or other thermodynamics data, have been made [3–6]. But the reaction behavior between UN and platinum-family metals has been scarcely reported. In the present study, the reactions of UN with Ru, Rh or Pd at several different nitrogen pressures and temperatures were carried out and the products were identified by X-ray diffraction and electron probe microanalysis (EPMA).

2. Experimental

UN was supplied by Mitsubishi Material. In the X-ray diffraction pattern of UN, the trace of UO_2 was observed. Ru, Rh and Pd powder with the purity more than 99.9% were obtained from Nakarai Tesque. The starting materials containing UN and Me with the desired molar ratio were pressed into pellets at 600 kg/cm^2 and heated in an electric furnace at temperatures from 873 to 1673 K under the nitrogen pressures from vacuum ($\sim 10^{-2}$ Pa) to 1 atm.

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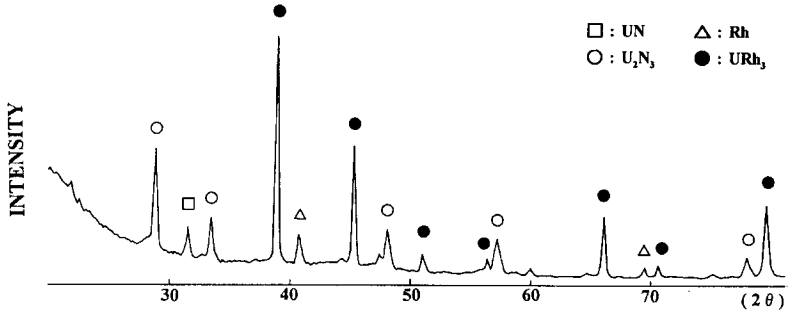

Fig. 1. X-ray diffraction pattern of the product in run No. 1-6.

The nitrogen pressure except for vacuum was controlled by Baratron type 122A supplied by MKS Japan.

The reaction products were identified by X-ray diffraction. The X-ray diffraction was performed at room temperature with Cu-Kα radiation on a Rigaku Rad r-A diffractometer equipped with a curved graphite monochromator.

The distribution of elements in the reaction products was investigated by EPMA using Topkon MINI-SEM 100 and Horiba EMAX-8000 units.

3. Results and discussion

3.1. The reaction behavior between UN and Ru and between UN and Rh

The experimental conditions and the results of a series of reactions between UN and Rh with the molar ratio of 1:3 are shown in Table 1. The X-ray diffraction pattern for the product of Run No. 1-6 is shown in Fig. 1. In this figure, it is seen that URh_3 is formed, but the peaks of UN, Rh and U_2N_3 are also observed. SEM (scanning electron microscope) and EDXA for this product shown in Fig. 2 exhibit three distinct areas. In one area U and Rh coexist, in one area only Rh exists, and in the other area only U exists. This corresponds to the results from the X-ray diffraction pattern.

The results of the X-ray diffraction and EDXA analyses for the reaction products obtained from UN and Ru and UN and Rh with the molar ratio of 1:3 are summarized in

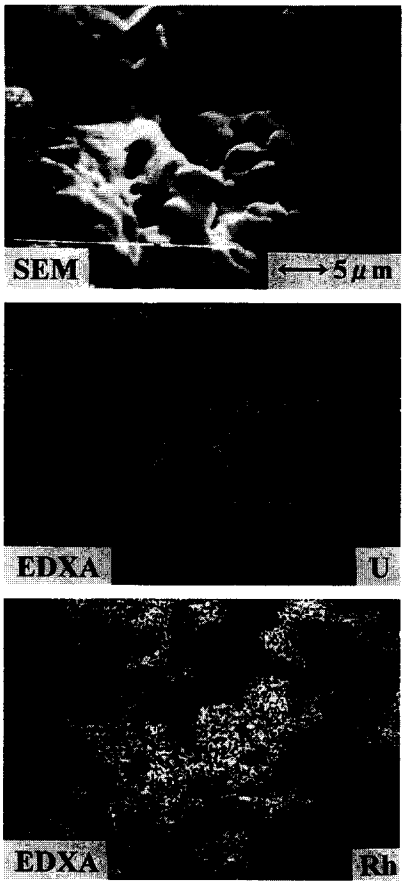

Fig. 2. The representation of SEM and EDXA for the product in run No. 1-6.

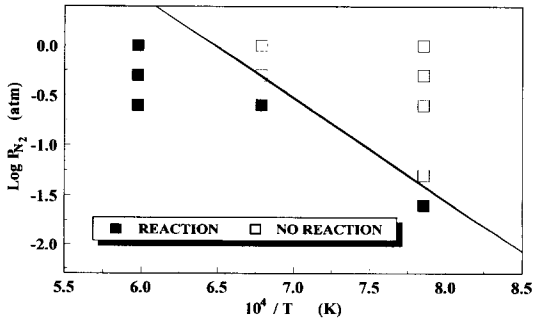

Fig. 3. Effect of nitrogen pressure on URu_3 formation as a function of temperature.

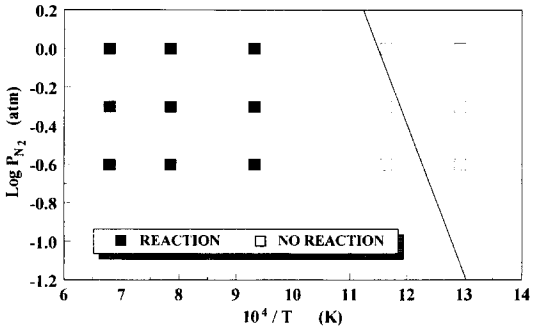

Fig. 4. Effect of nitrogen pressure on URh_3 formation as a function of temperature.

Figs. 3 and 4, respectively, with the equilibrium curves for the reactions [7]

$$U_2N_3 + 6Ru \rightarrow 2URu_3 + \tfrac{3}{2}N_2,$$

$$U_2N_3 + 6Rh \rightarrow 2URh_3 + \tfrac{3}{2}N_2.$$

In these figures, the closed square shows the formation and the open square shows the absence of URu_3 or URh_3 in the product. In the region below the equilibrium curve URu_3 or URh_3 is stable. Obviously URu_3 and URh_3 are formed in the thermodynamically stable region, although

Table 1
Experimental conditions and identification of the products of the reactions between UN and Rh

Run No.	Pressure (atm)	Temperature (K)	Products		Residues	
1-1	vacuum	873			UN	Rh
1-2	vacuum	1073	URh_3		UN	Rh
1-3	vacuum	1273	URh_3		UN	Rh
1-4	0.25	873			UN	Rh
1-5	0.25	1073	URh_3	U_2N_3	UN	Rh
1-6	0.25	1273	URh_3	U_2N_3	UN	Rh
1-7	0.25	1473	URh_3	U_2N_3	UN	Rh
1-8	0.5	873			UN	Rh
1-9	0.5	1073	URh_3	U_2N_3		Rh
1-10	0.5	1273	URh_3	U_2N_3		Rh
1-11	0.5	1473	URh_3	U_2N_3		Rh
1-12	N_2-flow	873		U_2N_3		Rh
1-13	N_2-flow	1073	URh_3	U_2N_3		Rh
1-14	N_2-flow	1273	URh_3	U_2N_3		Rh
1-15	N_2-flow	1473	URh_3	U_2N_3		Rh

URh_3 was not produced below 1073 K. This is because the reaction rate of UN and Rh is very low at low temperatures. The intermetallic compounds except for the UMe_3

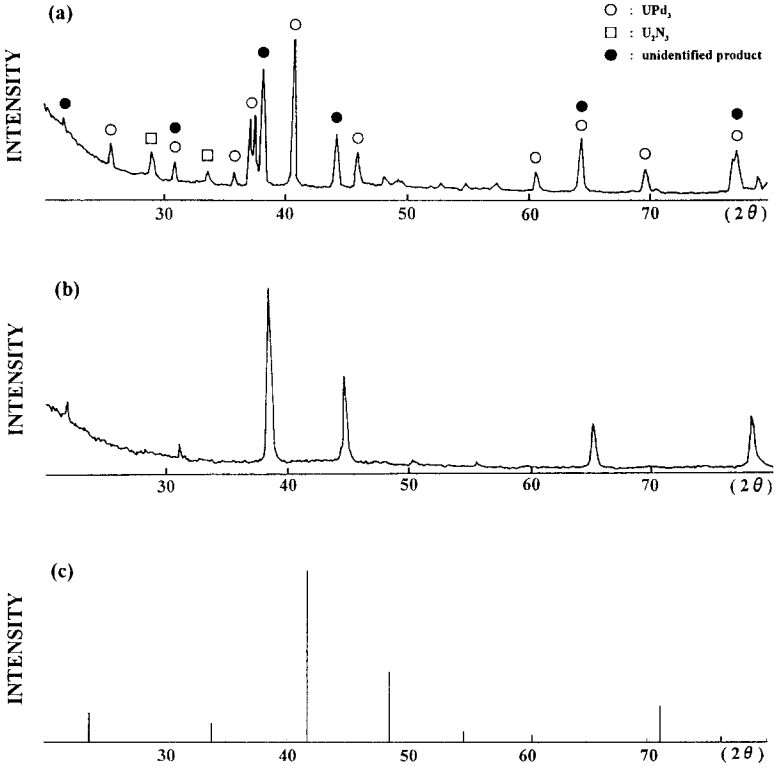

Fig. 5. (a) X-ray diffraction pattern for the product in run No. 2-14. (b) X-ray diffraction pattern for the product in run No. 3-7. (c) Simulated X-ray diffraction pattern for Cu_3Au.

Table 2
Experimental conditions and identification of the products of the reactions between UN and Pd

Run No.	Pressure (atm)	Temperature (K)	Products			Residues
2-1	vacuum	1173	UPd_3	U_2N_3	?	UN
2-2	vacuum	1273	UPd_3		?	
2-3	vacuum	1673	UPd_3			
2-4	0.25	1173		U_2N_3	?	
2-5	0.25	1273	UPd_3	U_2N_3	?	
2-6	0.25	1673	UPd_3			
2-7	0.5	1173		U_2N_3	?	
2-8	0.5	1273	UPd_3	U_2N_3	?	
2-9	0.5	1673	UPd_3	U_2N_3		
2-10	0.75	1173		U_2N_3	?	
2-11	0.75	1273	UPd_3	U_2N_3	?	
2-12	0.75	1673	UPd_3	U_2N_3		
2-13	N_2-flow	1173		U_2N_3	?	
2-14	N_2-flow	1273	UPd_3	U_2N_3	?	
2-15	N_2-flow	1673	UPd_3	U_2N_3	?	

?: unidentified product.

type compounds could not be detected in the reactions between UN and Ru and between UN and Rh.

3.2. The reaction behavior between UN and Pd

The experimental conditions and the results of a series of reactions between UN and Pd with the molar ratio of 1:3 are shown in Table 2. A compound which cannot be identified from the X-ray diffraction data was observed in addition to UPd_3. Fig. 5(a) shows the X-ray diffraction pattern of the product in Run No. 2-14. The pattern consists of the peaks of UPd_3, U_2N_3 and the unidentified compound. Since the starting mixture contained UN and Pd with the molar ratio of 1:3 and the products contained U_2N_3 in addition to UPd_3, this unidentified product is considered to be the intermetallic compound between U and Pd, which have a higher Pd content than UPd_3.

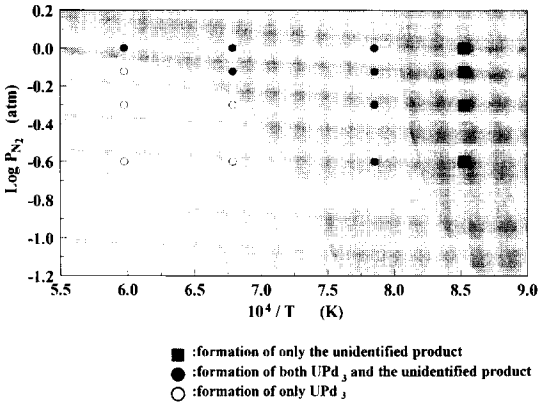

Fig. 6. Effect of nitrogen pressure on UPd_3 formation as a function of temperature.

The results of X-ray diffraction and EDXA analyses for the reaction products obtained from UN and Pd with the molar ratio of 1:3 are summarized in Fig. 6. In this figure, the open circle shows the formation of only UPd_3, the closed circle shows the formation of both UPd_3 and unidentified product, and the closed square shows the formation of only the unidentified product. It is found that the unidentified product forms at lower temperature and at higher nitrogen pressure than UPd_3.

3.3. Determination of the unidentified product

According to the phase diagram for the U–Pd system [8] (Fig. 7), the compounds which have the higher Pd contents than UPd_3 are UPd_4 and UPd_8. ASTM cards

Table 3
Experimental conditions and reactions for formation of the unidentified product

Run No.	Starting materials		Mixture ratio	Temperature (K)	Pressure (atm)	Result
3-1	UN	Pd	1:4	1073	vacuum	$\times_1$
3-2	UN	Pd	1:5	1073	vacuum	$\times_1$
3-3	UN	Pd	2:11	1073	vacuum	$\times_1$
3-4	UN	Pd	2:17	1073	vacuum	$\times_1$
3-5	UPd_3	Pd	1:4 (20 at.% U)	1273	vacuum	○
3-6	UPd_3	Pd	1:4.3 (19 at.% U)	1273	vacuum	○
3-7	UPd_3	Pd	1:4.6 (18 at.% U)	1273	vacuum	○
3-8	UPd_3	Pd	1:5 (16.7 at.% U)	1273	vacuum	$\times_2$
3-9	UPd_3	Pd	2:11 (15.4 at.% U)	1273	vacuum	$\times_2$

$\times_1$: X-ray diffraction pattern is too broad for identification.
$\times_2$: no formation of the unidentified product.
○: formation of only the unidentified product.

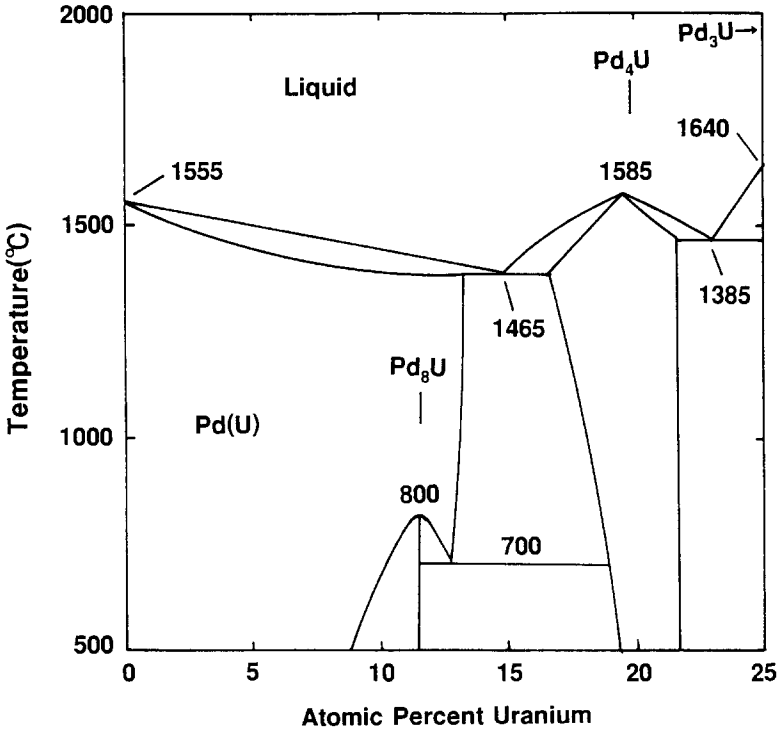

Fig. 7. The partial phase diagram for the U–Pd system [8].

concerning U–Pd intermetallic compounds do not exist. The detailed structural analysis data of UPd_3 ($TiNi_3$ type structure) is reported [9], but that of UPd_4 (Cu_3Au type structure) and UPd_8 (tetragonal) are not reported. It is scarcely reported that the intermetallic compounds except for the UMe_3 type compound were formed in the reactions of UN with platinum-family metals.

In order to determine the composition of the unidentified product, first, the reaction experiments between UN and Pd with several molar ratios larger than 3 were carried out. But the X-ray diffraction peaks of the reaction products were very broad, so that the identifications could not be carried out. Next, the reactions between pure UPd_3, which was produced from the reaction of UN with Pd, and Pd with several different molar ratios were carried out. The results are summarized in Table 3 with the experimental conditions. The pure unidentified compound was obtained when the mixture of UPd_3 and Pd containing 18 to 20 at.% U were heated at 1273 K in vacuum. The X-ray diffraction pattern of the product in Run No. 3-7 is shown in Fig. 5(b). Fig. 5(c) shows the peak positions of Cu_3Au. From this figure it is suggested that the unidentified compound has a Cu_3Au type structure with the lattice constant of 0.4060 nm (for $UPd_{4.6}$). Therefore it can be concluded that the $UPd_{4.0-4.6}$ phase with Cu_3Au type structure is formed in addition to UPd_3 during the reaction of UN with Pd. The structure refinement of the $UPd_{4.0-4.6}$ phase with Cu_3Au type structure is now in progress.

4. Conclusion

The experiments for the reactions between UN and Ru, Rh or Pd at several different nitrogen pressures and temperatures were carried out. The products were identified by X-ray diffraction and EPMA.

From the reactions between UN and Ru and between UN and Rh with the molar ratio of 1:3, URu_3 and URh_3 were produced as the intermetallic compounds, respectively. These compounds were formed in the region of temperature and nitrogen pressure where both the compounds are thermodynamically stable, although URh_3 was not produced below 1027 K.

In the reaction between UN and Pd, a compound which cannot be identified from the X-ray diffraction data was formed in addition to UPd_3. The pure unidentified compound which has the Cu_3Au type structure was obtained when the mixtures of UPd_3 and Pd containing U from 18 to 20 at.% were heated at 1273 K in vacuum. Thus in the reaction of UN and Pd, the UPd_4 phase with the Cu_3Au type structure is formed in addition to UPd_3.

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