

## RESEARCH AND DEVELOPMENT OF NITRIDE FUEL CYCLE FOR TRU BURNING

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The present status of the research and development of nitride fuel cycle for burning transuranium elements in actinide burner reactors and fast reactors at JAERI is described, especially focusing on the progress in the recent two years. The research and development cover fuel fabrication technology, property measurements such as thermal conductivity, basic irradiation tests at Japan Materials Testing Reactors(JMTR), electrorefining of actinide nitrides in fused salts, and the evaluation of mass balance in the reprocessing process of nitride fuel.

## 1. Introduction

Actinide nitrides provide advantageous thermal properties such as high thermal conductivity and high melting temperature. By applying the cold fuel concept[1] to fuel design for the transmutation of minor actinides (Np, Am and Cm), it would become possible to realize lower fuel temperature and hence lower fission gas release. Therefore, thinner cladding material might be acceptable and neutron spectrum could be harder. Furthermore, the mutual miscibility of actinide mononitrides might also lead to the fuel design with high concentrations of transuranium elements (TRUs). Considering the characteristics of nitride fuel, the actinide burner reactor (ABR) concept with a nitride fuel cycle has been proposed from Japan Atomic Energy Research Institute (JAERI) [2]. The research and development on nitride fuel cycle carried out at JAERI include fabrication technologies, property measurements, irradiation tests, and electrorefining of TRU-bearing nitride fuel. In addition to the above experimental studies, the mass balance in the pyroprocess has been evaluated. In the present report the progress of the studies on the nitride fuel cycle after the previous meeting[3] is mainly described.

## 2. Fuel Fabrication

### 2.1 Fabrication of nitride fuel particles by sol-gel method

The fabrication technology of nitride particle fuel by a sol-gel method has been investigated[3]. Minor actinides separated from the high-level waste (HLW) as nitrates will be converted to the solid particles by a sol-gel technique with a high yield. The gel particle is formed as a mixture of the actinide oxides and carbon, which is converted to mononitride by carbothermic reduction in a nitrogen atmosphere. The particles of uranium mononitride, UN, have been fabricated in order to study the fabrication process.

The feed solution with a C/U ratio of 2.75 was prepared by mixing uranium nitrate solution, carbon powder, hexamethylenetetramine (HMTA) and urea. The HMTA decomposes to form ammonia on heating to about 360K. The liquid droplets then turn into gel particles. The gel particles were washed, dried and calcined at 753K. The oxide with carbon was converted to nitride by first heating to 1,773K in N<sub>2</sub>. Further heating at 1,673K in N<sub>2</sub>-8%H<sub>2</sub> promoted the reaction of UO<sub>2</sub> with carbon through HCN and the removal of the residual carbon. Photo. 1 shows the UN particles thus produced. High purity UN particles with 660 ppm oxygen and 30 ppm carbon have been fabricated. Further efforts are being made:

- (1) Controlling the particle density.
- (2) Fabricating the mixed nitride of uranium and rare earth elements. The latter are substitutes for minor actinide.

### 2.2 Fabrication of nitride fuel pellets

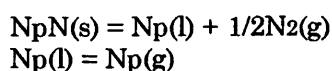
Pellets-type uranium-plutonium mixed nitride, (U,Pu)N, has been fabricated by a conventional route with carbothermic reduction of the dioxides with graphite, followed by ball-milling, compacting and sintering[4,5]. The carbothermic reduction is carried out at about 1,920K in H<sub>2</sub>-8%N<sub>2</sub> mixed gas flowing for about 36 ks.

For irradiation tests, the thermally stable pellets were fabricated by introducing relatively large pores in dense fuel matrix by use of pore former[5] so that pellet density could be kept about 85 %TD. Fine nitride powder was used to obtain dense matrix because of its poor sintering characteristics. Sintering was performed at about 2,000K for 18 ks in an Ar-8%H<sub>2</sub> atmosphere followed by the heat treatment at 1,730K in N<sub>2</sub>-8%H<sub>2</sub> mixed gas stream. The microstructure of the pellet is shown in Photo. 2, where black circles were pores introduced by pore former.

### 3. Fuel Property Measurements

The lattice parameters of the quasi-binary systems of plutonium mononitride, PuN, with UN and neptunium mononitride, NpN, were determined by X-ray diffraction analysis of the solid solutions. It is found that the NpN-PuN system shows completely mutual solubility over the whole range of compositions, similarly to the UN-PuN systems[6]. It is also indicated that its lattice parameter deviates positively from the Vegard's law, especially in the PuN-rich compositions as well as that of the system of UN-PuN. The deviation from the Vegard's law could be explained by the behavior of 5f electron.

Knudsen-effusion mass-spectrometric experiments of NpN and the solid solutions of NpN and PuN were carried out. It was reported from the preliminary experiments of NpN that NpN showed the congruent evaporation[3], but further studies have led to the conclusion that the NpN might be considered to decompose into liquid neptunium and nitrogen gas as follows;



The standard free energy of formation of NpN estimated from the data can be represented by the following equation[7];

$$\Delta G_f = -295,870 + 91T(\text{J/mol}).$$

With regard to the vaporization behavior of the solid solutions of NpN and PuN, Np(g) and Pu(g) were detected as predominant gas species. The temperature dependence of the partial pressures of Np(g) suggested the precipitation of liquid neptunium. On the other hand, the temperature dependence of the pressures of Pu(g) was rather complicated; at higher temperatures, it showed a similar behavior with PuN, but, at lower temperatures, the precipitation of liquid plutonium might be suggested.

The thermal diffusivities of actinide nitrides have been measured by use of a laser-flash method for estimating the thermal conductivities. The results on the thermal conductivities of UN, PuN, NpN and the solid solutions of UN-PuN were reported in earlier papers[8,9]. It is confirmed from the estimated values that the thermal conductivity of actinide mononitrides decreases with the atomic number of heavy metals as shown in Fig. 1. The thermal conductivities of the solid solutions of NpN and PuN were also determined. The solid solutions have a similar temperature dependence with NpN and PuN and show intermediate values between those of NpN and PuN.

The details of the properties of the solid solutions of NpN and PuN will be presented at this meeting[10].

### 4. Irradiation Behavior

Four encapsulated fuel pins of uranium-plutonium mixed nitride, (U<sub>0.8</sub>Pu<sub>0.2</sub>)N, were irradiated at JMTR up to the maximum burn-up of 5.5%FIMA at maximum heating rates of 650 - 730 W/cm as shown in Fig. 2. Thermal stable nitride pellets were fabricated for the tests as described above. The typical characteristics of fuel pins are shown in Table 1. No pin failure was observed in all the cases. The preliminary results of FP gas release from the nitride fuel are plotted in Fig. 3 as a function of burn-up, together with those of mixed carbide fuel irradiated in JMTR and Japan Research Reactor-2 (JRR-2). It is obvious that nitride fuel shows very low fission gas release; 2~3 % at the burn-ups of 4~5%FIMA because of its advantageous thermal characteristics and also the stabilization of fuel matrix by introducing the thermal stable pellets. Furthermore, it is confirmed that the maximum diameter increase rate of the fuel pins was about 1 %/%FIMA or less and the fission gas retained in fuel matrix does not significantly accelerate gas swelling of nitride fuel, at least up to the burn-up of 5.5%FIMA.

At present, two pins of mixed nitride fuel are under irradiation in the experimental fast reactor 「JOYO」 for a target burn-up of 4.5%FIMA as a joint research with JAERI and Power Reactor and Nuclear Fuel Development Cooperation (PNC).

## 5. Reprocessing Technology

### 5.1 Estimation of process and mass balance evaluation

The process of the molten-salt electrorefining of nitride fuel is similar to that of metal fuel: nitride fuel is anodically dissolved and the actinide metals are deposited on the dual cathodes[11], which consists of a solid cathode for the recovery of U and a liquid-Cd cathode for that of TRUs. Simulation calculations for nitride FBR fuel were made with use of the PALEO code to determine the amounts of actinides recovered in the electrorefiner and to estimate decontamination factors of fission products. The PALEO code, which is similar to the TRAIL code[12], calculates electrochemical behavior for Pu or U using diffusion layer model. In this calculation, the basic data such as standard potentials of actinides and lanthanides were taken from Ref. 13, and rare earth elements were represented by Ce which is one of the most difficult elements to be separated from actinides. It was found from preliminary calculation that the Ce concentration in the salt should be lower than 4.0wt% to keep the decontamination factor of about 5.

Equilibrium concentrations of main elements in LiCl-KCl eutectic melt were set to be 7.0wt% for Pu, 4.0wt% for U, 0.19wt% for minor actinides(Am) and 4.0wt% for rare earth(Ce) so that the Pu concentration in the output actinides from the electrorefining process might be almost same as that in the input actinides. The anode and cathode potentials were controlled to be -0.50V and -1.4V versus Ag/0.1wt%AgCl during electrorefining. As a result of the simulation calculations, the time dependent concentration of each element in the salt is shown in Fig.4. At the first stage, Pu, Ce, Am and then U are well resolved, and U is deposited on the solid cathode. After exchanging the cathodes, Pu, U, Ce and Am are deposited on the liquid Cd cathode. The process time is about 7 hours for the first stage, and about 2.5 hours for the second stage.

In order to keep the rare earth concentration in salt around 4.0wt%, some amount of the salt(6.7% of the salt) have to be removed at each batch from the electrorefining vessel. The removed salt first goes through a stripping step with Cd-Li, and then an extraction step with Cd-U. The process calculation was made using the distribution coefficients(wt% in salt/wt% in Cd)[14]; 1 for U, 2 for Pu, 4 for minor actinides, 40 for rare earths, and 1,000 for alkali and halogen. Considering the Pu recovery rate and the rare earth concentration in Pu, the values of 1 for U distribution coefficient in the stripping process and 3 for Cd/salt ratio in extraction process were selected. The stripping and extraction steps remove almost all the actinide from the salt to Cd and leave about 72% of the rare earth in the spent salt. Actinides recovered in the Cd solution are returned to the electrorefiner.

Table 2 summarizes the mass flow in the electrorefining and salt treatment processes. The annual processing capacity is set to be 44 ton-HMeq(heavy metal equivalent) which corresponds to the amount of spent fuels from 4GWe nitride FBR. Average burnup of the discharged fuels is 100GWD/ton for core fuels and 12 GWD/ton for blanket fuels. About 220kg-HMeq per day are processed when the annual working day is assumed to be 200 days. Without considering the process loss, 99.45% of U and 99.95% of Pu can be recovered after adding those from the salt process.

### 5.2 Electrolysis of actinide nitrides

Anodic dissolution of UN in the eutectic melts of LiCl and KCl has been studied to provide a basis for the feasibility study of the electrorefining of irradiated nitride fuels[13]. The threshold potential of the anodic dissolution of UN was observed as shown in Fig. 5, where the working electrode was first cathodically polarized to -2.40 V and then potential was raised from the rest potential, about -1.6 V, to -0.2 V. It was consistently explained with the thermochemical

database of pure substances. The anodic dissolution of UN as  $U^{3+}$  into LiCl-KCl begins at the standard electrode potential of  $E: = -0.82$  V referring to the equilibrium  $Ag/Ag^+$ . It is considered that the threshold potential is determined by the formation of solid  $UCl_3$  on UN. At present the possibility of direct nitriding of actinides in molten Cd-alloys is investigated.

Laboratory-scale electrorefiners for handling NpN and PuN have been installed in gloveboxes of  $5\text{ m}^3$  in which purified argon gas is circulated at a rate of about  $50\text{m}^3/\text{hr}$  and the concentrations of oxygen and water impurities are kept less than 1 ppm. The photograph of the argon gas atmosphere gloveboxes is shown in Photo. 3. The experiments are planned to start in 1996.

## 6. Summary

The present status of the research and development of nitride fuel cycle for TRU burning at JAERI is described. The fabrication technology of nitride fuel particles by a sol-gel method has been investigated and UN particles with high purity have been successfully fabricated, beside that pellet-type mixed nitride fuel by a conventional route. The properties of NpN-PuN solid solutions such as lattice parameter, thermal conductivity and evaporation behavior were determined. From the irradiation tests of mixed nitride fuel pins at JMTR, it is confirmed that nitride pellets shows very low FP gas release as expected. The pyroprocess for nitride fuel was estimated and the mass balance in the process was described.

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Table 1 Typical characteristics of nitride fuel pins irradiated at JMTR

<b>Fuel pin</b>		
Pin length	(mm)	250
Fuel length	(mm)	100
Outer diameter	(mm)	9.40
Cladding material		20% CWSUS316/Ferritic SUS
Cladding thickness	(mm)	0.51
Inter diameter	(mm)	8.38
Smear density	(%TD)	80
<b>Fuel pellet</b>		
Material		(U,Pu)N
Pu/(U+Pu)		0.20
Pellet diameter	(mm)	8.18 - 8.23
Pellet density	(%TD)	83 - 86
Pellet/cladding diameter gap	(mm)	0.15 - 0.20
Bonding material		He

Table 2 Mass flow in the electrorefining and salt treatment process

(1GWe x 4 FBRs equivalent) (kg/day)

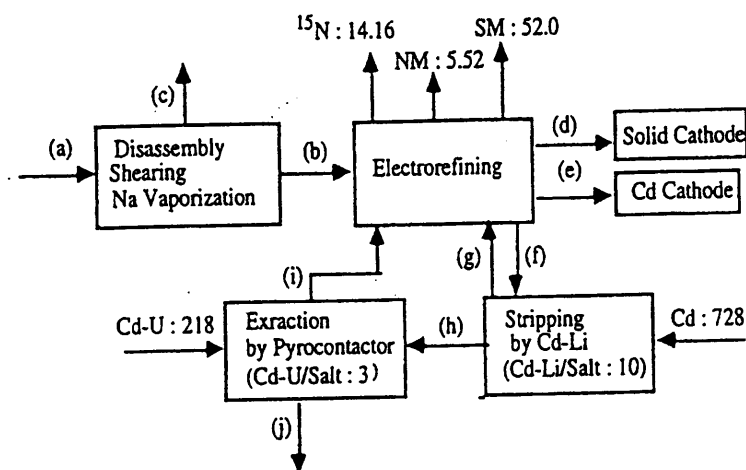
Element	(a)	(b)	(c)	(d)	(e)
U	200.40	200.40		180.58	22.71
Pu	22.72	22.72			22.71
MA	0.88	0.88			0.88
ALM	1.32	1.32			
RE	2.61	2.61			0.52
NM	5.52	5.52			
HL	0.14	0.14			
<sup>15</sup> N <sub>2</sub>	14.16	14.16			
VFP	1.48		1.48		
Na	16.88		16.88		
SM	800.00	52.00	748.00		

Element	(f)	(g)	(h)	(i)	(j)
U	2.91	2.65	0.26	3.15	1.49
Pu	5.10	4.25	0.85	0.835	0.015
MA	0.138	0.099	0.039	0.038	0.001
ALM	1.32	0.01	1.31		1.31
RE	2.91	0.58	2.33	0.24	2.09
HL	0.14		0.14		0.14

MA : Minor Actinide      RE : Rare Earth      NM : Noble Metal      HL : Halogen  
 ALM : Alkali              VFP : Vaporous FP      SM : Structural Material

(a) - (j) : See bellow





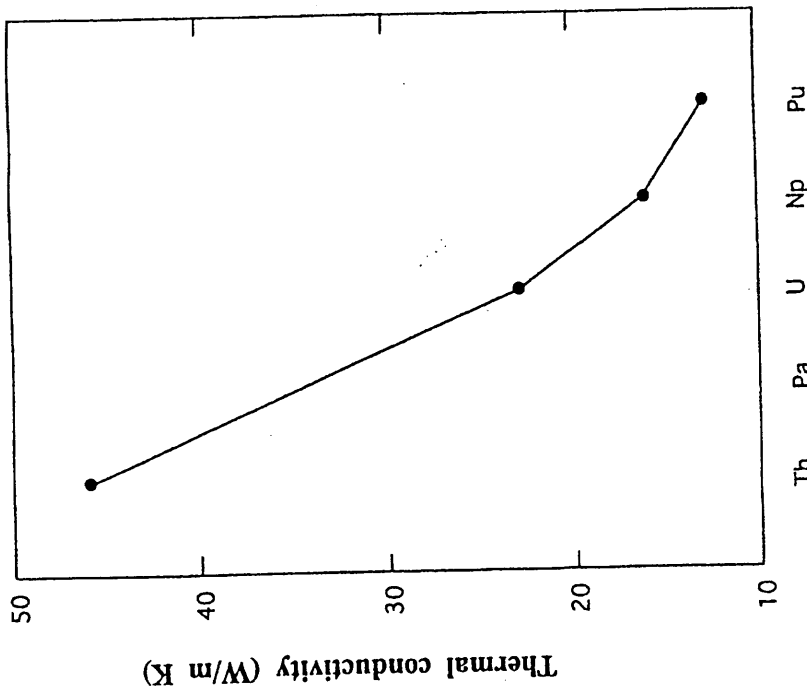


Fig. 1 Thermal conductivity of actinide mononitrides

Test No.	Reactor	No. of pins	Dia. (mm)	Linear power (kW/m)	Burnup (%FIMA)	'87	'89	'91	'93	'95	'97	'99
1	JMTR	2	9.4	65	4.1	Irradiation						PIE
2	JMTR	2	9.4	73	5.5	Irradiation						PIE
3	JOYO*	2	8.5	(80)	(4.5)	Irradiation						PIE

\* Under collaboration research program with PNC — Irradiation — PIE

Fig. 2 Irradiation program of nitride fuel

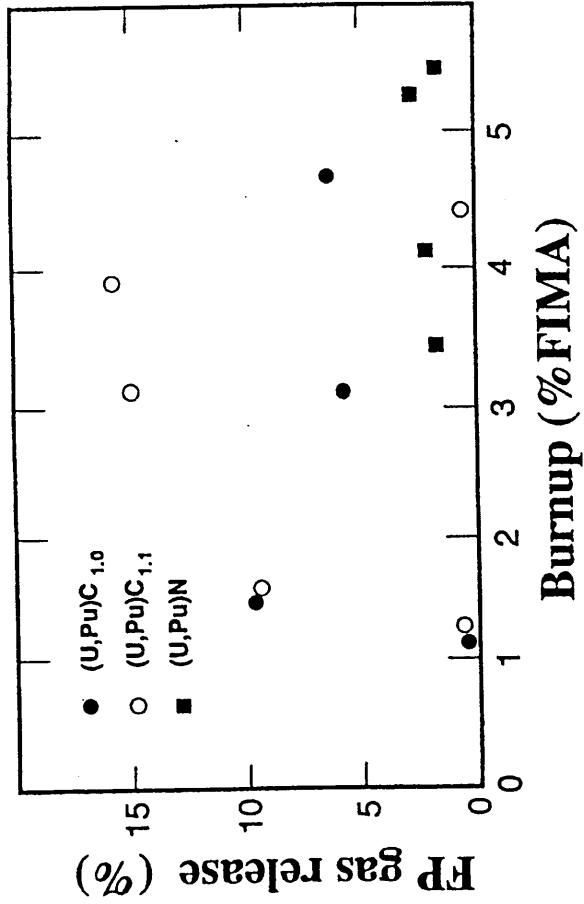


Fig. 3 FP gas release from carbide and nitride fuels irradiated in JRR-2 and JMTR

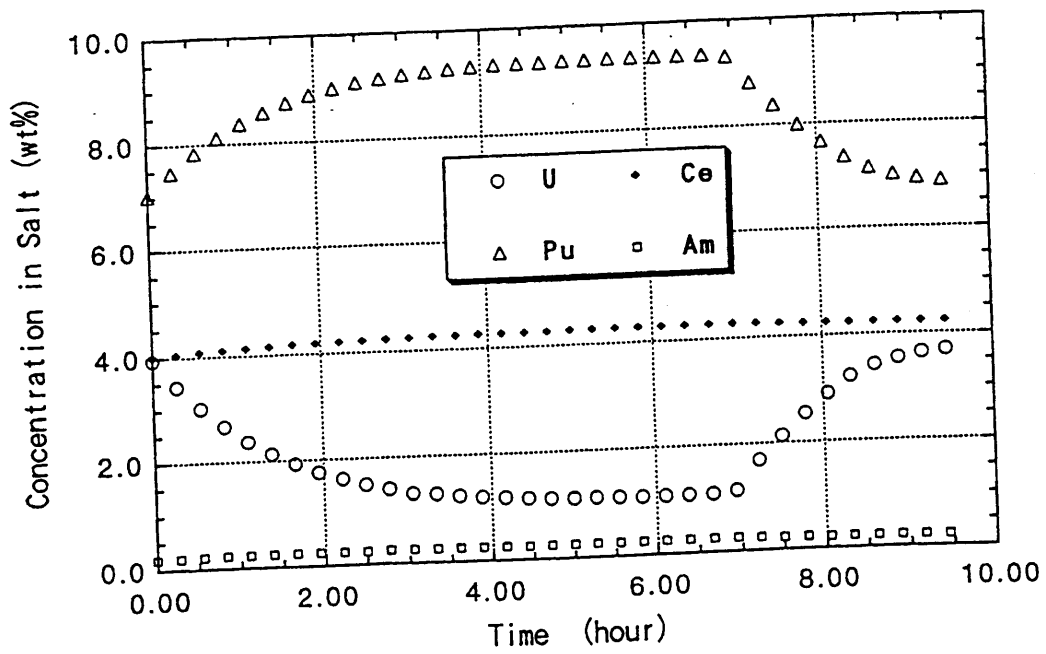


Fig. 4 Element concentration in salt at electrorefining of nitride fuel (U/Pu/Am/Ce=4.0/7.0/0.19/4.0),

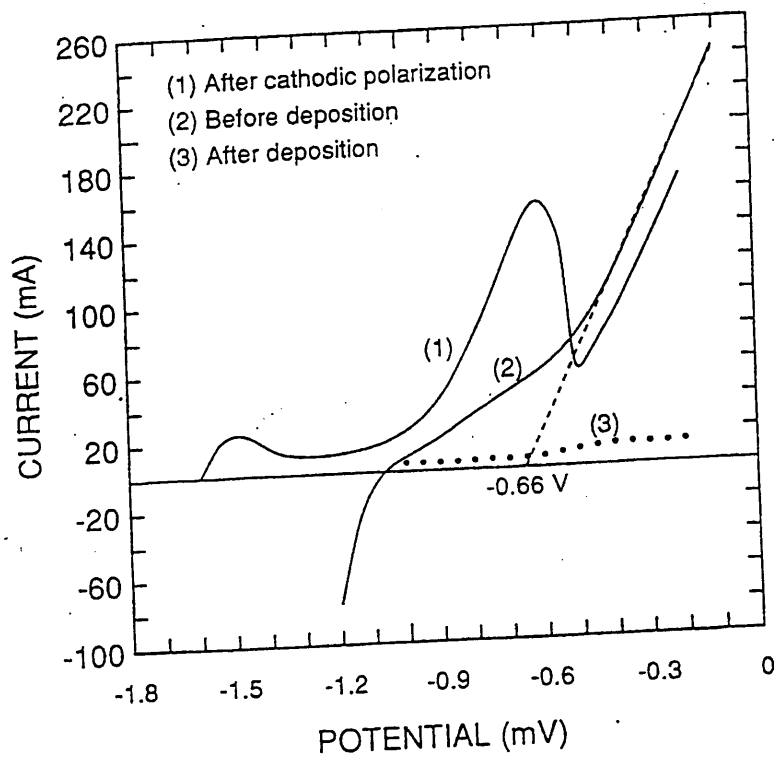


Fig. 5 Results of potentiodynamic measurements of UN

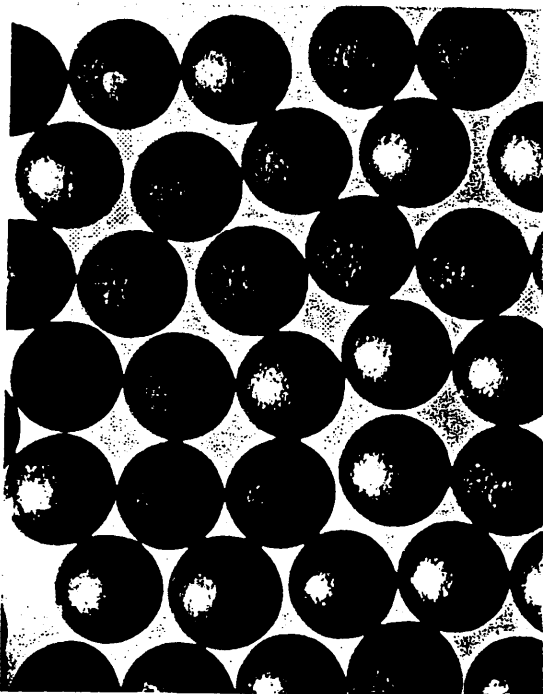


Photo.1 UN particles fabricated by sol-gel process followed by carbothermic synthesis.

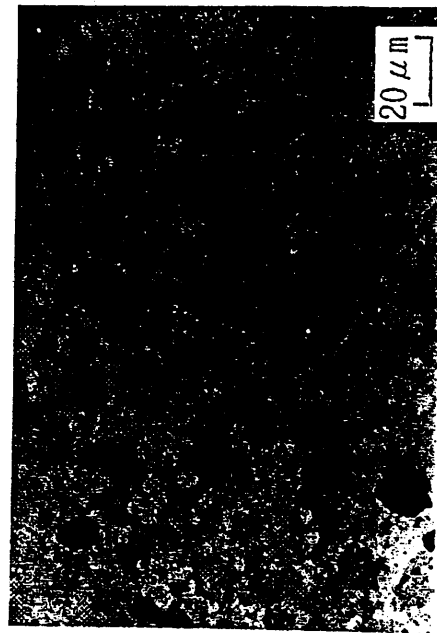


Photo.2 Microstructure of thermal stable nitride pellet

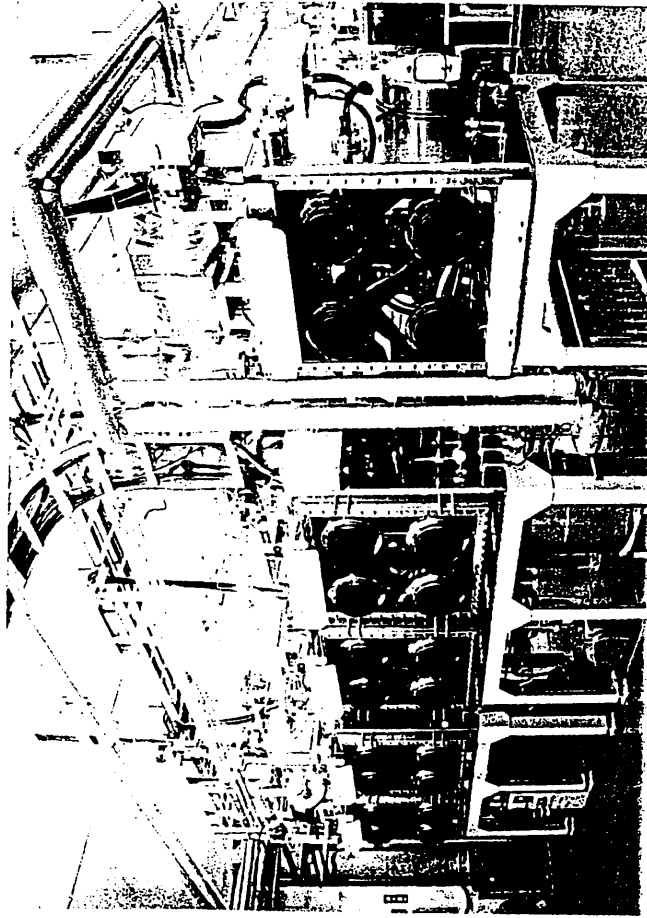


Photo.3 Appearance of gloveboxes in which electrorefiners for PuN and NpN are installed