



B.3.2. SOLID TRU FUELS AND FUEL CYCLE TECHNOLOGY

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B.3.2.1. NITRIDES AND ALLOYS

Alloys and nitrides are candidate solid fuels for transmutation. The fuel element is the sodium-bonded type as shown in Fig. 1. Actinide metals and nitrides have good compatibility with Na. Since the lattice parameters of the nitrides are close to each other [1], one may expect that UN, NpN, PuN, AmN and CmN are miscible with each other. This is not the case for actinide metals. At present, Am-based and Np-based alloys are proposed, because the mutual solubility of Am and Np is considered to be small [2]. The lower melting points and rather low thermal conductivities of transuranium alloys would limit the linear heat rating of the fuel elements [3]. These are the reasons why the nitrides are preferred to the alloys. However, the alloy fuels are still considered important alternatives, since it would be easier to fabricate them than the nitrides. However, it is uncertain whether one may apply the simple method of injection casting, which has been successfully employed for the fabrication of the U-Zr and U-Pu-Zr alloy rods.

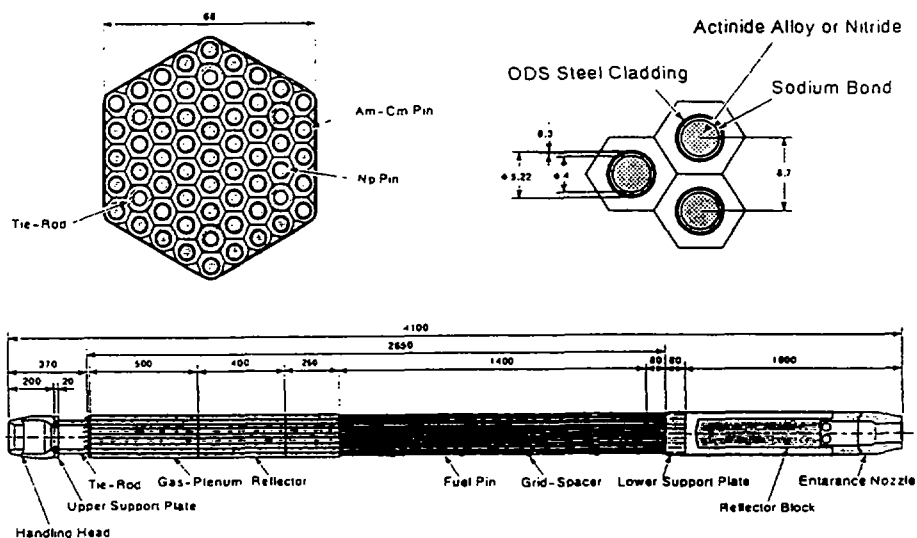


FIG. 1. Sodium-bonded fuel element and assembly.

The favorable thermal properties of the nitride fuels make full utilization of a cold-fuel concept possible [4]: (1) lower fuel temperatures and hence lower fission gas release and smaller swelling, and (2) a thinner cladding to achieve a high heavy-metal loading. A fuel would be called a "cold fuel", when its operating temperature is less than one third of the melting point. The melting point of the actinide nitrides is ~3000 K. There is an irradiation database of nitrides even for (U, Pu)N, but it is much smaller than those for the (U, Pu)O₂ and U-Pu-Zr alloys. However, the existing irradiation data suggest the tameness of (U, Pu)N under cold-fuel condition [4].

On the other hand, for the metallic fuels, there are phenomena whose mechanistic understanding has

not yet been reached: the anisotropy in swelling, the component redistribution under a thermal gradient, the variation of apparent thermal conductivity with porous structure development and bond-sodium intrusion into pores etc. [5]. The reaction between stainless steel cladding and actinide alloys is also severe at higher temperatures, and imposes a performance limit [6]. JAERI has prepared (U, Pu)N fuel elements and irradiated them in a thermal spectrum in JMTR [7]. UN and PuN were prepared by carbothermic reduction of powder mixtures of respective oxides and carbon in flowing $H_2 + N_2$. Then UN and PuN were mixed and sintered to form (U, Pu)N. The irradiation test of (U, Pu)N in the fast reactor, JOYO, was begun in August, 1994, as a JAERI/PNC joint program. Suzuki et al. [8] have prepared NpN by carbothermic synthesis. Thermal conductivity [9] and high-temperature vaporization [10] of NpN have been studied by the same group. The thermal conductivity of NpN was intermediate between UN and PuN. Thermal properties will be further studied for (U, Pu, Np)N.

B.3.2.2. NITRIDE FUEL CYCLE TECHNOLOGY

The scheme of the nitride fuel cycle is shown in Fig. 2. For the nitride fuel cycle, technical developments are being made on (1) the internal gelation method to form (oxide + carbon) gel microspheres from the actinide nitrates and (2) the electrorefining process for reprocessing irradiated nitride fuels.

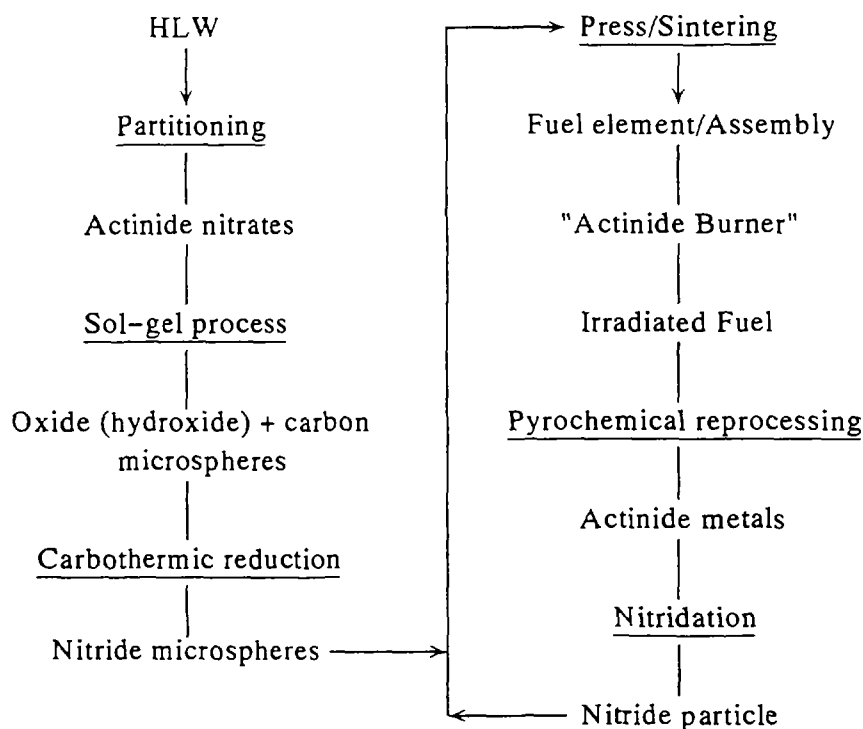


FIG. 2. Scheme of TRU nitride fuel cycle.

B.3.2.3.1. Nitride fabrication by sol-gel process

The internal gelation method is presently being studied because of the simplicity of feed solution preparation compared with the external gelation method, particularly when one wants to obtain multicomponent ceramics. In the internal gelation method, hexamethylenetetramine (HMTA), added to the solution, decomposes on heating to form ammonia which then reacts with the actinide nitrates. Then the solution of actinide nitrates with a carbon suspension turns into a solid mixture of oxide (hydroxide) and carbon in the form of microspheres. Normally the droplets of feed solution are heated in an oil column, but the use of a microwave heating for the internal gelation process has been proposed by Ledergerber et al. [11] Because of its potential to reduce the treatment of alpha contaminated oil, a 2.5 GHz microwave heating apparatus has been developed for this gelation process (Fig. 3) [12]. Also, in order to prevent the instability of the feed solution by the α -decay heat, techniques to mix the actinide nitrate solution and the HMTA solution right above the droplet-forming nozzle are being developed [13]. The gel microspheres are heat treated in a nitrogen atmosphere and converted to the nitride.

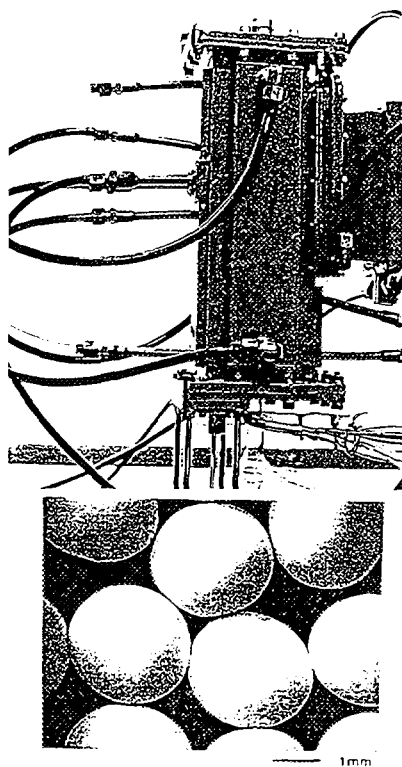


FIG. 3. Microwave gelation apparatus and ammonium uranate gel microspheres.

FIG. 4 shows a stability diagram for the U-C-N-O system at an arbitrary nitrogen partial pressure of $p^*(N_2) = 0.1$ atm at 1823 K [14]. The mixture of UO_2 and carbon is heated in a nitrogen atmosphere to form Uranium carbonitride, $U(C, N)$, and oxynitride, $UO_{2-y}N_{3y/4}$. The amount of the latter decreases with time; so does the fraction of UC in $U(C, N)$. Carbon activity, $a(C)$, and $p^*(O_2)$ are given by the upper abscissa and left ordinate, respectively. Progress of the carbothermic reaction is measured by the cumulative evolution of CO. The dashed line gives the equilibrium partial pressure of CO, $p^*(CO)$. $p^*(CO)$ at $a(C)=1$ is ~ 0.03 atm. As the reaction proceeds, C/U decreases to further reduce the equilibrium CO pressure, $p^*(CO)$. That is, in order to obtain UN, one has to supply nitrogen in a large excess to effectively remove CO from the system. Though excess N_2 from the process exhaust can be purified and circulated, the demand on ^{15}N -enriched N_2 makeup could be larger than that simply expected from the reaction stoichiometry. This is another incentive to recycle ^{15}N from the pyrochemical reprocessing.

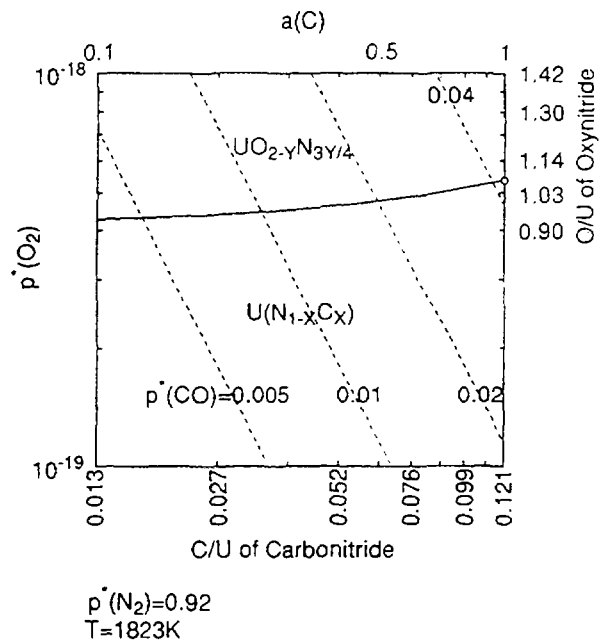


FIG. 4. Stability diagram of U-C-N-O system at 1823 K with $p^*(N_2) = 0.92$ atm.

B.3.2.3.2. Pyrochemical reprocessing

The irradiated fuels are reprocessed with molten-salt electrorefining techniques. The configuration of the electrorefiner can be common for the nitride and alloy fuels. For reprocessing nitride fuels, the electrorefiner has to be flushed with an inert gas to purge N_2 from the anode. ^{15}N -enriched N_2 is recycled to the nitride refabrication.

The anode basket contains either nitride or alloy fuels. The cathode is either a solid metal rod or a liquid metal bath such as molten Cd depending on the combination of actinide elements in the molten salt bath. A molten Cd cathode would be preferred to recover transuranium elements in the presence of U^{3+} in the molten salt phase.

The recovered N_2 can be fed to the process to convert actinide metals to nitrides. Conversion can be made in a liquid cadmium bath: actinide metals dissolve into Cd, react with N_2 which is in contact with Cd, and segregate as nitrides on the bottom of the bath. Cd can be readily distilled away from the nitrides.

The anodic dissolution of UN has been studied in laboratory-scale experiments [15]. UN powder was contained in a graphite anode basket. The counter electrode was a molybdenum rod. The LiCl-KCl- UCl_3 melt was contained in a recrystallized alumina crucible. The Ag/AgCl reference electrode consists of pure silver in LiCl-KCl-10 mol% AgCl. The measurements were done at 773 K. Fig. 5 shows that the anodic dissolution of UN occurs with the characteristic potential at about -0.66 V against the reference electrode. The pertinent reaction is the formation of solid UCl_3 on UN:



$$\begin{aligned} \Delta G &= \Delta G^{\circ}(UCl_3) - \Delta G^{\circ}(UN) - 3\{\Delta G^{\circ}(AgCl) + RT \ln X_{AgCl}\} \\ &= -192,030 \text{ J/mol} \end{aligned}$$

$$E = \Delta G/3F = -0.66 \text{ V}$$

where ΔG° is the free energy of formation, X_{AgCl} is the mole fraction of AgCl in the reference electrode, and F is the Faraday constant. Above this characteristic potential UN becomes unstable.

Electrolytic decomposition of UN was made with the working-electrode potential of -0.20 V. Almost all UN was dissolved, and α -U was deposited on the counter electrode. Similar runs have been made in LiCl-KCl- $CdCl_2$ melt, where Cd-U alloys were deposited on the cathode. Further tests with (U, Ln)N, PuN and NpN are scheduled (Ln: lanthanides). Table I shows the standard electrode potentials of actinide and

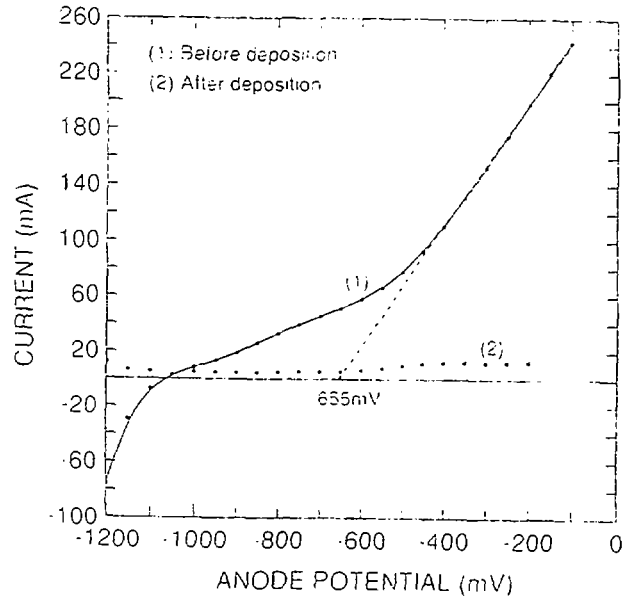


FIG. 5. Current and electrode potential for UN contained in a graphite anode basket in LiCl-KCl- UCl_3 melt at 773 K. The reference electrode was LiCl-KCl-10 mol% AgCl.

TABLE I. STANDARD ELECTRODE POTENTIALS IN LiCl-KCl EUTECTIC MELT AT 773 K.

Reaction	$E^\circ(\text{Ag})/\text{V}$
$\text{Li}^+ + e = \text{Li}$	-2.68
$\text{La}^+ + e = \text{La}$	-2.17
$\text{Li}^+ + e + (1/6)\text{N}_2 = \text{LiN}_{1/3}$	-1.88
$\text{Pu}^{3+} + 3e = \text{Pu}$	-1.81
$\text{U}^{3+} + 3e = \text{U}$	-1.61
$\text{La}^{3+} + 3e + (1/2)\text{N}_2 = \text{LaN}$	-1.42
$\text{Pu}^{3+} + 3e + (1/2)\text{N}_2 = \text{PuN}$	-1.00
$\text{U}^{3+} + 3e + (1/2)\text{N}_2 = \text{UN}$	-0.82
$\text{Cd}^{2+} + 2e = \text{Cd}$	-0.51
$\text{Ag}^+ + e = \text{Ag}$	0

fission-product metals and nitrides as well as those of structural metals, which were calculated from the thermodynamic data in the literature.

B.3.2.3.3. Fundamental database

In order to assess the feasibility of a P-T scheme, the database of basic properties has to be enlarged. The thermodynamic database has to be expanded in three major areas: (1) actinide alloys and intermetallics, (2) actinide-containing molten salts and (3) transuranium nitrides, particularly americium nitride. In JAERI, a pure

substance and solid-solution database, related to actinide burning, is being created.

With our present knowledge, it is difficult to design a metal fuel with high concentrations of MA. Systematic studies of MA-transition metal alloying behavior are being made. Alloying behavior among U, Np, Pu and Am appears to be predicted with the Brewer model [2, 16], though the accuracy of prediction has yet to be examined for each system. Even with the U-Pu binary system, further refinement of the alloy theory seems to be necessary to realize satisfactory agreement with the experimental phase diagram [2]. Figures 6 and 7 show predicted ternary phase diagrams of U-Pu-Am and Np-Pu-Am, respectively. In the U-Pu-Am system, the liquid miscibility gap in the U-Am binary would close with the addition of a small amount of Pu. As for the Np-Am binary, the addition of small amount of Pu would not prevent the segregation of the Np-rich liquid at lower temperatures. Further theoretical refinement will be possible by referring the results of systematic experimental studies of the alloying behavior of transuranium elements such as those being made by Gibson and Haire [17].

The volatility of americium may be troublesome in any type of P-T scheme. For instance evaporative loss of americium during the sintering of the nitride fuel has to be avoided. Thermodynamic properties of AmN have to be studied to optimize the fabrication process. An initial estimate of the free energy of

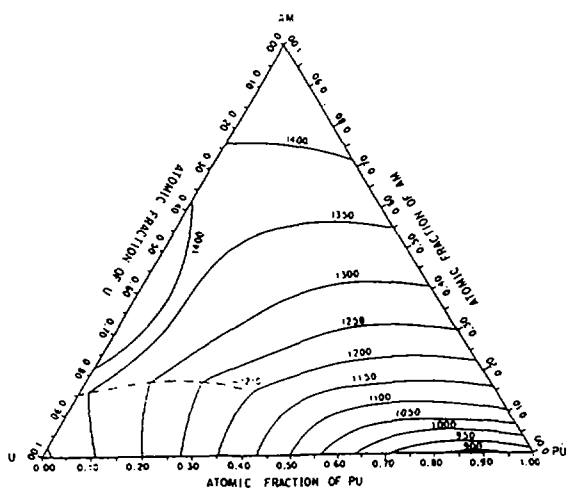


FIG. 6. Predict liquidus of U-Pu-Am ternary system.

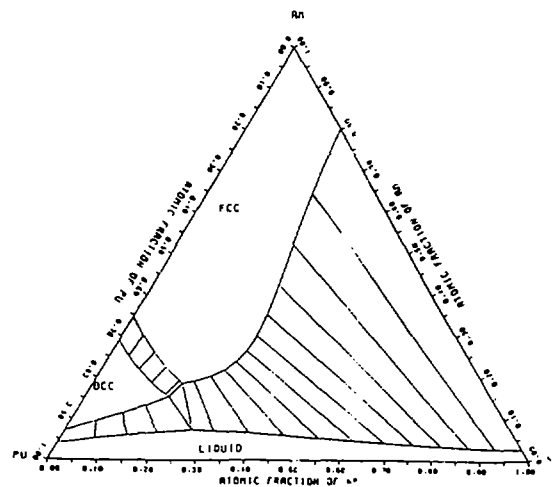


FIG. 7. Predicted isotherm of Np-Pu-Am ternary system at 1000 K.

formation, ΔG_f° , of AmN has been made from the vaporization behavior of impurity ^{241}Am in reactor-grade PuN [18]. $\Delta G_f^\circ(\text{AmN})$ appears not to be significantly different from those of UN and PuN. This gives a much higher vapor pressure of Am over AmN compared with Pu over PuN. If so, either a technique to lower the sintering temperature has to be devised or the application of low-density fuel has to be considered.

As long as one seriously considers the use of Plutonium and the recycle of the other transuranium elements in nuclear technology, the thermodynamic behavior of actinide(An)-noble metal alloys such as An-Pd alloys has to be better defined. The fission yields of noble metals are much greater from the transuraniums than from ^{235}U , and they form very stable intermetallics with actinides. The existence of stable intermetallics would cause a significant actinide loss during reprocessing.

REFERENCES

- [1] KOCH, G., et al.: Gmelin Handbuch der Anorganischen Chemie, Transurane, Teil C: Die Verbindungen, Springer Verlag.
- [2] OGAWA, T.: J. Alloys and Compds., 194 (1993) 1.
- [3] OGAWA, T., et al.: JAERI-M 89-123 (1989).
- [4] BLANK, H.: J. Less-Common Metals 121 (1986) 583.
- [5] WALTERS, L. C.: Nucl. Technol. 65 (1984) 179.
- [6] VOHEN, A. B., et al.: Trans. ANS 66 (1992) 202.
- [7] ARAI, Y., et al.: JAERI-Research 95-008 (1995).
- [8] SUZUKI, Y., et al.: J. Nucl. Sci. Technol. 31 (1994) 677.
- [9] ARAI, Y., et al.: J. Nucl. Mater. 211 (1994) 248.
- [10] NAKAJIMA, K., et al.: 1995 Annual Mtg. Atomic Energy Society of Japan, paper No. K9., Tokyo, March, 1995.
- [11] LEDERGERBER, G.: Trans. ANS 40 (1982) 55.
- [12] YAMAGISHI, S., et al.: JAERI-Tech 94-010 (1994).
- [13] YAMAGISHI, S.: 1995 Annual Mtg. Atomic Energy Society of Japan, paper, No. L48, Tokyo, March, 1995.
- [14] OGAWA, T., et al.: JAERI internal document.
- [15] KOBAYASHI, F., et al.: J. Am. Cer. Soc. (submitted).
- [16] BREWER, L.: J. Alloys and Compds. 213/214 (1994) 132.
- [17] GIBSON, J. K., et al.: J. Alloys and Compd. 213/214 (1994) 106.
- [18] OGAWA, T., et al.: J. Alloys and Compds. (in press).