

Crystallochemistry of actinide nitrides ($U_{1-y}Pu_y$)N and effect of impurities

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Abstract – Investigations on actinide nitrides has been done in our Laboratories for Fast Breeder Reactors since the seventies and some properties are reported to show the interest for these fuels.

Today, the actinide nitrides are reconsidered as possible fuels for the future fission reactors (GFR and LMFR selected by the international forum Generation IV). The results of new investigations on crystal structure of mixed mononitrides (U,Pu)N, and the effects of oxygen and carbon contaminations on this structure are presented.

The cubic "NaCl-fcc" type structure of actinide nitrides AnN with space group $O5/h-Fm3m$ does not respect the "Vegard law" model for the mixed nitrides ($U_{1-y}Pu_y$)N. These nitrides are usually considered with strong metallic character associated with partial ionic bonding, but the ionic contribution in the $An-N$ bonding determined in this work is very important and near 41.6% for UN and PuN. From results published on resistivity of mixed nitrides, the data on bonding must be also modified for partial covalence. This is in good agreement with the experimental lattice parameters which are not compatible with dominant metallic bonding. The numbers of bonding electrons in the nitrides ($U_{1-y}Pu_y$)N are reevaluated and the low values proposed comparatively with those previously published confirm the strong ionic character with high concentration of An^{3+} ions.

The solubility of oxygen and carbon in actinide nitrides ($U_{1-y}Pu_y$)N are discussed from measurements on volumic concentration of actinide oxide phase, total oxygen and carbon contents, and lattice parameter of nitrides. The oxygen solubility limit in UN is near 1000ppm, with a lightly higher value of 1200ppm for the mixed nitride ($U_{0.8}Pu_{0.2}$)N. The effects of oxygen or carbon atoms in the lattice of ($U_{1-y}Pu_y$)N are analysed..

INTRODUCTION

The mixed uranium plutonium nitrides and the plutonium nitride are considered since many years as possible nuclear fuels [1-3]. R&D nitride programs including irradiation tests, were carried out in the USA for FFTF reactor or space applications as far back as 1963 [4, 5]. Many studies have been done since 1965 in the laboratories of the CEA in France and the European JRC TUI in Germany on mixed nitrides with about 20at.% of plutonium, for advanced fuels of Sodium cooled Fast Breeder Reactors [6-8]. Advanced fabrication processes have been developed also in collaboration with PSI (Switzerland). But unfortunately, the validation on nitride fuels by tests in pile is relatively limited comparatively with oxide fuels. Few irradiations of fuel pins were performed in reactors like Phenix, Silene or HFR [9-12], and for most of them, the Post Irradiation Examinations are not yet totally explored. However, mixed nitrides with 45 and 60at% Pu are prepared for future irradiation in the reactor BOR60 in Russia.

Outside of Europe and USA, researches on mixed nitride fuels have been developed in Japan during more than 15 years, and this knowledge is

now used in the Sodium Fast Reactors program [13]. Nitride fuels had been also produced in India after 1980 for small Sodium cooled Fast Neutron Reactors with very low thermal power [14].

MOTIVATION FOR NITRIDE FUELS

The very high melting point (>3000K), the good chemical stability up to 2000K (except in water), the industrial fabrication process available and the reprocessing by the PUREX process or by pyrochemistry without difficulties are in favor of nitride fuels. However, the main advantages of actinide nitrides for future nuclear fuels, are the high density of actinides ($13.5g/cm^3$) and the relatively high thermal conductivity (15 – 22W/m.K between 773 and 1773K, ten time higher than conductivity of oxides). Nevertheless, nothings is perfect and three difficulties must be reported for the uses of actinide nitrides : the relatively high pyrophoricity under air atmosphere, particularly for powders; the decomposition of mononitrides in vapor and low melting point phase at high temperature; and the transmutation of ^{14}N in

long-lived radiotoxic isotope ^{14}C . The handling in glove boxes under inert atmosphere, the conditioning of fuel under nitrogen pressure ($>3.5 \times 10^5 \text{ Pa}$), and the use of enriched ^{15}N nitrogen are industrial solutions to remove these drawbacks. The actinide carbides, carbonitrides or oxycarbonitrides could be also other alternatives to investigate for materials.

Up to now, the nuclear fuels of power reactors in the world are oxides. The use of actinide nitrides has been relatively limited with no industrial scale. More, the background on oxide fuels is incomparably larger than the one on nitride fuels, and there is no problem or unacceptable limit for reactor safety provided by the oxide fuel which impose to change the situation. However, difficulties to increase the burn up with oxide fuels could be one reason to develop other fuels for the nearest future. But unfortunately the nitrides are practically excluded in Water Reactors and therefore in the next series of "European Pressurized water Reactor". On the other hand, for the reactors of future generations developed for 2040, the efficiency is an important parameter to optimize. That is included in the specifications of the Very High Temperature Reactors and the Gas Fast Reactors studied in the international Forum Generation IV. The temperature of coolant gas is for instance significantly increased (limit up to 1600°C). For safety reasons and in order to solve some difficulties from the Science of Materials, high thermal conductivity is requested for the fuels in these reactors. After analysis of preliminary bibliographic studies including the minimal wastes production criteria, $(\text{U}_{0.78}\text{Pu}_{0.2}\text{Am}_{0.02})\text{N}$ has been selected in the list of fissile materials for the GFR.

Our satisfactory results from irradiations "NIMPHE" of mixed nitride $(\text{U}_{0.8}\text{Pu}_{0.2})\text{N}$ $>80\%$ theoretical density, in the Fast Breeder Reactor Phenix with linear power $450\text{-}730\text{ W/cm}$, and burn up at $6.2\text{-}7.5\text{ at.}\%$, show a good behaviour and a low swelling for the nitrides comparatively to the carbides.

This new investigation on crystallochemistry of mixed nitrides $(\text{U}_{1-y}\text{Pu}_y)\text{N}$ has been done to determine the different bonding in the actinide nitrides. These structural aspects could be very useful to predict the variation of some physical and chemical properties like thermal conductivity or compatibility with fission products which are important for the behaviour of the nitride fuels in the future reactors.

AnN CRYSTALLOCHEMISTRY

The crystal structure of actinide nitrides AnN is cubic (fcc), NaCl-type, $\text{O}_h^5\text{-Fm}3\text{m}$. The deviation from stoichiometry in $(\text{U}_{1-y}\text{Pu}_y)\text{N}_{1+x}$ nitride is very limited, and no interstitial nitrogen atoms is proposed in the literature for the actinide mononitrides. The bonding usually considered for these nitrides in the previous works is mixture of ionic and metallic bonding, with dominant metallic character like in lanthanide nitrides. Few authors consider nevertheless exclusively covalent bonding, and the covalent bonding cannot be totally excluded. Therefore, the species in pure mixed nitrides $(\text{U}_{1-y}\text{Pu}_y)\text{N}$ could be U_{metal} , $\text{U}_{\text{covalent}}$, U^{4+} , U^{6+} , Pu_{metal} , $\text{Pu}_{\text{covalent}}$, Pu^{4+} , Pu^{3+} , $\text{N}_{\text{covalent}}$, and N^{3+} . Some radii of these species are reminded in the Table 1, and the unit crystal cells are presented on Fig.1 for the different type of bonding with the respect of atom sizes.

Table 1. Atom radius in actinide nitrides (from Sutton; Pauling; Shannon and Prewitt).

Radius, Å	U	Pu	N	O	C
covalent	1.52	1.53	0.75	0.66	0.77
metallic	1.53	1.62	0.71	[1.46]	-
$r_{\text{I}}^{3+}(\text{CN}6)$	1.04	1.01	1.48	1.36	[0.15]
$r_{\text{I}}^{4+}(\text{CN}6)$	0.90	0.86	-	-	-

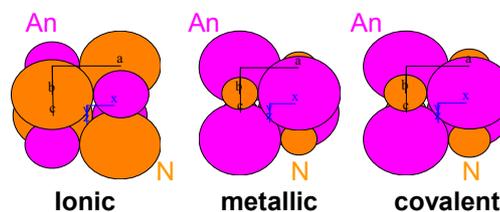


Fig. 1. Crystal structure of actinide mononitride for different bonding : $\text{An} = \text{U}, \text{U}^{4+}, \text{Pu}, \text{Pu}^{3+}, \text{ or } \text{Pu}^{4+}$; $\text{N} = \text{N} \text{ or } \text{N}^{3+}$

The variation in the lattice parameter of mixed mononitrides can be analysed from the results published by different laboratories. This variation is described on Fig. 2 [13, 15, 16]. The cubic structure of mononitride is compatible with all compositions of mixtures $(\text{U}_{1-y}\text{Pu}_y)\text{N}$. Therefore this nitride can be considered as single phase solid solution for all y . But a significant deviation from the Vegard's law is also shown, as well as for mixed nitrides of U/Pu than U/Np. This deviation can be compared with the published results for mixed carbides $(\text{U,Pu})\text{C}$.

Practically, insignificant variation of crystal cell parameter of solid solution can be observed for low concentrations of one of the actinide in the mixed nitrides : <25at% for $(U_{1-y}Pu_y)N$, but that can reach <40at% for $(U_{1-y}Np_y)N$. The substitution domain of actinides for the stability on the size of crystal cell of nitrides seems to be affected by the couple of actinides, but no clear correlation can be done with radius of these actinides. For more balanced compositions, the actinide concentration dependence on the lattice parameter of mixed nitrides is strong and relatively similar for the actinide couples studied $(U_{1-y}Pu_y)N$ and $(U_{1-y}Np_y)N$:

$$a = a_0 + (3(+/-0.3) \times 10^{-4}) \text{at\%An.}$$

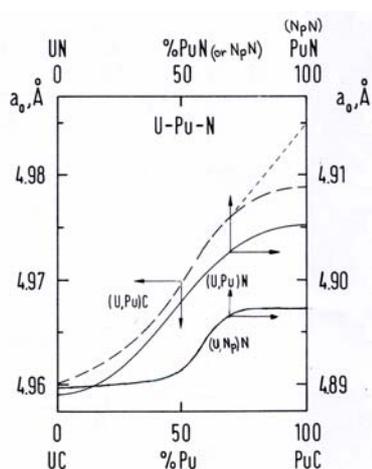


Fig. 2. Lattice parameter of mixed nitrides $((U,Pu)C$ from [15]; $(U,Pu)N$ from [16]; $(U,Np)N$ from [13])

Our results on measurement of lattice parameter of $(U,Pu)N$ at room temperature with very low content of impurities are reported in Table 2 and compared with theoretical parameters estimated from the radius of the different atoms.

Table 2. Lattice parameters of $(U,Pu)N$

Bonding	Lattice parameters, Angstroms			our results
	from Metallic	from Covalent	from Ionic radii	
UN	4.48	4.54	Ar^3N^2/Ar^4N^2 5.04 / 4.74	4.889
$(U_{0.8}Pu_{0.2})N$	-	-	-	4.891
PuN	4.66	4.56	4.98 / 4.68	4.905
b (in $a = a_0 + b\%/Pu$)	0.0018	0.0002	-0.0006	0.00023

These results confirm the strong ionic character for bonding in actinide mononitrides which governs the crystal lattice and which is the reason for the high values for parameters. The ionic compound compatible with the

experimental parameters is $An^{3+}N^{3-}$. This necessity to have important concentrations of trivalent actinide ions in $(U,Pu)N$ is original in solid state chemistry of actinides because uranium is considered to be stable under tetravalent or hexavalent oxidation state in compounds and nitrogen is oxidizing gas.. However our results of spectrophotometric measurements on actinide compounds previously published have shown typical bands for U^{3+} on UN spectra.

IONIC BONDING and ELECTRONIC STRUCTURE

The theoretical ionicity in diatomic heteronuclear An-N bonding can be evaluated by the Phillips-Van Vechten theory and the Pauling theory :

$$i\% = 16[X_{an}-X_N] + 3.5[X_{an}-X_N]^2.$$

Electronegativity data from Pauling and Allred-Rochow have been used :

$$X_N = 3.07; X_U = 1.22; X_{Pu} = 1.22.$$

The ionic character for molecule can be also correlated with electric dipole moment μ :

$$i\% = 100x (\mu_{obs.}/\mu_{calc.})$$

with $\mu_{calc.} = (q.e.a/2)$; where a is the lattice parameter.

Finally the ionic bonding character in AnN is relatively important: $i\% = 41.6\%$ for U-N and Pu-N, and the experimental dipole moment would be about 9.8 Debye.

On the other hand, the results of electrical resistivity measured on mixed nitride $(U_{0.8}Pu_{0.2})N$ by Keller for $T < 1200K$ do not show the typical metallic character [17].

In conclusion, the ionic bonding is dominant in nitrides $(U,Pu)N$, the metallic character is weak in mixed nitrides and covalent bonding could be important (up to 58%).

From these results, it is possible to determine the part of localized electrons on the actinide by the Pauling theory. The number of bonding electrons E_b is for instance given for covalent bonding by : $r = r(1) - 0.3 \log E_b$, where r is covalent radius of atom and $r(1)$ radius for single bond. Comparison with $[An-N]$ distance in nitride gives the total number of bonding electrons :

$$[An-N] = a/2 = r_{An}(1) + r_N(1) - 0.6 \log E_b$$

The valence electrons are $5f + 6d + 7s$ for actinides and $2s + 1p$ for nitrogen. The results on the numbers of bonding electrons and localized electrons are reported in Table 3. The number of bonding electrons found in $(U,Pu)N$ are between 4.09 and 4.31. These values are significantly lower than results published by Arai [18]. On the contrary, the localized electrons between 3.7 and

Table 3. Bonding electrons in (U,Pu)N

Compound	Lattice parameter, Angstrom	Valence electrons	Bonding electrons 100% covalent	Bonding electrons lono-covalent	Localized electrons #
UN	4.889	9	7.65	4.09	3.71 (1.35 [9])
PuN	4.905	11	7.61	4.31	5.39 (3.40 [9])
(U _{0.8} Pu _{0.2})N	4.891	9.4	7.64	4.12	4.06

5.4 are more larger than them previously published.

OXYGEN and CARBON IMPURITIES

The solubility of oxygen in the actinide mononitrides has been determined from image analysis on ceramographies of uranium nitrides and mixed (U,Pu)N nitrides, and measurements of total oxygen content in the different nitrides. X-Ray-Diffraction has been also used to control the different phases.. The samples had been prepared in our laboratory from pure nitride powder made in inert atmosphere glove boxes by hydration/nitridation process. Pellets of these powders had been pressed and sintered during <15h at temperature between 1720 and 1800°C after addition and mixing of small amounts of actinide oxide. The volumic concentrations of actinide oxide phase are estimated from the surface ratio of oxide phase recorded at room temperature on ceramography of sintered nitrides by an optical microscope. The bulk distribution of oxide phase is supposed to be homogeneous, and the oxygen solubility is considered to be independent of temperature. All the samples had been cooled in the same conditions, however it will be necessary to control definitively this hypothesis by XRD measurements at high temperature.

The variation of volumic concentration of oxide phase in the nitride is proportional to the total oxygen content with a threshold showing the oxygen solubility limit. The results for UN are reported on Fig 3.

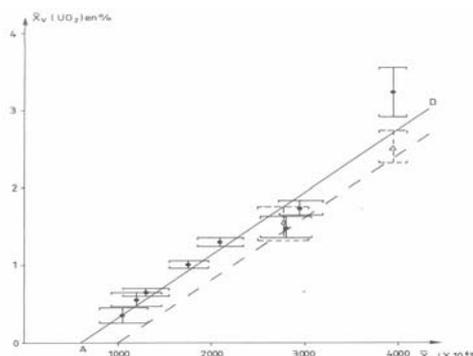


Fig.3. Variation of volumic concentration of UO_{2+x} vs total oxygen content in UN pellets

The threshold for the uranium oxide phase detected in uranium nitride gives an oxygen solubility limit in UN at <1000.10⁻⁶. The variation of the lattice parameter of UN with soluble oxygen was not possible to detected by XRD, however important oxidation of samples can occur during preparation for XRD.

The same technique used for (U_{0.8}Pu_{0.2})N gives an oxygen solubility limit of <1200.10⁻⁶.

For carbon impurity AnN and AnC are completely miscible and there is no solubility limit.

REFERENCES

- 1 R. Pascard, Nucl. Metallurgy, 13, 1967, 345.
- 2 Plutonium 1970 and other actinides, Metallurgical Soc. AIME, New York, 1970, C. H. de Novion, et al., 509; C. A. Alexander et al., 95.
- 3 HJ. Matzke, Science of advanced LMFBR fuels, Elsevier Science Publishers B. V. , 1986.
- 4 R. A. Wullaert, et al. , US Report BMI-1638, 1963.
- 5 R. A. Potter, J. L. Scott, US Report NASA-CR-134498, 1974.
- 6 K. Richter, et al., Report EUR-6154 EN, 1978.
- 7 H. Bailly, IAEA-TECDOC-352, 1985, 95.
- 8 F. Delvoe, CEA report R-5434, 1988
- 9 H. Bernard et al., IAEA-TECDOC-466, 1988, 43.
- 10 J. L. Faugère et al., ANP 92, Tokyo Japan, Oct 1992.
- 11 G. Pautasso et al., J. Nucl. Mater. 158, 1988, 12.
- 12 H. Blank, Report EUR-13220 EN, 1991.
- 13 Y. Arai et al., Proceedings Gobal 95, Versailles France, Sept. 1995, 538 ; Proceedings Global 97, Yokohama Japan, Oct. 1997, 664.
- 14 C. Ganguly et al., Nucl. Technol., 11, 1985, 71.
- 15 R. Pascard, Pulvermet. In der Atom., Proc. 4th Plansee Seminar, 1962, 387.
- 16 V. J. Tennery et al., J. Amer. Ceram. Soc. 54, 1971, 247.
- 17 D. L. Keller, US Report BMI-1809, 1967.
- 18 Y. Arai, et al., J. Sol. State Chem., 115, 1, 1995, 66