CONFIRM: COLLABORATION ON NITRIDE FUEL IRRADIATION AND MODELLING

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The main objectives of the CONFIRM project of the European 5th Framework Programme are modelling, optimisation and fabrication of a uranium-free fuel for Accelerator-Driven Systems (ADS). Project partners are KTH (Stockholm), CEA (Cadarache), Studsvik Nuclear, BNFL (Risley), ITU (Karlsruhe) and SERCO (Harwell). In a first phase, plutonium fuel in a zirconium nitride matrix with high linear rating and high burnup will be irradiated in the Studsvik test reactor. The contribution of PSI is the production of (Pu,Zr)N pellets, the fabrication of four helium-bonded fuel rodlets, and their transport to Studsvik. Nitride pellets of low oxygen and carbon content, but with a rather high porosity, could be fabricated by means of the carbothermal reaction.

1 INTRODUCTION

The recycling of minor actinides, such as americium and curium, is necessary for an effective reduction of the long-term radioactive inventory of spent fuel by partitioning and transmutation. In order to avoid further production of plutonium, recycling of the minor actinides has to be carried out in a uranium-free matrix. Reactors with a fast neutron spectrum, i.e. fast reactors or sub-critical Accelerator Driven Systems (ADS), are dedicated to this kind of waste transmutation.

In previous research programmes, oxides were regarded as the preferred fuel option, and vast experience in the irradiation to high burnup has been accumulated over the years. However, nitride fuel has the advantage of higher thermal conductivity compared to oxide fuel and, with regards to the standard reprocessing procedure, better solubility in nitric acid. The N-15 requirement for suppressing C-14 production has already been reported [1].

Its high thermal conductivity, high melting point, and its good compatibility with the coolant (Na, NaK), makes zirconium nitride a prime candidate as an inert matrix material [2].

In a first phase, (Pu,Zr)N will be irradiated in the Studsvik reactor to test its performance at high linear rating (40-50 kW/m), and under high burnup (>10%) conditions. The forthcoming European 6th Framework Programme will include post-irradiation examination of this fuel, as well as the modelling, fabrication and irradiation of (Am,Zr)N.

The perceived safety problems related to the decomposition of nitride fuels under the above-mentioned irradiation conditions are currently being addressed [3-5] by the severe accident modelling groups at the former AEA-T, now SERCO (Harwell, UK) and KTH (Stockholm).

2 THERMO-CHEMICAL MODELLING OF CARBOTHERMAL REDUCTION

The carbothermal nitridation of zirconia solid solutions with cerium and neodymium, as inactive substitutes, and with uranium and plutonium as active elements, has been studied using thermogravimetry and gas chromatography, and the data compared against thermodynamic calculations of the enthalpies of formation for the binary zirconium nitride [6, 7].

An easy-to-handle and well-controlled reaction was utilised to convert metal oxides to their nitrides. The chosen carbothermal nitridation method [8] could be used with the PSI Sol-Gel route as well as with a powder route, and could easily be implemented in a used oxide fuel preparation route [9]. Of particular interest are the starting temperatures of the reactions and the possibility to shift the equilibrium towards the nitrides by removing CO as a by-product from the system.

Different groups have reported on the reactions assumed to be taking place during the carbothermal nitridation of uranium dioxide or plutonium dioxide in a nitrogen/hydrogen atmosphere [10-14]. From consideration of their results, the following reaction has to be considered for a stoichiometric oxide solid solution of a dopant metal based on zirconia with 20 at%:

$$\left(Zr_{0.8}M_{0.2}\right)O_2 + 2C + \tfrac{1}{2}N_2 \rightarrow \left(Zr_{0.8}M_{0.2}\right)N + 2CO$$
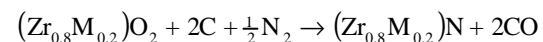
The Gibbs energy of reaction can be expressed as:

$$\Delta_r G^\circ = 0.8\,\Delta_f G^\circ\left(ZrN\right) + 0.2\,\Delta_f G^\circ(MN)$$
$$- \Delta_f G^\circ\left(Zr_{0.8}O_{1.6}\right) - \Delta_f G^\circ(M_{0.2}O_{0.4})$$
$$+ 2\Delta_f G^\circ\left(CO\right) + 2RT\ln\frac{p(CO)}{P^\circ} - \frac{1}{2}RT\ln\frac{p(N_2)}{P^\circ}$$

in which the standard Gibbs energy of reaction, $\Delta_r G°$, has been calculated using the databases of Kubaschewski et al. [15, 16].

For a realistic prediction of the carbothermal nitridation of the mixed metal oxides used in this study, a CO partial pressure of 0.01 mbar has been assumed. From the results, a starting temperature for the reaction of about 1375K to 1475K, depending on the dopant, is predicted. Higher temperatures, and a lower CO partial pressure, should accelerate the reaction.

These modelling studies were performed in the framework of a PhD programme related to the topic of mixed zirconium/plutonium nitride fuel fabrication [7].

3   FUEL FABRICATION

Nitride Powder Fabrication

For the fabrication of $(Pu_{0.2}Zr_{0.8})N$ and $(Pu_{0.3}Zr_{0.7})N$, Zirconia was first mixed with 20 at% and 30 at% of plutonium oxide, respectively. After homogenisation in an attrition mill, the oxide was mixed with carbon black in the ratio 1:2.5 to1:3.5 (see flow diagram in Fig. 1).
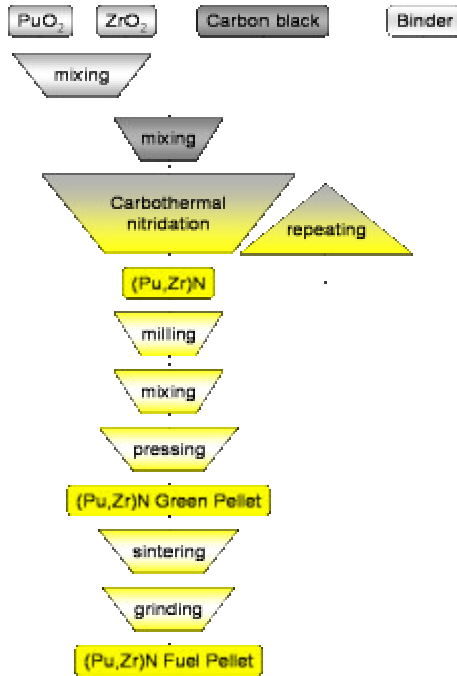

Fig. 1: Flow sheet for the (Pu,Zr)N fuel pellet fabrication process.

The resulting mixture was then treated in 100g batches in a sinter furnace with optimised temperature programmes (reaction levels at 1675 K for about 36 h, or 1875 K for about 24 h). For all thermal treatments, a nitrogen atmosphere was used. For decarburisation, the gas was doped with 8% hydrogen for a specified time before cooling down. In order to fulfil the specification for the oxygen content (<1wt%), the material was treated again under the same conditions, based on results from thermochemical modelling calculations and the experience gained during earlier experiments. The gas flow was all the time set at about 100 l/h.

Characterisation of the Nitride Powder

X-ray diffraction patterns were measured. Samples were pulverised, nickel powder was added as standard material, and the resulting mixture embedded in nail varnish. From the diffraction patterns obtained, the lattice constants were calculated, and estimates compared against theoretical values (combination of the known lattice constants of the binary compounds using Vegard's law).

Element analyses were performed from both powder samples and pellets, in order to determine the carbon, nitrogen and oxygen contents of the final materials. The analytical results are summarised in Table 1, and the histories of the precursors and products are shown in Fig. 2. The last three batches in the list have twice been carbothermally treated. Though the oxygen level is clearly lower than that observed after one carbothermal cycle, the carbon content stays constant, and the lattice constant gives no indication of a second phase.

Table 1: Analytical data derived from the nitride powder batches. The last three batches (shaded) have twice been carbothermally treated.

Batch	Lattice constant a [Å]	Standard deviation	Lattice constant a [%theoretical a]	C-content [wt%]	Standard deviation	O-content [wt%]	Standard deviation	N-content [wt%]	Standard deviation	N-content [%theror.N-content]
N-80Zr-20Pu-1104	4.6456		100.06	1.7574	0.0308	3.6342	0.2228	5.2744	1.0244	50.76
N-80Zr-20Pu-1116	4.6582	0.0043	100.33	0.0618	0.0017	4.4506	0.3005	6.4488	0.6817	62.07
N-80Zr-20Pu-1125	4.6561	0.0085	100.28	1.9558	0.0077	3.5516	0.1688	6.5260	0.0191	62.81
N-70Zr-30Pu-1126	4.6815	0.0043	100.12	1.4250	0.0282	1.0854	0.1537	8.1262	0.0836	86.79
N-70Zr-30Pu-1127	4.6424	0.0047	99.29	1.2167	0.0136	2.3105	0.0556	7.4616	0.1019	79.70
N-80Zr-20Pu-1134	4.6466	0.0053	100.08	1.5895	0.0134	2.8996	0.1149	7.9342	0.0551	76.36
N-80Zr-20Pu-1135	4.6366	0.0136	99.86	1.7380	0.1456	3.0902	0.0732	7.4806	0.3143	72.00
N-70Zr-30Pu-1137	4.6824	0.0075	100.14	1.4838	0.0404	1.9670	0.0224	7.7064	0.0178	82.31
N-80Zr-20Pu-1140	4.6666	0.0028	100.51	1.8294	0.0064	2.3384	0.0870	7.9686	0.0268	76.70
N-80Zr-20Pu-1143	4.6290	0.0021	99.70	1.0828	0.0366	2.8672	0.2124	6.2224	1.2389	59.89
N-80Zr-20Pu-1154	4.6488	0.013	100.13	1.4876	0.0328	0.4407	0.0496	9.1902	0.0434	88.45
N-70Zr-30Pu-1155	4.6742	0.0039	99.97	1.2640	0.0963	0.3872	0.0156	8.6202	0.0181	92.07
N-80Zr-20Pu-1156	4.6511	0.0032	100.18	1.1758	0.1009	1.0943	0.0727	8.3322	0.0662	80.20

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PuO2        ZrO2        Carbon Black                                Starting Material

(Pu0.2Zr0.8)O2+C    (Pu0.2Zr0.8)O2+C       (Pu0.3Zr0.7)O2+C           Mixed Oxide Powder

N-80Zr-20Pu-1104  N-80Zr-20Pu-1116   N-80Zr-20Pu-1134  N-80Zr-20Pu-1135   N-70Zr-30Pu-1126  N-70Zr-30Pu-1127   Nitride Powder 1st Carborduction

N-80Zr-20Pu-1125      N-80Zr-20Pu-1140      N-70Zr-30Pu-1137      Mixed Nitride Powder

N-80Zr-20Pu-1156      N-80Zr-20Pu-1154      N-70Zr-30Pu-1155      Nitride Powder 2nd Carboreduction

P-80Zr-20Pu-025 (1-12)   P-80Zr-20Pu-030 (1-15)   P-70Zr-30Pu-026 (1-12)  P-70Zr-30Pu-029 (1-12)   Green Pellets

N-80Zr-20Pu-1170 (1-12)  N-80Zr-20Pu-1177 (1-12)  N-70Zr-30Pu-1171  N-70Zr-30Pu-1173   Sintered Pellets

N-80Zr-20Pu-1176      N-80Zr-20Pu-1177      N-70Zr-30Pu-1171  N-70Zr-30Pu-1173   Fuel Pellets
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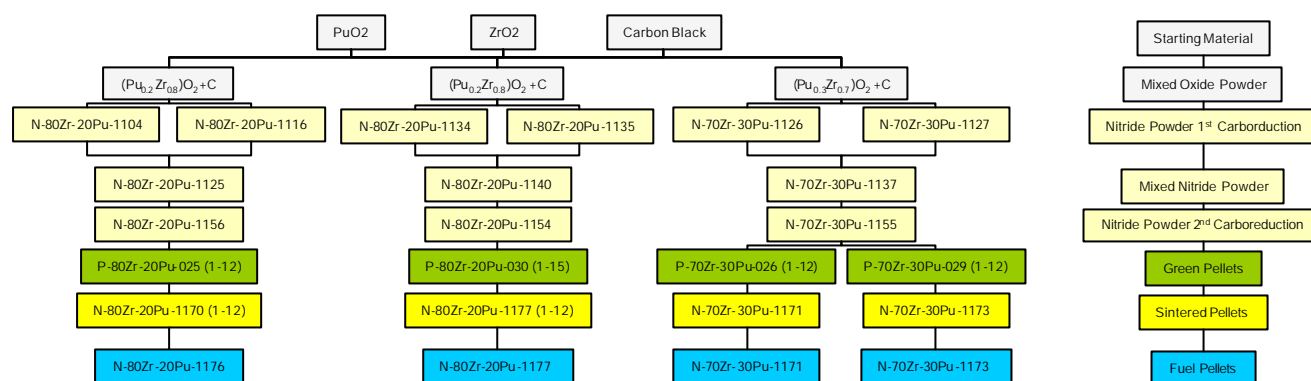
Fig. 2: History of the fuel pellet batches. Batch numbers are shown on the left, and the legend on the right.

Pellet Fabrication

The (Pu,Zr)N powder so obtained was pressed with an 8 mm diameter tool in an automatic hydraulic press; 0.5-1.0 wt% zinc stearate was added to the powder as lubricant. Two green pellets of each fabrication batch were checked for cracks by means of bubble tests: no indication of cracks was found. All green pellets were visually checked, and the green density determined. The pellets were then sintered, using a sintering technique already employed previously by S. Daumas [14] for uranium/zirconium nitride pellets. The procedure consisted first of a de-waxing step at 973K, attained via a ramp of 450 K*h^{-1}, and then maintained for 3 hours. During this step, all the organic material inside the pellets should be removed.

Then, at a rate of 300 K*h^{-1}, the pellets were further heated to 1423 K, and finally, at a rate of 67 K*h^{-1}, to a maximum of 2023 K, which was then maintained for 7 hours. This phase was followed by controlled cooling, at a ramp rate of 250 K*h^{-1}, to 1273 K. From this temperature, the furnace cooled down naturally. The atmosphere in the reaction tube was nitrogen, except at the end of the process when a nitrogen atmosphere with 8% hydrogen was used.

After sintering, the pellet diameter was ground to the specified diameter on a centreless grinder. At the final inspection, the weight, height and diameter of all pellets were measured, and each was checked visually for cracks, chips and general cleanliness.

Characterisation of the Nitride Pellets

The density of the nitride pellets was calculated from the dimensions and weight. In order to compare the results of different mixed zirconium nitrides, the results of the measurements are given as a percentage of the theoretical density, as calculated via Vegard's law.

The analytical data of the pellets are summarised in Table 2. In contrast to the nitride powder, the oxygen impurity in the pellets could be reduced further. The carbon level could also be reduced to around 1 wt%. The ceramography (see Fig. 3) of a nitride pellet exhibits a large open porosity, corresponding to a density range of 78-81.5% of the theoretical density.

The calculations for ideal irradiation conditions predict a porosity of only 15% [17].

Some of the (Pu,Zr)N pellets have been sent to CEA Cadarache for the measurement of the thermal conductivity. Additionally, (U,Zr)N pellets from pre-tests were sent to SERCO, Harwell for high temperature stability analysis. The melting point of plutonium containing ZrN is assumed to be about 100 K below that of (U,Zr)N [3]; measurements for (Pu,Zr)N will follow.
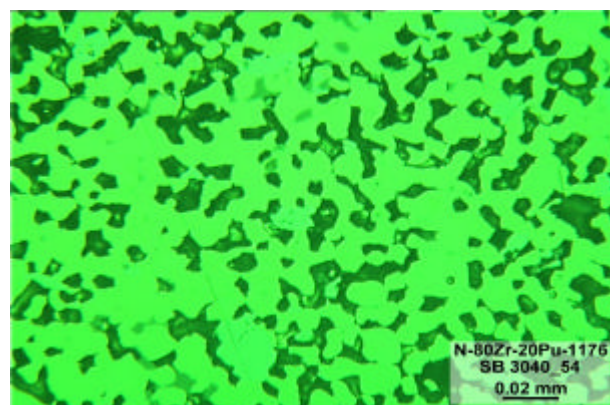

Fig. 3: Polished ceramographic sample of a (Pu,Zr)N fuel pellet showing a porosity of 18.5%.

Fabrication of Hafnium Nitride End Pellets

For the end-pellet production, commercial hafnium nitride powder was pressed with the 6.15 mm diameter tool in a manual hydraulic press. No carbothermal reduction step was necessary. The green pellets were visually checked, and the green density determined. Sintering was similar to that undertaken for the fuel pellets. The pellet diameter was first ground to the specified value on a centreless grinder. During the grinding process, due to the low pellet density, some difficulties arose in ensuring the roundness of the pellet and the end-capping.

During final inspection, the pellets were first carefully checked visually for roundness, cracks, chips and cleanliness, and then the diameter, height and weight of each was carefully measured. The oxygen and carbon level of HfN pellets gave no problems. The porosity of the end pellets is not critical, and is therefore not specified.

Table 2: Analytical data for the fuel pellet (N-70Zr-30Pu-… and N-80Zr-20Pu-…) and end-pellet batches (N-100Hf-…).

Batch	Lattice constant [Å]	Standard deviation	Lattice constant [%Ta]	C-content [wt%]	Standard deviation	O-content [wt%]	Standard deviation	N-content [wt%]	Standard deviation	N-content [%TN]	% of theoretical density
N-70Zr-30Pu-1171	Not measured, originates from the same nitride powder as N-70Zr-30Pu-1173										79.9
N-70Zr-30Pu-1173	4.6563	0.0226	99.59	0.7689	0.1307	0.1495	0.0284	8.8340	0.4619	94.35	80.7
N-80Zr-20Pu-1175*	4.6441	0.0102	100.02	0.5846	0.0143	0.1670	0.0134	9.5290	0.0185	91.71	77.7
N-80Zr-20Pu-1176	4.6429	0.0087	100.00	Not measured, originates from the same nitride powder as N-80Zr-20Pu-1175							81.5
N-80Zr-20Pu-1177	4.6500	0.020	100.15	1.1145	0.0044	0.2078	0.0424	9.7226	0.2956	93.58	78.2
N-100Hf-1172	4.5148	0.004	99.77	0.1808	0.0552	0.4096	0.0409	7.8107	1.6379	107.34	60.6
N-100Hf-1174	4.5145	0.0062	99.76	0.1808	0.0552	0.3152	0.1004	6.1197	1.8055	84.10	62.3

*Not used as fuel batch, only listed for analytical results

4 PIN DESIGN AND FABRICATION

CEA Cadarache provided PHENIX-type cladding tubes, together with the plenum springs for the fuel rods. The free plenum volume was calculated by PSI to be approximately 1998 mm^3, which is in good agreement with the input data for the NITRAF calculation carried out by SERCO (1805 mm^3). All other components of the fuel rod have been designed by PSI according to the specifications of the Studsvik reactor operator, and have been approved by Studsvik Nuclear AB. Figure 4 shows a complete fuel rod, composed of two fuel segments.

5 CONCLUSIONS AND OUTLOOK

It has been shown that the calculated Gibbs energy for carbothermic reduction agrees well with experimental results. Plutonium-zirconium-nitride fuel could be fabricated in the specified geometry, and with the appropriate chemical composition, particularly in regards to the impurities. Only the porosity turned out to be lower than the target value as estimated by the calculations. Evidently, the nitrides with a high oxygen and/or carbon level exhibit a high density,

whereas pure nitrides have relatively low densities. This fact has also been noticed by Arai and Nakajima [18], who argue the case for oxygen to be used as a sintering aid.

The helium-bonded pins were subsequently sent to Studsvik, where they were installed in the irradiation rig. The irradiation, with the rig filled with NaK as coolant, begins in Spring 2004. Following irradiation, PSI will be involved in the destructive testing of one of the pins, in the context of an EU 6th FW Programme.
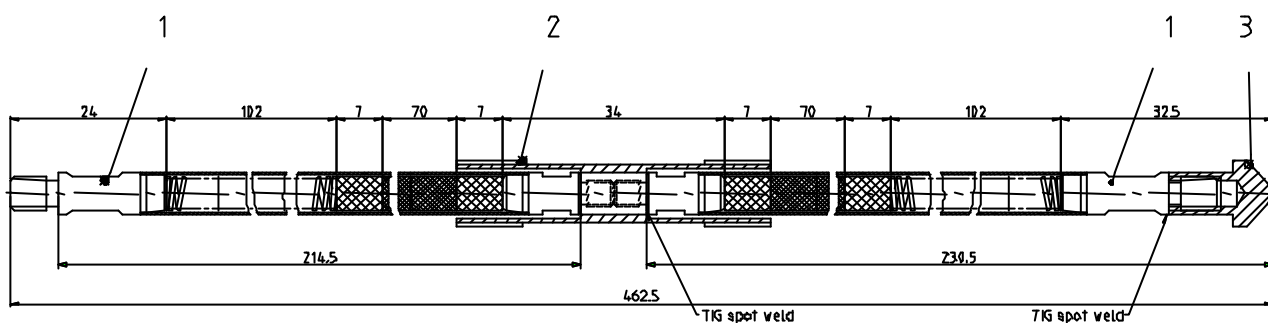
Fig. 4: Fuel rod composed of two segments. 1 upper/lower segment, 2 adapter, 3 end cap.

REFERENCES

[1] J. Wallenius, S. Pillon, "*N-15 Requirement for 2nd Stratum ADS Nitride Fuels*", Nuclear Application in the New Millenium *(Acc-App/ADTTA'01)*, Reno (Nevada), 2001.

[2] M. Burghartz, G. Ledergerber, H. Hein, R.R. van der Laan, R.J.M. Konings, "*Some aspects of the use of ZrN as an inert matrix for actinide Fuel*", Journal of Nuclear Materials, **288**, 233-236 (2001).

[3] R. Thetford, M.A. Mignanelli, "*The chemistry and physics of modelling nitride fuels for transmutation*", Journal of Nuclear Materials, **320**, 44-53 (2003).

[4] J. Wallenius, R. Thetford, T. Abram, S. Pillon, A. Fernandez, F. Ingold, P. Askeljung, "*CONFIRM-Collaboration On Nitride Fuel Irradiation and Modelling*", 6th Int. information exchange meeting on actinide and FP P&T, 11-13 December, Madrid, 2000.

[5] J. Wallenius, K. Tucek, W. Gudowski. "*Safety Analysis of Nitride Fuels in Cores Dedicated to Waste Transmutation*", *Actinide and Fission Product Partitioning and Transmutation*, Madrid, 2000.

[6] M. Streit, F. Ingold, M.A. Pouchon, L.J. Gauckler, J.-P. Ottaviani, "*Zirconium nitride as inert matrix for fast systems*", Journal of Nuclear Materials, **319**, 51-53 (2003).

[7] M. Streit, "*Fabrication and Characterisation of (Pu,Zr)N Fuels*", Diss. ETH No. 15402, ETH Zurich, Switzerland, 2004.

[8] Y. Arai, S. Fukushima, K. Shiozawa, M. Handa, "*Fabrication of Uranium-Plutonium Mixed Nitride and Thermally Stable Carbide Fuels*", in International Atomic Energy Agency, IAEA-TECDOC-466, 25-33, (1987).

[9] H. Bernard, P. Bardelle, D. Warin, "*Mixed Nitride Fuels Fabrication in Conventional Oxide Line*", in International Atomic Energy Agency, IAEA-TECDOC-466, 43-51, (1987).

[10] G. Pautasso, K. Richter, C. Sari, "*Investigation of the Reaction $UO_{(2+x)}$ +PuO_2 + C + N_2 by Thermogravimetry*", Journal of Nuclear Materials, **158**, 12-18 (1988).

[11] P. Bardelle, D. Warin, "*Mechanism and kinetics of uranium-plutonium mononitride synthesis*", Journal of Nuclear Materials, **188**, 36-42 (1992).

[12] G. Ledergerber, "*Internal Gelation for Oxide and Nitride Particles*", in Japan Atomic Energy Research Institute, Tokaimura, 1996, JAERI-Review 96-009, 1-21,

[13] G. Ledergerber, Z. Kopajtic, F. Ingold, R.W. Stratton, "*Preparation of uranium nitride in the form of microsperes*", Journal of Nuclear Materials, **188**, 28-35 (1992).

[14] S. Daumas, "*Etude et réalisation de support-matrices inertes par le procédé sol-gel pour l'incineration des actinides mineures*", PhD Thesis, Université Aix-Marseille I. (1997).

[15] O. Kubaschewski, C.B. Alcock, P.J. Spencer, in "*Materials Thermochemistry*". Pergamon Press, Oxford, pp 363 (1993),

[16] O. Kubaschewski, C.B. Alcock, "*Metallurgical Thermochemistry*", Pergamon Press, Oxford, pp 447 (1979).

[17] R. Thetford, M.R. Lingard, "*CONFIRM Precalculations: Ideal Operation and Power to Melt*", ARMM/P(02)17 (Issue 2), 2002 – BNFL COMMERCIAL; in Serco Assurance, 2002, SERCO, Oxfordshire (UK).

[18] Y. Arai, K. Nakajima, "*Preparation and characterisation of PuN pellets containing ZrN and TiN*", Journal of Nuclear Materials, **281**(2-3), 244-247 (2000).