FABRICATION AND PROPERTY MEASUREMENTS OF MA NITRIDE FUELS AND LLFP TARGETS

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Abstract

Research on MA nitride fuels and LLFP targets for transmutation of long-lived radioactive elements in JAERI is presented. Inert matrix fuels such as (Am,Y)N and (Am,Zr)N were synthesised by the carbothermic reduction method. Thermodynamic properties such as thermal expansion and heat capacity were measured in Tc-Ru alloy system. Some candidates of ^{129}I target were examined in thermal stability and compatibility with claddings. A new facility for handling MA elements for MA fuels and pyrochemical reprocessing is also introduced.

Introduction

For the management of high level, long-lived radioactive waste, large R & D efforts devoted to transmutation of long-lived radioactive elements are being done in Japan in the frame of the OMEGA program. The Japan Atomic Energy Research Institute (JAERI) has proposed the concept for transmutation of minor actinides (MA: Np, Am and Cm) using accelerator-driven systems (ADS), [1] where MA nitride is adopted as a fuel material of a sub-critical core. Besides MAs as major long-term radiotoxic elements in the waste, a few fission products such as ^{99}Tc and [129]I, which are very long-lived isotopes and potentially mobile, are also considered in the transmutation study.

In the double-strata fuel cycle concept, the nitride fuel has been chosen as a candidate because of the possible mutual solubility among the actinide mononitrides and excellent thermal properties besides supporting hard neutron spectrum. AmN [2,3] and (Cm,Pu)N [4] have already been synthesised by the carbothermic reduction technique using oxide powders as starting materials. The nitrides without oxides were successfully prepared in an excess carbon condition to prevent the formation of oxides. This carbon-rich condition was chosen from the properties that MA elements reduce the stability of carbides and increase the stability of oxides. For the heterogeneous recycling of Am and Cm without U, solid solution or dispersed fuels, so-called Inert Matrix Fuels (IMF), can be used in order to attain the requirements of the target for ADS such as chemical and physical stabilities at high temperature and high radiation fluence. In JAERI, the solid solution nitrides of Am with an inert matrix such as YN and ZrN are being studied on fabrication technique, [5] thermodynamic properties and so on.

The concept of transmutation of ^{99}Tc and [129]I to stable nuclides is an attractive option to reduce the long-term risk of the storage of high-level radioactive waste from nuclear reactors. They can be transformed into stable isotopes by a single neutron capture. Tc metal has been found to be an excellent target material for transmutation. [6,7] In JAERI, some experimental studies on transmutation of Tc have started. [8-10] Firstly, thermal properties such as thermal expansion, heat capacity and so on were measured on Tc-Ru alloy system, because Tc metal target changes to Tc-Ru alloy during irradiation. For I targets, literature survey and experimental studies on fabrication and characterisation of the candidates, $Ca(IO_3)_2$ and CuI, has already started. [10] More recently, compatibility with the cladding materials is being studied.

There is a very limited possibility in Japan to handle and fabricate fuels/targets containing significant amount of MAs such as Am and Cm. In addition an inert atmosphere is necessary for handling of MA nitrides and other MA compounds such as chlorides. Within a collaborative program between JAERI and the Japan Atomic Power Company (JAPC), a new facility, called the Module for TRU High Temperature Chemistry (TRU-HITEC), is under construction in NUCEF. It consists of three hot cells shielded by steel and polyethylene and one glove box, where a high purity argon atmosphere will be maintained. The limiting masses are 10 g of [241]Am and 0.02 g of [244]Cm. Many experimental apparatuses for MA fuels and pyrochemical reprocessing will be installed in the cells and glove box. The TRU-HITEC is expected to become operational in 2003.

Fabrication of MA nitrides

Fabrication of Am-based nitrides containing YN and ZrN as inert matrix was made in glove boxes of Waste Safety Testing Facility (WASTEF) of JAERI. [243]AmO$_2$, Y$_2$O$_3$ and ZrO$_2$ powders were used as the starting materials for fabricating (Am,Y)N and (Am,Zr)N. Mixed nitrides of (Am,Y)N and

(Am,Zr)N with varying Am contents were synthesised by the carbothermic reduction of tabletted oxides-carbon mixture. The synthesis of nitrides was achieved according to the following reaction.

$$MO_X + xC + 1/2 N_2 = MN + xCO$$

The initial carbon/metal ratios were chosen to be in 20-30% excess of the stoichiometric ratios, in order to obtain low oxygen containing nitrides without oxides. The carbothermic reduction heating was done at 1 573-1 773 K in flowing N_2 gas. For fabricating (Am,Y)N, a two-step heating was performed at 1573 K for AmN and 1 773 K for (Am,Y)N, because heating at higher temperature than that for AmN was needed to synthesise YN, as shown in Figure 1. For (Am,Zr)N, one-step heating condition at 1 573 K was chosen, because ZrN was easily synthesised at 1 573 K from ZrO_2. During heating, CO gas released was monitored by an infrared spectrometer to measure the conversion from oxides to nitrides. After confirming almost zero release of CO, the flowing gas was changed from N_2 to $N_2+4\%H_2$ gas mixture to eliminate the residual free carbon contained in the nitrides. The additional heating in $N_2+4\%H_2$ gas was done at 1 773 K. Characteristics of the products of carbothermic reduction were examined by X-ray diffraction and impurities (oxygen, carbon and nitrogen) analysis.

Figure 1. **Typical heating history and CO release in heating conditions for fabricating (Am,Y)N and (Am,Zr)N**
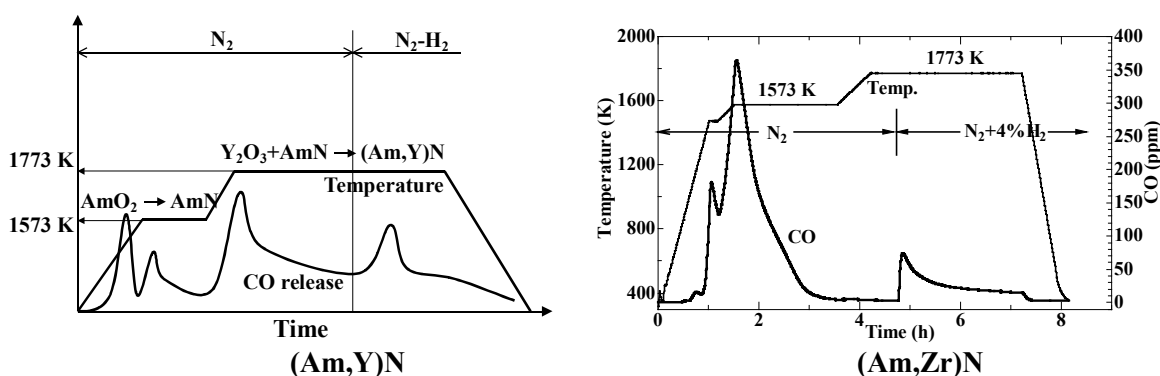

It was found from X-ray diffraction patterns of (Am,Y)N that (Am,Y)N solid solutions without any oxide phases were prepared. The lattice parameters were calculated to be 0.4901-0.4936 nm, as shown in Table 1, assuming that the crystal structure is a NaCl structure. These values are close to the lattice parameters of $(Am_xY_{1-x})N$ estimated from those for AmN and YN using Vegard's law. The chemical analyses of oxygen, carbon and nitrogen contained in the (Am,Y)N solid solutions are also summarised in Table 1. The high oxygen contents over 1wt% are mainly due to oxidation or hydrolysis reaction of (Am,Y)N during the short-time handling in air atmosphere after carbothermic reduction heating. However, the carbon contents are not changed by the reactions. As the result, the solid solutions of (Am,Y)N with low carbon contents below about 1wt% and without oxides were successfully synthesised under the present condition.

Table 1. **The Lattice parameters and the chemical analysis results for (Am,Y)N**

Am content (mol%)	Lattice parameter (nm)	Chemical analysis (wt%)		
		Oxygen	Carbon	Nitrogen
9.1	0.4901±0.0001	1.62	0.67	11.02
19.9	0.4921±0.0002	1.20	0.07	10.43
30.6	0.4936±0.0001	–	0.31	–

For fabrication of (Am,Zr)N, it was found that the carbothermic reduction reaction was almost completed during heating for 3 hrs at 1 573 K, as shown in Figure 1. The extra heating for eliminating free carbon in the sample was intermittently performed for 5 hrs at 1 773 K in flowing N_2+H_2 mixture on the next day. Figure 2 shows the powder X-ray diffraction patterns of the samples containing 10 and 30mol% Am. For the sample with low Am content of 10 mol% Am, the formation of single phase (Am,Zr)N solid solution without oxides such as AmO_2, Am_2O_3 and ZrO_2 was confirmed from the X-ray pattern. On the other hand, for the sample with high Am content of 30 mol% Am, no oxides were formed, but the double splitting of diffraction peaks was clearly observed. From the peak positions of pure AmN and ZrN, it is speculated that a two-phase (Am,Zr)N solid solution with low and high AmN compositions was formed during the carbothermic reduction heating. The lattice parameter of $(Am_{0.1}Zr_{0.9})N$ solid solution was in good agreement with the calculated value of 0.4636 nm based on the Vegard's law using our measured lattice parameters of AmN (0.4992 nm) and ZrN (0.45965 nm).

Figure 2. **X-ray diffraction patterns of (Am,Zr)N containing 30 mol% and 10 mol% Am**
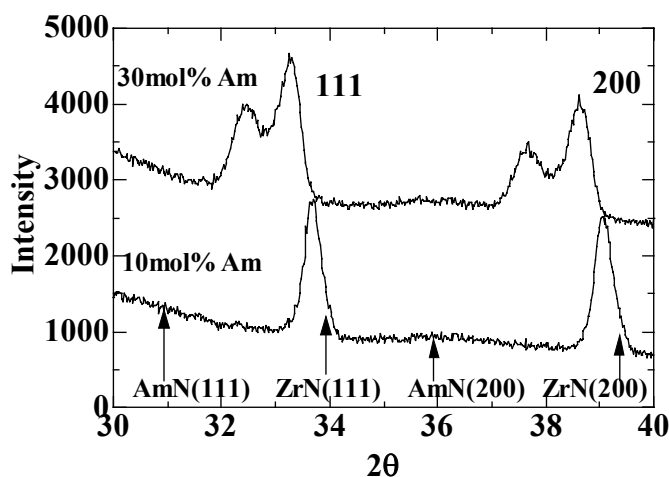
The compositions of the two phase (Am,Zr)N solid solution for 30mol% Am were estimated from the lattice parameters to be 14.5 and 43.1mol% AmN. The chemical analyses indicate that the (Am,Zr)N solid solutions have low oxygen contents less than 0.4wt%, but their carbon contents are higher than those for the (Am,Y)N solid solutions, as shown in Table 2. The difference of oxygen and carbon contents between (Am,Zr)N and (Am,Y)N is mainly due to a difference of the oxygen or carbon affinity between Zr and Y. From only this limited result, the reason for formation of the two phase (Am,Zr)N solid solution can not be determined. In case of PuN-ZrN [11] and UN-ZrN systems, [12] it has been found that they are completely miscible to form the solid solutions in the whole range of composition. From the chemical analyses, the nominal compositions of the $(Am,Zr)(N_{1-x-y}O_xC_y)$ solid solutions are estimated to be $Am_{0.1}Zr_{0.9}(N_{0.894}O_{0.023}C_{0.083})$ and $Am_{0.3}Zr_{0.7}(N_{0.908}O_{0.032}C_{0.060})$, assuming that all the measured oxygen is present in the M(N,O,C) as MO, and that the carbon is present as MC and free carbon. It is supposed that the relatively high carbon content for the Zr-rich nitride is mainly due to higher stability of ZrC compared with Am_2C_3. The free carbon contents were also estimated to be 0.65wt% and 0.23wt% for $Am_{0.1}Zr_{0.9}(N,O,C)$ and $Am_{0.3}Zr_{0.7}(N,O,C)$, respectively.

Table 2. **The lattice parameters and the chemical analysis results for (Am,Zr)N**

Am content (mol%)	Lattice parameter (nm)	Chemical analysis (wt%)		
		Oxygen	Carbon	Nitrogen
10.0	0.4635±0.0001	0.30	1.47	10.35
30.0	0.4654±0.0003	0.34	0.70	8.42
	0.4767±0.0013			

Fabrication and property of LLFP targets

[99]Tc targets

The cylindrical samples of Tc metal and Tc-Ru alloys for measurements of thermal properties such as thermal expansion and heat capacity were prepared by liquid casting technique using an arc-melting furnace and a water-cooled copper mould, where mixed powder of Tc and Ru metals was used as starting materials. The samples were annealed at 1 573 K for 1 h in a vacuum before measurements. Characteristics of the Tc-Ru alloys were examined by SEM-EDX and XRD. Figure 3 shows a rod sample of Tc metal and a disk sample of Tc-Ru alloy.

Figure 3. **(a) Rod sample of Tc metal with a diameter of 4 mm**, and **(b) disk sample of Tc0.26Ru0.74 alloy with a diameter of 5 mm**

(a)   (b)
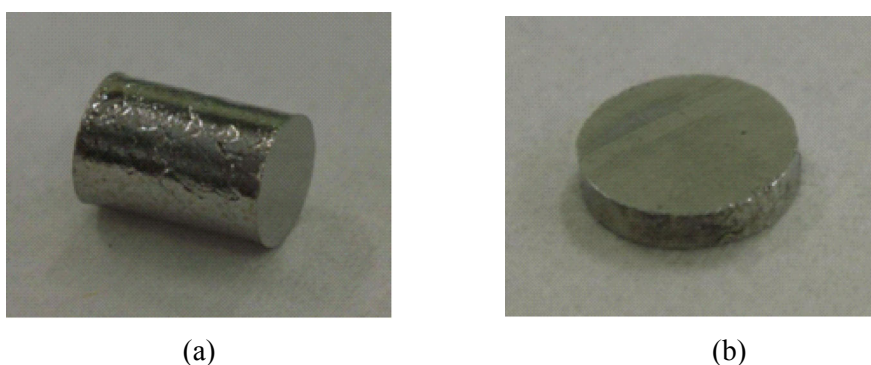
The thermal expansions of Tc-Ru alloys were measured up to 1 300 K with a push-rod dilatometer, where a quartz rod was used as push-rod and the expansion was directly measured with a linear variable differential transformer. The measurements were done in flowing purified Ar gas of 50 ml/min and at a heating rate of 5 K/min. Figure 4 shows the measured thermal expansions of Tc-Ru alloys including Tc, Ru pure metals and cladding candidates of SUS316 and 21/4Cr-1Mo steel. It was found that the thermal expansion of Tc metal is larger than that of Ru metal and that the thermal expansion of Tc-Ru alloys decreased lineally with increasing Ru concentration.

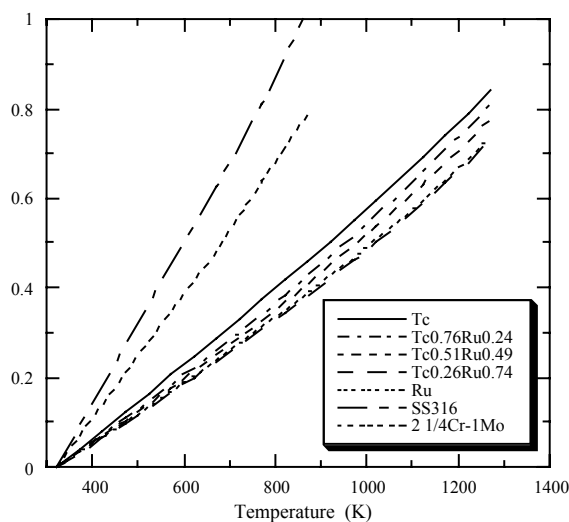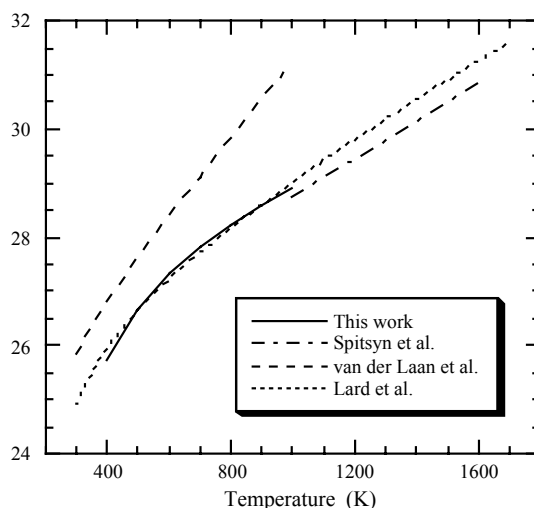Figure 4. **Thermal expansions of Tc-Ru alloys**

Legend:
Tc
Tc0.76Ru0.24
Tc0.51Ru0.49
Tc0.26Ru0.74
Ru
SS316
2 1/4Cr-1Mo

X-axis: Temperature (K)

Figure 5. **Heat capacities of Tc metal**

Legend:
This work
Spitsyn et al.
van der Laan et al.
Lard et al.

X-axis: Temperature (K)

The specific heat capacities of Tc, Ru pure metals and $Tc_{0.51}Ru_{0.49}$ alloy were measured from R.T. to 1 100 K with a differential scanning calorimeter (Netzsch DSC 404), where a sapphire disk was used as standard. The measurements were done in flowing purified Ar gas of 50 ml/min and at a heating rate of 10 K/min. Figure 5 shows the heat capacities of Tc metal. It was found that the specific heat capacity of Tc metal was larger than that of Ru metal, and that the measured specific heat capacity of $Tc_{0.51}Ru_{0.49}$ alloy agreed very well with the calculated value using the Neumann-Kopp rule.

[129]I targets

From the literature survey, two kinds of iodine compounds, $Ca(IO_3)_2$ and CuI, were chosen as tentative candidates of [129]I targets, because CuI and $Ca(IO_3)_2$ are stable in air or moisture atmosphere compared with other iodide compounds such NaI, MgI_2, CaI_2 etc. In JAERI, their thermal stability and compatibility with cladding materials at high temperature are being examined. The sample disks of

CuI and Ca(IO$_3$)$_2$ with theoretical densities of 86%TD and 71%TD, respectively, were prepared by conventional powder method, where the as-pressed disks were heat-treated at 573 K for three hours in flowing argon gas. Figure 6 shows heat-treated disk samples of Ca(IO$_3$)$_2$ and CuI.

Figure 6. **Heat-treated disks of Ca(IO$_3$)$_2$ and CuI with a diameter of 11 mm**

Ca(IO$_3$)$_2$ CuI
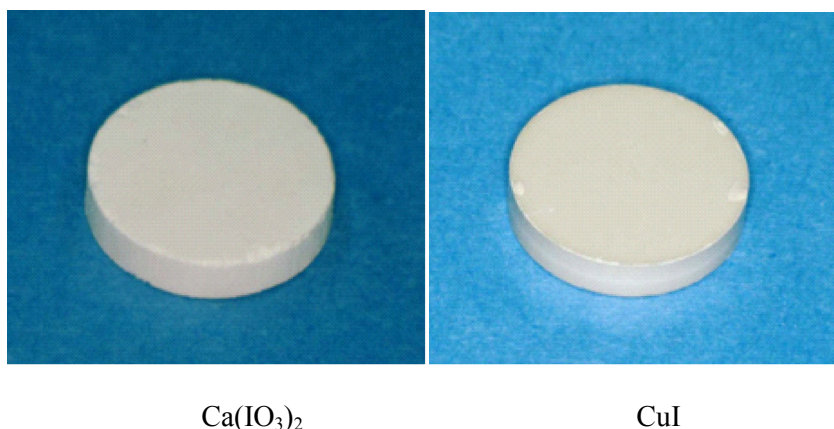
For the compatibility test, some candidates of cladding materials, SUS316 and 2.25Cr-1Mo steel and liner material, Cu, were used. The disks of CuI and Ca(IO$_3$)$_2$ were sandwiched by plates of the claddings, and then sealed in He-filled quartz tubes. The tubes were heated at 723 K for 100 or 500 hours. The experimental conditions and the results of the compatibility examination are summarised in Table 3. It was clearly found that the compatibility of CuI with SUS316 and 2.25Cr-1Mo steel is significantly better than that of Ca(IO$_3$)$_2$ and that Cu is very effective liner material to avoid the corrosion of the claddings.

Table 3. **Experimental conditions and compatibility results for CuI and Ca(IO$_3$)$_2$**

Sample		Heating conditions		Corrosion
Compound	Metal plate	Temperature (K)	Time (h)	
CuI	SUS316	723	100	Slight
CuI	2.25Cr-1Mo steel	723	100	Moderate
CuI	Cu	723	100	No
CuI	Cu	723	500	No
CuI	Cu	623	500	No
Ca(IO3)2	SUS316	723	100	Moderate
Ca(IO3)2	2.25Cr-1Mo steel	723	100	Severe

TRU-HITEC – A new facility for TRU High Temperature Chemistry

The main purpose of the TRU-HITEC is to obtain the fundamental data for MA fuels and pyrochemical reprocessing. The TRU-HITEC has a set of tools to prepare Am-based ceramics in a large scale, and a high purity argon gas atmosphere will be maintained, where impurities of oxygen and moisture are O$_2$ <1 ppm and dew point <-70°C. Figure 7 shows a schematic diagram of TRU-HITEC, which consists of three hot cells shielded by steel and polyethylene and a glove box shielded by leaded acrylic resin. The hot cells and glove box are connected with each other. Each cell is equipped with a wide window made of leaded glass and acrylic resin, and three master-slave manipulators. At the rear of the cell, windows, ports for gloves and suits are arranged to access installed apparatuses by hands. The installation is equipped with two sets of molten-salt

electrochemical cells for pyrochemical reprocessing, cathode processing furnace, high temperature furnace (up to 2 273 K), oxygen potential measurement device, TG-DTA, inspection device, high-temperature XRD and so on. The TRU-HITEC is now under construction and will be available in 2003.

Figure 7. **Schematic diagram of TRU-HITEC**
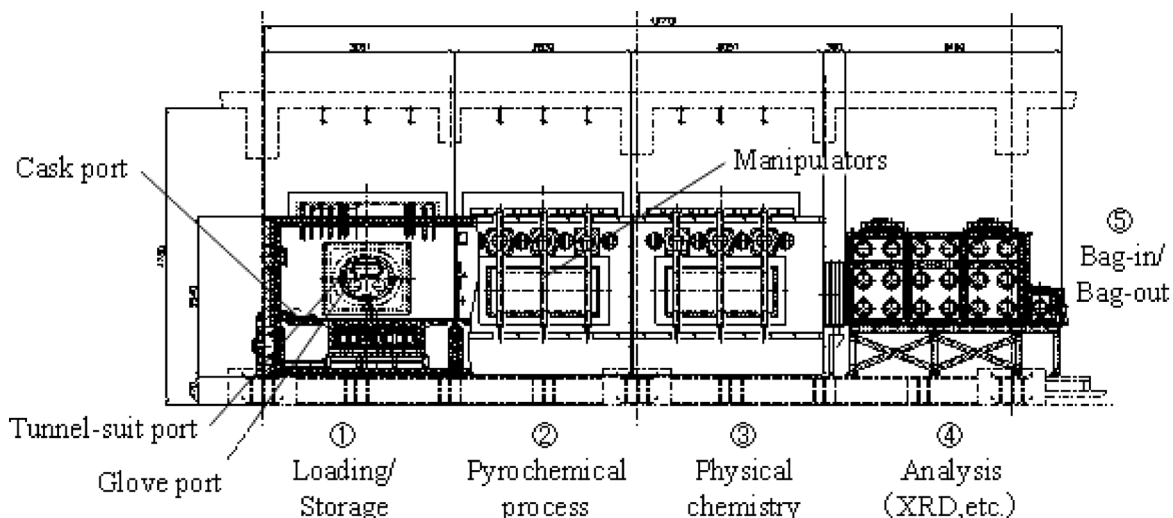
Concluding remarks

The recent results on MA nitride fuels and LLFP target development carried out in JAERI were presented. U-free Am-based nitride fuels diluted by inert matrix such as YN and ZrN were prepared by carbothermic reduction technique for the first time. The thermodynamic properties such as thermal expansion and heat capacity of Tc-Ru alloys were measured to build a database of the Tc metal target. Experimental studies on fabrication and characteristics of I targets were made to select the suitable chemical forms and claddings. A new facility, a Module for TRU High temperature Chemistry (TRU-HITEC), for handling a large scale of [241]Am besides U, Np and Pu is now under construction and will be available in 2003.

REFERENCES

[1] T. Mukaiyama *et al.* (1995), *Partitioning and Transmutation Program OMEGA at JAERI*, Proc. Int. Conf. Global'95, 11-14 September 1995, p.110.

[2] M. Takano, A. Itoh, M. Akabori *et al.* (1999), *Synthesis of Americium Mononitride by Carbothermic Reduction Method*, Proc. Int. Conf. Global'99, Jackson Hole, US, 29 August-3 September 1999, p.110.

[3] M. Takano, A. Itoh, M. Akabori *et al.* (2001), *Synthesis of Americium Mononitride by Carbothermic Reduction Method*, Proc. Int. Conf. Actinides-2001, Hayama, Japan, 4-9 Nov.

[4] M. Takano, A. Itoh, M. Akabori *et al.* (2001), *Carbothermic Synthesis of (Cm,Pu)N*, J. Nucl. Mater., 29424.

[5] A. Itoh, M. Akabori, M. Takano *et al.* (2001), *Fabrication of Americium-based Nitrides by Carbothermic Reduction Method*, Proc. Int. Conf. Actinides-2001, Hayama, Japan, 4-9 Nov.

[6] R.J.M. Konings, A.D. Stalios, C.T. Walker, N. Cocuaud (1998), *Transmutation of Technetium: Results of the EFTTRA-T1 Experiment*, J. Nucl. Mater., 254, 122.

[7] R.J.M. Konings, N. Cocuaud (1998), *Transmutation of Technetium: Results of the EFTTRA-T2 Experiment*, J. Nucl. Mater., 274, 336.

[8] Y. Shirasu, K. Minato (2002), *Thermal Expansions of Technetium-Ruthenium Alloys*, J. Alloys and Comp., 335, 224.

[9] Y. Shirasu, K. Minato (2002), *Heat Capacities of Technetium Metal and Technetium-Ruthenium Alloy*, J. Alloys and Comp., 337, 243.

[10] K. Minato, Y. Shirasu, K. Nishihara (2001), *Fundamental Properties of Targets for Transmutation of Technetium-99 and Iodine-129*, Proc. Int. Conf. Global 2001, Paris, France, 9-13 Sept.

[11] Y. Arai, K. Nakajima (2000), *Preparation and Characterization of PuN Pellets Containing ZrN and TiN*, J. Nucl. Mater., 281, 244.

[12] H. Holleck (1986), in: A.J. Freeman, C. Keller (eds.), Handbook of the Physics and Chemistry of the Actinides, vol.4, North-Holland, Amsterdam, p. 209.