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Evaluation of high plutonia (44% PuO_2) MOX as a fuel for fast breeder test reactor

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ABSTRACT

Uranium plutonium mixed oxide (MOX) containing up to 30% plutonia is the conventional fuel for liquid metal cooled fast breeder reactor (LMFBR). Use of high plutonia (>30%) MOX fuel in LMFBR had been of interest but not pursued. Of late, it has regained importance for faster disposition of plutonium and also for making compact fast reactors. Some of the issues of high plutonia MOX fuels which are of concern are its chemical compatibility with liquid sodium coolant, dimensional stability and low thermal conductivity. Available literature information for MOX fuel is limited to a plutonium content of 30%. Thermodynamic assessment of mixed oxide fuels indicate that with increasing plutonia oxygen potential of the fuel increases and the fuel become more prone to chemical attack by liquid sodium coolant in case of a clad breach. In the present investigation, some of these issues of MOX fuel have been studied to evaluate this fuel for its use in fast reactor. Extensive work on the out-of-pile thermo-physical properties and fuel-coolant chemical compatibility under different simulated reactor conditions has been carried out. Results of these studies were compared with the available literature information on low plutonia MOX fuel and critically analyzed to predict in reactor behaviour of this fuel containing 44% PuO_2. The results of these out-of-pile studies have been very encouraging and helped in arriving at a suitable and achievable fuel specification for utilization of this fuel in fast breeder test reactor (FBTR). As a first step of test pin irradiation programme in FBTR, eight subassemblies of the MOX fuel are undergoing irradiation in FBTR.

1. Introduction

Uranium plutonium mixed oxide fuels containing plutonium up to 30% have been in use since a long time in conventional fast breeder reactors. Only in few cases, sodium bonded MOX test pins containing ‘Pu’ up to 40% has been irradiated in EBR-II [1]. Of late, there has been renewed interest to use high plutonia MOX fuel as test irradiation pins as part of a fuel development programme. High plutonia MOX can also be used in fast reactors for ‘Pu’ burning without any breeding. It can as well be used for fast test reactor. The present investigation is a part of high plutonia MOX (44% PuO_2) fuel development programme in India for use in fast breeder test reactor.

As part of this fuel development programme some important thermo-physical properties and chemical compatibility of the fuel with liquid sodium coolant have been carried out. Phase stability, coefficient of linear thermal expansion, thermal conductivity and high temperature hardness have been experimentally measured. The data obtained have been analyzed in the light of the available literature data for MOX fuel containing 30% PuO_2. Out-of-pile chemical compatibility of this fuel with sodium coolant has been studied by carrying out isothermal annealing of welded closed capsules containing sodium and MOX pellets under different experimental conditions. The extent of reaction was evaluated by X-ray radiography, visual examination, measurement of volume and weight change, X-ray diffractometry and metallography. The following paragraphs highlight the result of these studies.

2. Experimental

2.1. Fuel pellet fabrication

MOX fuel has been fabricated by powder metallurgical route consisting of milling, compaction and sintering. The flow sheet followed for fabrication of the fuel along with quality control and process control steps is given in Ref. [2]. UO_2 and PuO_2 powders were first weighed and then milled together in an attritor to get the required enrichment and homogeneity. The milled powder was precompacted and granulated followed by compaction using a multistation rotary press. The pressing parameters and tool sizes are optimized to get good quality annular pellets. The compacted pellets were sintered at 1650 °C for 4 h in $N_2 + 7\% H_2$ atmosphere. The pellets were subjected to various quality control checks for

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Table 1
Specification of MOX.

Fuel	UO_2–PuO_2
PuO_2	44 ± 1%
O/*M*	1.98 ± .02
Operating peak linear power	250 W/cm
Fissile column length	430 ± 1.5 mm
Flow through SA	1.8 kg/s
Peak burnup	100000 MWd/t
Clad OD/ID	6.60 ± 0.02/5.70 ± 0.02 mm
Pellet OD/ID	5.52 ± 0.08/1.8 ± 0.2 mm
Linear mass of pellet	2.20 ± 0.10 g/cm
Pellet density	94 ± 2% TD
Insulation pellet length	6 mm

acceptance. Table 1 presents the specification of the sintered pellets.

2.2. Thermo-physical property measurement

2.2.1. Phase stability and coefficient of thermal expansion

Studies on phase stability and measurement of coefficient of linear thermal expansion were carried out using a horizontal dilatometer. A graphite sample holder and a push rod assembly were used in conjunction with an LVDT, maintained at constant temperature. For phase stability studies, sintered pellet was heated continuously from ambient to a maximum of 1200 °C, under high purity Argon cover gas. The change in length was monitored as a function of temperature both during heating and cooling. These experiments were carried out number of times under different experimental conditions of maximum temperature and heating rate and a plot of $\Delta L/L$ vs. temperature was obtained. Any phase instability during heating/cooling will be manifested by sudden expansion/contraction at any particular temperature. The linear thermal coefficient of expansion between ambient to 1200 °C was also estimated from the length change data and an expression for the percentage change in thermal expansion as a function of temperature was obtained.

2.2.2. Thermal diffusivity/conductivity

Thermal conductivity (k) data was determined from the thermal diffusivity (α, cm^2/s), specific heat (C_p, J/g) and density (ρ, g/cm^3) using the relation,

$$k = \alpha.\rho.C_p. \tag{1}$$

Thermal diffusivity was experimentally measured between 800 K and 1800 K by laser flash method. The details of the experimental procedure are given in reference [3]. The density (ρ) of the sample which is a function of temperature was corrected using the thermal expansion data generated in this study. The heat capacity of MOX fuel was obtained from literature for UO_2 [4] and PuO_2 [5] and using Neumann Kopp's relation assuming ideal solution behavior.

2.2.3. Fuel-coolant chemical compatibility

Out-of-pile chemical compatibility of MOX fuel with liquid sodium coolant was carried out by isothermal annealing of MOX pellets in liquid sodium at 700 °C and 800 °C for times ranging from 29 h to 500 h, in welded closed capsules. The size of the experimental capsules and the internal arrangements were different for different studies, suitable to different experimental conditions. The variables were time and temperature of heating, sodium purity (in terms of 'O' content), sodium to fuel volume ratio, physical state of the MOX pellet with respect to sodium i.e. direct contact with sodium or MOX pellets in artificially created breached D9 welded pins.

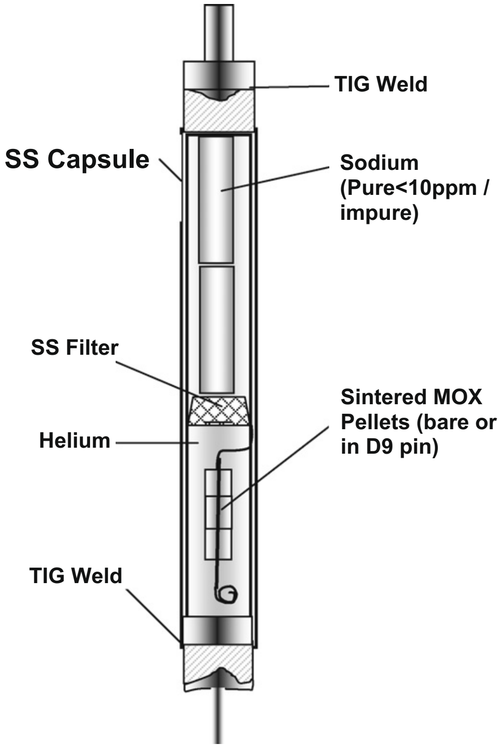

Fig. 1. Typical schematic diagram of MOX sodium compatibility capsule; type of capsules with 'Ti' sponge [high purity sodium ('O' <10 ppm)]; without 'Ti' sponge; high sodium to fuel ratio; MOX pellets in welded D9 pin.

Capsule design: Typical capsule design is shown in Fig. 1. It has essentially got two compartments, 'A' and 'B' separated by a stainless steel mesh used for filtration of liquid sodium from extraneous impurities like oxides of sodium or 'Ti' sponge used to purify the sodium. Compartment 'A' contains either fuel samples as pellets or a small welded pin in D9 tube or with longitudinal cuts of sizes 370 μm thick and lengths 1, 2 and 3 mm long made by laser. This capsule configuration simulates the conditions of a major leak of sodium in case of breached fuel pin in a reactor when MOX pellet comes in direct contact with large volume of sodium. Sodium purity varied from highly pure to that containing 100 ppm 'O' (maximum).

Heating procedure: The welded capsules were first radiographed by X-ray radiography and then heated at 700 °C for 2 h in a vertical furnace with compartment 'B' (containing sodium) at the bottom end. In some of these experiments sodium was further purified by 'Ti' sponge. The capsule was made upside down in hot condition when purified liquid sodium percolates through the stainless steel mesh and comes in contact with MOX pellets or the small welded D9 fuel pins. Intermittent X-ray radiography was carried out to observe any dimensional changes or physical changes in the pellets developed during heating. After each radiography, the capsule was again loaded in the furnace with compartment 'B' in the upright position so that solid sodium again comes down the mesh and comes in contact with the fuel pellet or the leaked pins. After the stipulated time period, the final radiography was done and the outer capsule was cut open. The condition of the pellet/pin was visually examined and pin diameter was measured.

Sodium removal: After completion of heating schedule sodium from the pellet was removed by either vacuum distillation or by dissolution in methyl/ethyl alcohol. In case of vacuum distillation, MOX pellets were heated to 450 °C for 2–3 h in vacuum of $10^{-1.5}$ torr. Alternately MOX pellets were immersed in ethyl alcohol when sodium is dissolved in alcohol and the pellets were

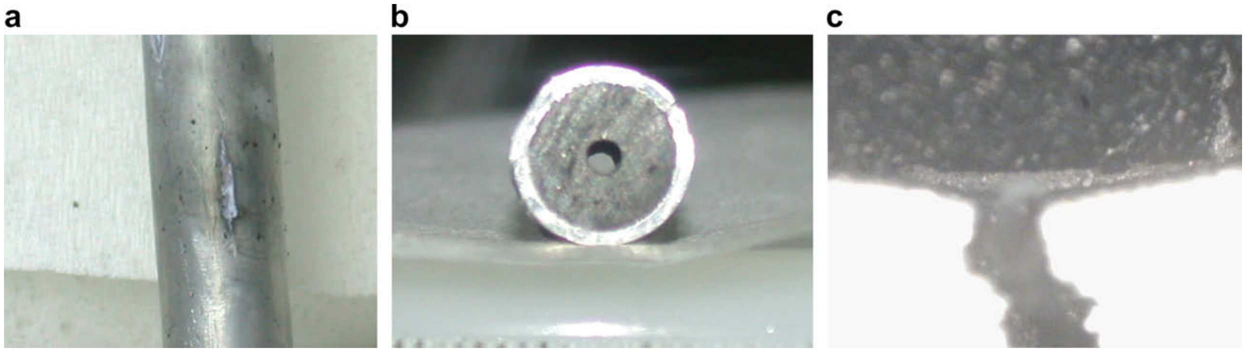

Fig. 2. Photograph of MOX fuel pellets in D9 cladding tube after 350 h at 700 °C; (a) D9 pin showing 'Na' entry through the artificially created breach; (b) cross section of the D9 Pin with annular MOX pellet; (c) breach in D9 cladding and the MOX pellet.

recovered for subsequent metallographic study. In case of test capsules containing MOX pins, the pins were sliced at the middle of the longitudinal defect using a slow speed cut off wheel along with the MOX pellets so that the cut section shows the cross section of the pellet and the D9 clad (Fig. 2). After sodium extraction, MOX pellets were weighed and samples were studied by X-ray diffractometry and metallography. Metallography was carried out by vacuum impregnation technique, as the pellets become fragile after heating.

3. Results and discussion

3.1. Phase stability

A typical results showing percentage expansion vs. temperature is shown in Fig. 3. As there was negligible change in the length of the sample, it can be deduced that there was no phase transformation in the temperature range from ambient to 1200 °C. However, the slight change in the sample size observed after the cycle can be attributed to the thermal lag between the heating and cooling rates and this effect is expected to be more pronounced at higher heating/cooling rates. Dimensional stability of MOX pellet is most important during reactor start up and shut down operation when fuel temperature could go down to as low as 453 K during reactor shut down and may go up to temperature above 723 K during start up. For safe operation of the reactor it is expected that the fuel should not undergo any phase change in this temperature range. Apart from dimensional instability any phase separation may lead to different 'Pu' redistribution between the phases and its effect on reactor operation. Phase stability of MOX fuel containing high plutonia has been reported by Markin et al. [6] and Sari [7]. They have observed that mixed oxide fuel with an (O/M) ratio of 2.00 would exist as single phase. However, for (O/M) ratio less than 2, it will exist as two phase mixture below 723 K and single phase at high temperature. No data on phase stability is available for MOX fuel with 44% PuO_2. However, Markin and Street [6] observed using high temperature X-ray that six oxides of $(U_{0.58}\,Pu_{0.42})O_{2-x}$ with O/M ratio between 1.79 and 2.00 become single phase from two phase cubic in the temperature range 473–773 K depending upon the (O/M) ratio. Sari et al. [7] also carried out similar studies by hydrogen reduction and using high temperature XRD and ceramography. Markin et al. [6] reported this phenomenon would occur for plutonium content of more than 30%, however, Sari et al. [8] observed that this is possible even for MOX containing 20% Pu. So, hypostoichiometric MOX will become two phase with different (O/M) ratio and Pu content and to maintain equilibrium the 'Pu' distribution will also be different. Markin's data of 42% Pu is close to the composition of interest in this study i.e. 44% PuO_2. Markin observed a transition at 723 K for (O/M) of 1.98 and for still higher (O/M) ratio the transition temperature will be lower. The (O/M) ratio of MOX fuel in this study was 1.98 ± 0.02 and no measurable phase transition could however be detected by dilatometry in the heating/cooling curve between ambient to 1200 °C. This was also supported by X-ray diffractometry studies when one of the samples, after a heating and cooling cycle indicated single phase.

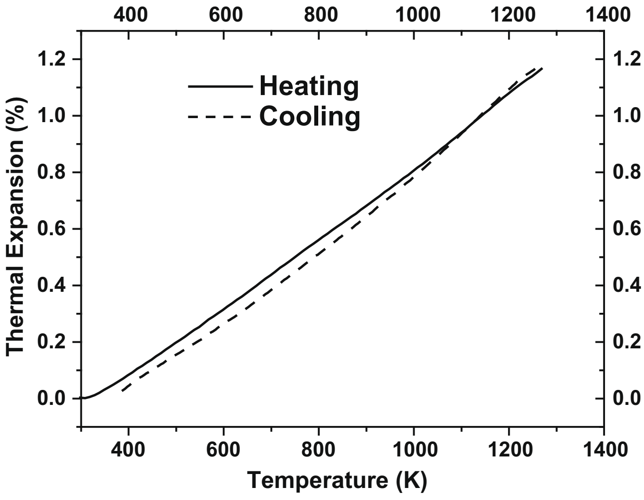

Fig. 3. Thermal expansion and phase stability of MOX fuels.

3.2. Coefficient of thermal expansion

Coefficient of linear thermal expansion was determined from the plot of change in length vs. temperature (Fig. 3). Percentage $(\Delta L/L)$ could be expressed as a function of temperature by the following relation:

$$(\Delta L/L)\times 100 = -0.071 + 0.001.T - 1.692\times 10^{-7}.T^2 + 2.0182\times 10^{-10}.T^3 \tag{2}$$

$(R^2 = 0.99;\ SD = 0.0499;\ Accuracy = \pm 6\%)$

The average coefficient of linear thermal expansion was found to be 12.52×10^{-6}/K (ambient to 1000 °C) and the same for MOX containing 30% PuO_2 is 10.65×10^{-6}/K obtained from MATPRO [8]. The MATPRO data was calculated from an expression which is valid from 5 to 30% PuO_2. It is observed that thermal expansion of MOX containing 44% PuO_2 is slightly higher that that of MOX containing 30% PuO_2.

3.3. Thermal conductivity

Thermal conductivity data was corrected for porosity (p) to 95% TD from 82% TD using the following relation [4]:

$$k_0 = k_p(1 - \beta.p), \tag{3}$$

where $\beta = 206–0.5t$, $t = T(\mathrm{K})/1000$, [4] the data obtained could be expressed by the following relation:

$$k = 1/(-0.61 + 1.42 \times 10^{-3} - 3.93 \times 10^{-7}.T^2). \tag{4}$$

Fig. 4 shows the plot of thermal conductivity as a function of temperature for UO_2, MOX (PuO_2: 44%; this study) and MOX (5–30% PuO_2;) corrected to 95%TD. It was observed that thermal conductivity decreases with increase in temperature and follows a 1/(A + B.T) relation, typical of dielectric solids when mode of heat conduction is phononic in the low temperature range. Thermal conductivity of MOX containing 44% PuO_2 was found to be 1.803 W/m K while the same for MOX containing 30% PuO_2 was 2.326 W/m K at 1000 °C. The lower thermal conductivity of MOX fuel is attributed to the effect of PuO_2 content. MATPRO data however does not take into account the effect of PuO_2 and had recommended a common single relation for PuO_2 content varying between 5–30% PuO_2. Gibby [9] and Martin [10] have carried out extensive work on MOX fuel containing up to 30% PuO_2. Gibby concluded that the effect of PuO_2 content is more at lower temperature than that at high temperature and at each temperature thermal conductivity decreases with increase in PuO_2 content and attains a minima at around 50%. The lower thermal conductivity of MOX fuel will not be much concern as the pellets used are annular and hence the temperature gradient from the fuel centre to the periphery will be less.

3.4. Fuel-coolant chemical compatibility

Thermodynamic assessment [11–15] of MOX fuel up to 30% PuO_2 indicates that the formation of a fuel sodium reaction product (FSRP) depends on the oxygen potential of the fuel (O/M ratio) and 'O' content in sodium. Thermodynamic calculation on the MOX fuel containing 44% PuO_2 ($O/M = 1.98$) also indicates that there is possibility of such a reaction, as with addition of PuO_2, the oxygen potential of fuel increases making the fuel more prone to 'Na' attack. The formation of FSRP could be controlled by limiting the availability of 'O' at the reaction site. The source of oxygen could either be from fuel or 'Na'. The reaction product is of the type Na_3MO_4 [M = U + Pu] having a density of 5.6 g/cm^3 compare to 11 g/cm^3 of MOX. Hence the formation of FSRP results in a volume increase which could be catastrophic if the reaction continues to proceed. However, when clad breach is small, this voluminous product, Na_3MO_4, plugs the gap. The formation of FSRP should manifest itself by volume increase and a proportional weight increase. The formation of FSRP can also be detected by metallography, X-ray diffractometry of the reacted fuel. In this study X-ray radiography measurements of the dimension of the fuel pellet after heating at 700 °C for 310 h and 800 °C for 190 h indicate volume increase of 21% and 26.1%, respectively, and the weight increase was in the range of 1.85–2.24% only. Similarly in another test, the percentage volume increase for MOX pellet at 700 °C was measured as a function of time up to 29 h and the maximum volume increase was 40% till saturation. These results agree with the extrapolated result of 23% from Housseau et al. [13]. The maximum volume increase observed by Mignanelli and Potter [14] for UO_2–30%PuO_2 was 9.01% at 800 °C after 17 h for an initial O/M ratio of 1.996. The corresponding weight change was 1.03%. Housseau et al. [14] also observed a maximum volume increase of 9% for UO_2–30%PuO_2 at 750 °C for 500 h, with an initial O/M of 2.00. The same for 76% PuO_2 at 750 °C for 500 h with an initial O/M of 2.00 showed a volume increase of about 38% and that for 100% PuO_2 is about 51%. However, in none of the tests mentioned in literature or in this study the net weight increase was commensurate with the volume increase e.g. for $MO_{1.996}$ (30% PuO_2) at 800 °C after 17 h, volume increase was 9.01% while the weight increase was only 1.03% [15]. Hence, the total volume increase may not be due to the formation of the reaction product alone. In these studies, it was observed that MOX pellets undergo cracking without loss of integrity and presence of residual elemental sodium was observed (Fig. 5) within the pellet cross section in the pores and the cracks even after distillation of sodium. This phenomenon has also been reported in literature. So, the large volume increase observed can be attributed to the crack formation and sodium ingression into pores and cracks. The weight increase could be partly due to the presence of residual sodium within the pellets (even after sodium distillation under vacuum) and partly due to FSRP formation. In this study, about 20 capsules containing MOX pellets and sodium under different conditions were heated at temperatures 700 °C and 800 °C for times up to about 500 h. However, XRD of the fuel samples after the test could not detect the compound Na_3MO_4, possibly due to the small extent of reaction product. Moreover, the pellets remain integral and did not lose shape. So, it was concluded from this study that sodium fuel reaction will not create any serious safety issue since the reaction product will be very small and there will be sufficient time gap between the detection of delayed neutron signal from a leaky pin and discharge of fuel or fission fragments in to the coolant channel.

RBCB (run beyond clad breach) experiment in the literature [16] seems to indicate the formation of FSRP as a very thin layer (150 μm) at the pellet-clad interface. However, it can be well accommodated since the hot fuel creeps if the matrix density of the fuel is of the order of 90% TD or lower. Further the FSRP formation is reported to be localized to the defect site. As a supportive

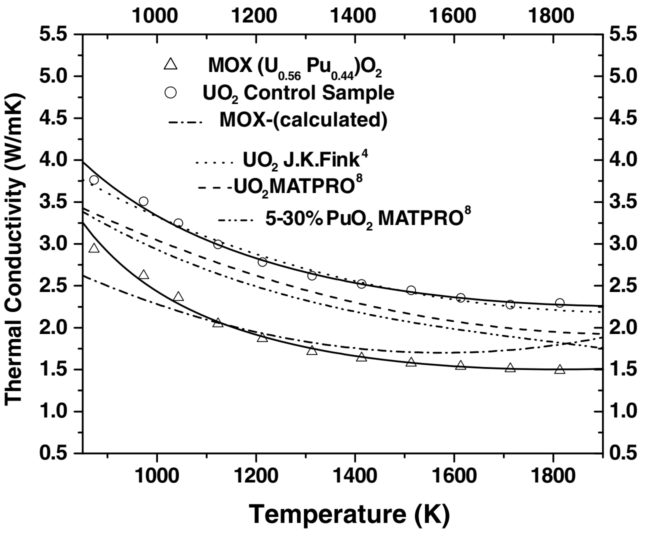

Fig. 4. Thermal conductivity (corrected to 95% TD) of MOX and UO_2 as a function of temperature.

Fig. 5. MOX pellets at 700 °C after 400 h. Showing cracks and sodium patches on the surfaces of pellet.

evidence of the operation of failed LMR oxide fuel element in European fast reactors it has been suggested that a small defect develops very slowly and a large defect in ‘end-of-life’ pins resulted in limited fuel loss. The formation of FSRP is important in high burn up fuel and the physical properties of FSRP and kinetics are beneficial. This may protect open cracks and in no case, have hazardous condition affecting reactor safety, been experienced.

4. Conclusions

As part of MOX fuel development programme, thermo-physical and thermo-chemical properties of hitherto unknown MOX fuel containing 44% PuO_2 have been measured to address the issues of this fuel, like phase stability, low thermal conductivity and fuel-coolant chemical interaction. It was observed that there was no phase instability of the MOX fuel up to 1200 °C. Thermal conductivity of this fuel was slightly lower than that of MOX containing 30% PuO_2 but as it consists of annular pellets, this small difference in thermal conductivity should not have serious impact on the fuel centre temperature.

The fuel-coolant chemical compatibility studies show that although thermodynamically there is a possibility of reaction between fuel ($O/M = 1.98$) and sodium, out-of-pile experiments did not reveal any detectible reaction product. So, even if it is formed in small quantities, the resulting volume increase of the reaction product could be accommodated within the fuel having lower smear density and may not cause any serious safety issue of hindering the sodium flow in the coolant channel. Also, the kinetic of the reaction is slow and determined by the availability of ‘O’ and ‘Na’ at the reaction site. The results of these studies have been encouraging and based on these observations eight sub assemblies of MOX fuel containing 44% PuO_2 has been undergoing irradiation in FBTR.

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References

[1] E.A. Aitken, S.K. Evans, G.F. Melde, B.F. Rubin, in: Proceedings of the Conference on Fast Reactor Fuel Element Technology, Amer. Nucl. Soc., April 13–15, 1971, p. 459.
[2] J.P. Panakkal, J. Nucl. Mater. (in press), doi: 10.1016/j.nucmat.(2007).09.024.
[3] A.K. Sengupta, S. Majumdar, C. Ganguly, D.S.C. Purushotham, P.R. Roy, Am. Ceram. Soc. Bull. 65 (7) (1986) 1057.
[4] J.K. Fink, J. Nucl. Mater. 279 (2000) 1.
[5] International Atomic Energy Agency, Thermophysical Properties of Materials for Watercooled Reactors, IAEA-TECDOC-949, 1997, p. 51.
[6] T.L. Markin, R.S. Street, J. Inorg. Nucl. Chem. 29 (1967) 2265.
[7] C. Sari, U. Banedict, H. Blank, J. Nucl. Mater. 35 (1970) 267.
[8] IAEA TECDOC 949, June (1997).
[9] R.L. Gibby, J. Nucl. Mater. 38 (1971) 163.
[10] D.G. Martin, J. Nucl. Mater. 152 (2–3) (1988) 94.
[11] P.E. Blackburn, in: Proceedings of the International Symposium on ‘Behaviour and Chemical State of Irradiated Ceramic Fuels’, Vienna, 7–11 August 1972, p. 393.
[12] M.G. Adamson, E.A. Aitken, in: Thermodynamics of Nuclear Materials, vol. I, 1974, p. 233.
[13] M. Housseau, G. Dean, F. Perret, in: Proceedings of the International Conference on ‘Behaviour and Chemical State of Irradiated Ceramic Fuels’, Vienna, 7–11 August 1972, p. 349.
[14] M.A. Mignanelli, P.E. Potter, J. Nucl. Mater. 125 (1984) 182.
[15] M.A. Mignanelli, P.E. Potter, J. Nucl. Mater. 130 (1985) 289.
[16] R.V. Strain, J.H. Bottcher, S. Ukai, Y. Arii, J. Nucl. Mater. 204 (1993) 252.