Journal of Alloys and Compounds 271/273 (1998) 557–562

Actinide transmutation: new investigation on some actinide compounds

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Abstract

Mixtures of actinide oxides with other oxides have been studied for transmutation of long-lived isotopes in nuclear power reactors and for optimization of plutonium consumption in fuels. These materials are solid solutions or composites selected with criteria used for classical fuels, and pellets with uranium, neptunium or plutonium have been prepared and characterized. The actinide phases analyzed in composites with magnesia are not fully compatible with the phase diagrams previously published. The results of specific heat measured on $(Y,U)O_{2+x}$ solid solution show a deviation from Kopp's law, and the effect of substitution of multivalent actinides by trivalent ions is discussed. Irradiation damage produced by fission products have been studied by simulation with ion irradiation. The good behavior of the actinide compounds with magnesium oxide, and the favorable effect of addition of actinide oxide in inert matrices had been observed.

Keywords: Actinides oxides; Plutonium; Neptunium; Transmutation; Thermal properties; Irradiation damage

1. Introduction

The actinides produced in nuclear fuels constitute an important part of the high level radioactive waste. Quantities and radiotoxicity of neptunium, plutonium, americium, and curium present in the irradiated fuels unloaded each year from the 55 French Pressurized Water Reactors (more than 550 kg, 11 800 kg, 450 kg and 55 kg respectively) may not lead to choose the direct storage of the spent fuels for very long time. Today the plutonium is partitioned from the irradiated fuels at the La Hague reprocessing plant, and in the near future, the neptunium could be also partitioned without difficulties. Therefore, investigations to reduce the radiotoxicity of these actinides are in progress and a promising scenario is to increase the consumption of plutonium by fission and to transmute the long-lived isotopes in the nuclear power reactors (isotopes involved are ^{237}Np, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu, ^{241}Am, ^{243}Am, and ^{245}Cm). An important effort in basic research on these transuranium elements occurs now, and various studies are developed in a wide international collaboration program including two parts: solution chemistry for partitioning of americium and curium from irradiated fuels in reprocessing plants, and solid state physics and chemistry of Np, Pu, Am, or Cm compounds for the selection of the best materials for fission or transmutation targets. This study on fabrication, characterization, thermophysical properties, and irradiation damages of actinide compounds is included in the second part.

2. Actinide compound criteria

The targets are pins made with pellets of actinides dispersed in inert matrices in order to optimize the elimination of the long-lived actinide isotopes by irradiation (multirecycling or once-through options). The compatibility with the nuclear technology available today (Pressurized Water Reactors and Fast Neutron Reactors using oxide fuels) imposes a priority for investigations on oxides. However, other materials like nitrides, intermetallic compounds or alloys will be considered in a second stage [1] and they are not presented here. The inert matrices are transparent to the neutrons and their properties must be similar or better than properties of $UO_{2\pm x}$: melting point (above 2000°C), thermal conductivity, behavior under irradiation (swelling), accommodation to the fission and transmutation products, and chemical stability. Refractory mixtures of actinide oxide with non-actinide oxides transparent to the neutrons and relatively stable under neutron irradiation have been selected (Table 1). The majority of these mixtures produce ceramic–ceramic composites (cer-

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0925-8388/98/$19.00
PII: S0925-8388(98)00154-6

Table 1
Actinide compounds selected and studied.

An	M=Y	M=Ce		M=U
Composition of (M, An)O_2 solid solutions				
U	$(Y_{0.6}U_{0.4})O_{2\pm0.1}$[a]	$(Ce_{0.6}U_{0.4})O_{2\pm0.02}$[a]		UO_2[a]
Pu		$(Ce_{0.6}Pu_{0.4})O_{2\pm0.02}$		$(U_{1-y}Pu_y)O_{2\pm0.02}$[b]
Composition of M_mO_n–AnO_2 composites (molar ratio are in brackets)				
An in AnO_2	M_mO_n			
	Al_2O_3	MgO	$MgAl_2O_4$	$Y_3Al_5O_{12}$
U	[0.8/0.2][a]	[0.9/0.1][a]	[0.74/0.26][a]	[0.4/0.6][a]
Np	[0.8/0.2]	[0.9/0.1]	[0.66/0.34]	
	[0.93/0.07]	[0.75/0.25]		
Pu		[0.9/0.1]		

[a] compound irradiated with ions.
[b] $0<y<0.5$.

cers) of actinide oxide dispersed in inert matrix. The heterogeneity in distribution of actinide in pellets is a strongly influent parameter for properties and behavior under irradiation, and two types of microstructure have been developed: microdispersed actinide oxide phase in inert matrix, or calibrated macromass of actinide oxide uniformly distributed in inert matrix to control the heterogeneity. There are also few solid solutions and mixed oxides of Y_2O_3 or CeO_2 with actinide oxides have been studied.

3. Fabrication and characterization of pellets

The pellets of actinide compounds were prepared by dry mixing of oxide powders, then cold pressing and sintering at high temperature (>1500°C) under controlled atmosphere. The oxygen potential in our furnace had been calibrated with zirconia probe. This dry process was used for compatibility with the fabrication units working today and for limitation of production of waste (the industrial fabrication scale would be several tons per year). The process was systematically tested previously with uranium before to prepare the transuranium compounds. The microstructure and the composition of sintered pellets have been controlled by optical microscopy and X-ray Diffraction (XRD). The effect of actinide on microstructure of sintered pellets of microdispersed MgO–$AnO_{2\pm x}$ composites is presented on Fig. 1. The two phases MgO and actinide oxide are distinctively visible on micrographies. The actinide oxide phases (in white on micrographies) are larger for uranium, and their grain sizes are lightly decreasing from uranium to plutonium. The XRD analyses reported in Table 2 confirm partially the published results on actinide oxide phases [2–8]: stoichiometric dioxide is present after sintering at 1750°C under reducing atmosphere of dry Ar+5%H_2 ($\Delta G(O_2)=-500$ kJ mol^{-1} at 1750°C) for uranium and neptunium, whereas plutonium oxide is reduced with dissociation in two phases ($PuO_{1.98}$ and α cubic ⟨Pu_2O_3⟩) after sintering at 1500°C under slightly more oxidizing atmosphere of Ar +5%H_2+2500 ppm H_2O ($\Delta G(O_2)=-380$ kJ mol^{-1} at 1500°C). These results are in good agreement with the stability of tetravalent uranium and neptunium in ionic solids, comparatively with plutonium more easily reduced to trivalent ion. However, contrary to the published Np–O phase diagram [3] which predicts actinide metal precipitates for the oxygen potential used, no neptunium metal has been observed by XRD in neptunium composites. The Np metal would be visible on XRD spectrum because its content is approximately at the same level than cubic α⟨Pu_2O_3⟩ in plutonium composite. This α cubic ⟨Pu_2O_3⟩ phase detected in our pellets by X-ray Diffraction at room temperature, is the cubic phase previously reported by Gardner et al. [8] which is produced below 300°C by an eutectoid reaction. This phase is in equilibrium with PuO_{2-x} (cubic fluorite structure) between room temperature and 300°C. Its structure is based on pseudo body-centered cubic lattice, bixbyite type with space group T_h^7 (Ia3) like Mn_2O_3, and our results on the lattice parameter ($a=1.1036\pm0.0013$ nm) are slightly lower than published data $1.105<a<1.107$ [8–10]. The stoichiometry $PuO_{1.515}$ proposed by Gardner et al. had been estimated by extrapolation from results on lattice parameters, but it has never been confirmed by direct analysis. On the other hand, our results of XRD determine the composition limit $PuO_{1.98}$ for the second cubic phase PuO_{2-x} (fluorite cell) at room temperature (unit cell dimensions $a=0.5398\pm0.0001$ nm). At high temperature, there is only the cubic phase with fluorite type cell, and its composition for the conditions used during sintering of PuO_2–MgO pellets which are typical for industrial fabrications, is estimated from published data [11,12] at $PuO_{1.97}$. Therefore, the molar composition of the plutonium oxide dispersed in MgO at room temperature is: 0.021 α$PuO_{1.515}$+0.979 $PuO_{1.98}$. Similar unpublished results were previously obtained in our laboratory with

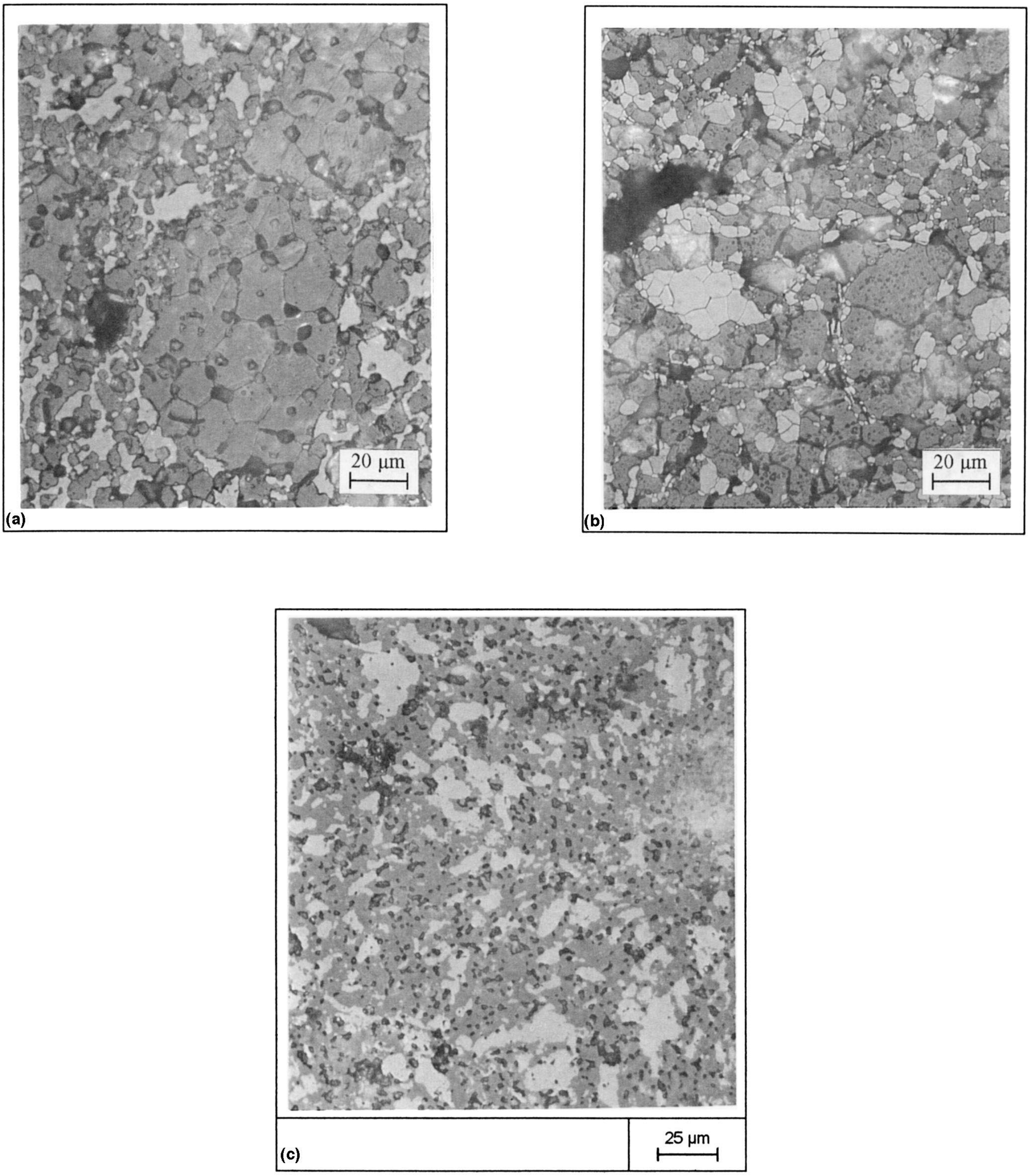

Fig. 1. Microstructure of MgO–AnO_2 microdispersed composites. a. MgO–UO_2; b. MgO–NpO_2; c. MgO–PuO_2.

pellets of 0.015 $\langle PuO_2\rangle$–0.985 MgO and 0.038 $\langle PuO_2\rangle$–0.962 Al_2O_3 sintered under dry Ar+H_2. In the present work, 2500 ppm H_2O were added to the atmosphere during sintering, and the needles of Widmanstatten precipitates typical for microstructure of $\alpha\langle Pu_2O_3\rangle$ [13] are not observed on micrography of PuO_2–MgO composites.

Finally, our results associated with thermodynamics of actinide oxides [8,14–16] confirm the necessity to use an

Table 2
Sintering conditions and composition of MgO–AnO$_2$ microdispersed composite pellets.

Composite	Sintering conditions		Composition,
	Temperature,°C	Atmosphere	analyzed by XRD
MgO–UO$_2$	1750	Ar+5%H$_2$	MgO+UO$_2$
MgO–NpO$_2$	1750	Ar+5%H$_2$	MgO+NpO$_2$
MgO–PuO$_2$	1500	Ar+5%H$_2$+O 2500 ppm H$_2$	MgO+PuO$_{1.98}$ +α⟨Pu$_2$O$_3$⟩

oxidizing atmosphere at low temperature for Pu, Am or Cm composites to avoid the dissociation in two actinide oxides by an eutectoid reaction. For ⟨PuO$_2$⟩–MgO composite for instance, the oxygen potential must be maintained above −350 kJ mol^{-1} at temperatures below 700°C.

4. Thermal properties of actinide oxide compounds

Thermal properties of actinide compounds are measured in glove-boxes in our laboratory, and new results for solid solutions are presented on Fig. 2 and Fig. 3. The thermal conductivity K, is calculated from specific heat C_p and thermal diffusivity a: $K=a\rho C_p$ (ρ is the density of material). The specific heat was measured by Differential Scanning Calorimetry and the thermal diffusivity was measured on disk by laser flash technique. The results of measurement of specific heat on pellets of the solid solution (Y$_{0.6}$U$_{0.4)}$O$_{2.0\pm0.1}$ can be compared on Fig. 2 with data from calculation with the Kopp's law for mixtures [17,18]. The Kopp's law for solid solutions of oxides (M$_{1-y}$An$_y$)O$_{2+x}$ is:

$$C_p[(M_{1-y}An_y)O_{2+x}] = (1-y)C_p[MO_{2.0}] + yC_p[AnO_{2.0}] + x/2C_p[O_2].$$

For sesquioxide compounds M$_2$O$_3$, the equivalent specific heat to C_p[MO$_{2.0}$] is 0.5(C_p[M$_2$O$_3$]+C_p[O$_2$]). The experimental data are significantly higher than calculated data, in the range of temperature studied. The mechanism for heat transfer in oxides between room temperature and 1400°C is governed essentially by the phonons, and therefore the deviation from Kopp's model is probably induced by the structure of defects and bonding energies in crystals. The mixed oxide (Y$_{0.6}$U$_{0.4)}$O$_{2\pm x}$ crystallizes with cubic fluorite cell like UO$_2$. In these crystals, uranium cannot be exclusively tetravalent because yttrium remains only trivalent and composition of mixed oxide is not ($\mathrm{Y}^{3+}_{0.6}\mathrm{U}^{4+}_{0.4}$)O$_{1.7}$ with high concentration of oxygen vacancies (more than one by M$_4$O$_8$ unit cell). On the other side, the limit for ionic composition is the stoichiometric compound ($\mathrm{Y}^{3+}_{0.6}\mathrm{U}^{6+}_{0.3}\mathrm{U}^{4+}_{0.1}$)O$_2$ with clusters between Y^{3+}, U^{4+}, and U^{6+} but the low oxygen potential used during sintering avoids the oxidation of significant amount of uranium cations to hexavalent ions. The C_p data calculated with the Kopp's law for stoichiometric compound are 30%

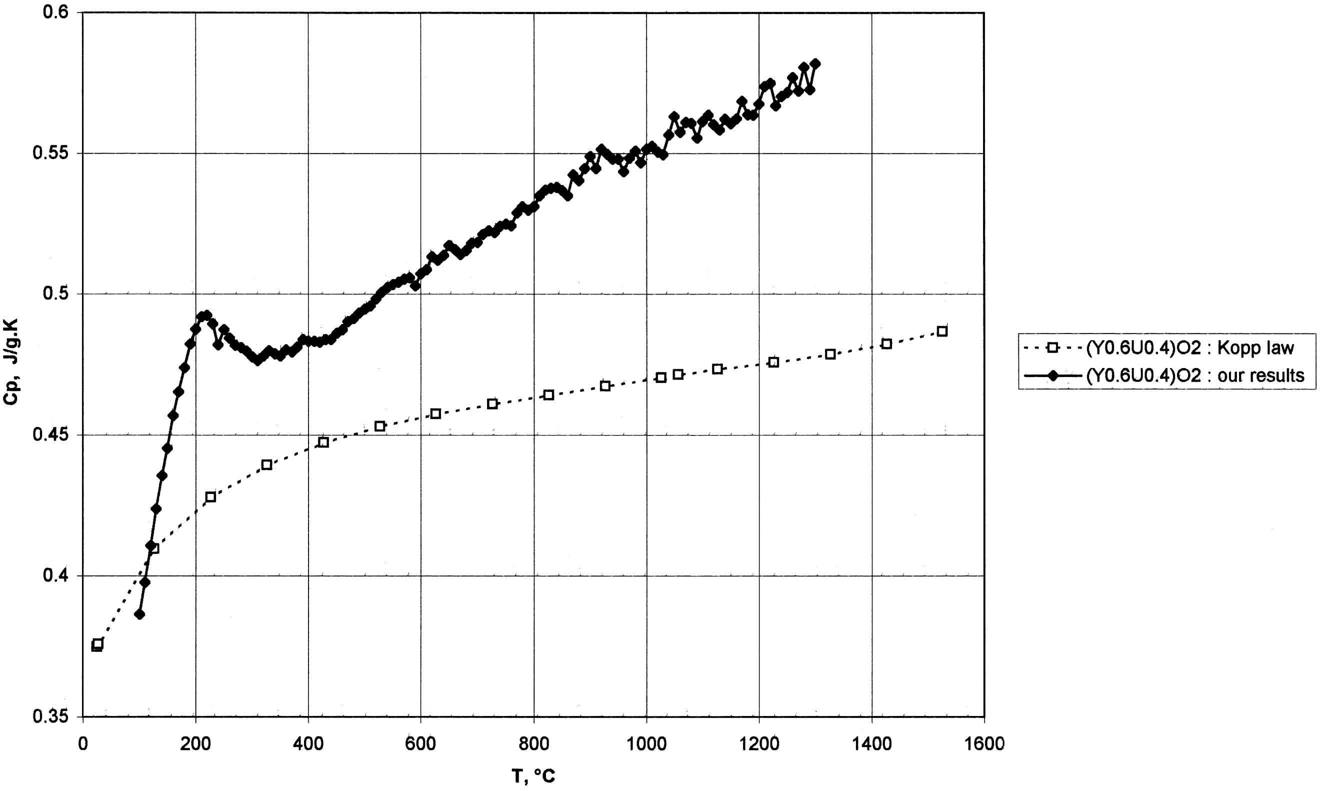

Fig. 2. Specific heat of (Y$_{0.6}$U$_{0.4}$)O$_{2\pm0.1}$.

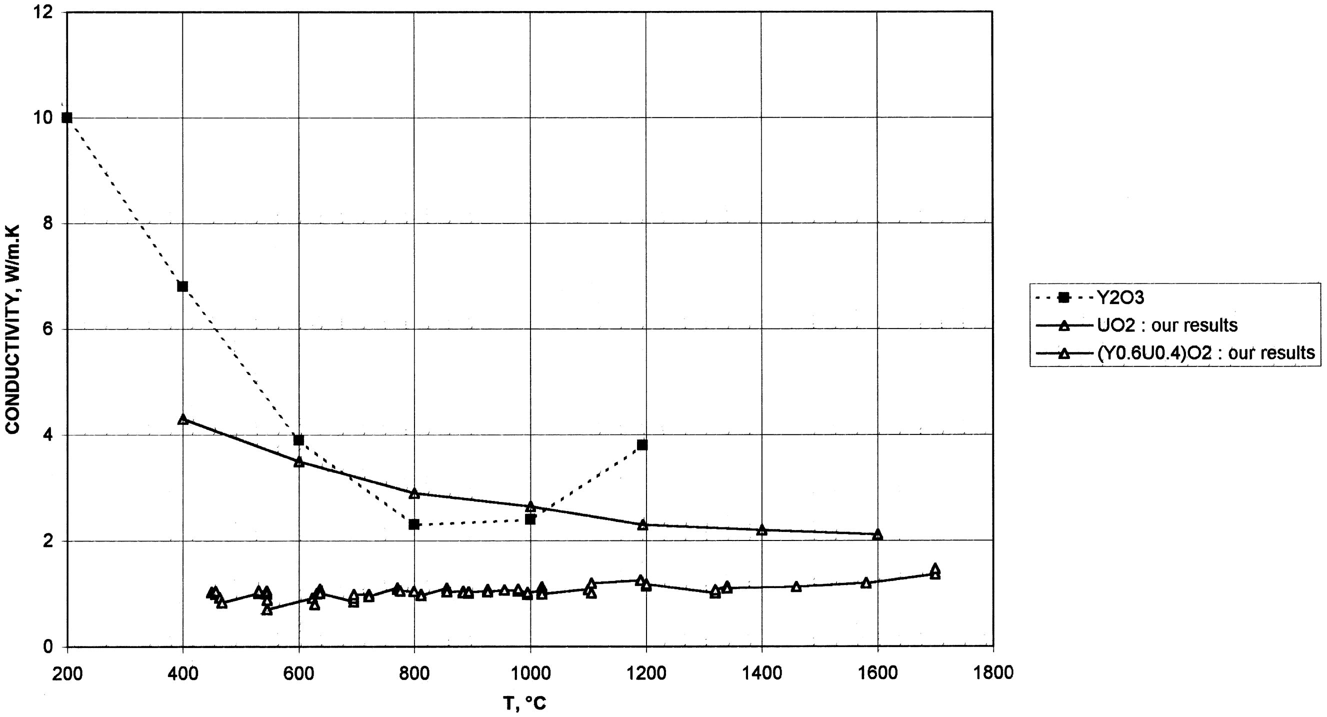

Fig. 3. Thermal conductivity of $(Y_{0.6}U_{0.4})O_{2\pm 0.1}$, 95% density.

lower than experimental results (0.05 J $(g\,K)^{-1}$. Distribution of oxygen vacancies and substitutions between U and Y on cation sites in cubic fluorite type crystals become an important parameters for the thermal and transport properties of $(Y_{0.6}U_{0.4})O_{2\pm x}$. More generally, the substitution of cations in cubic ionic oxides cannot be considered systematically like homogeneous dilution, and these conclusions are particularly suitable for solid solutions of actinide oxides with trivalent ions (Np, Pu, Am, Cm, Y or lanthanides). The authors of published studies on solid solutions use very often specific heat data calculated with the Kopp's law, but data must be controlled by experimental measurements for accurate result on thermal properties. The results on thermal conductivity of $(Y_{0.6}U_{0.4})O_{2\pm x}$ are presented on Fig. 3. The specific heat above 1300°C used for the calculation has been extrapolated and these results confirm the misfitting with thermal conductivity data estimated by the law of mixtures.

5. Behavior under irradiation with ions

Uranium oxide compounds (solid solutions and composites) had been irradiated at the GANIL (Caen, France) at room temperature by krypton or cadmium ions, with energy from 100 MeV to 1 GeV, and fluency to 4.10^{13} ions cm^{-2}. The samples were thin disks cut from pellets of material prepared in our laboratory (see Table 1), with polished face perpendicular to ion beam. These irradiations are good simulations for damage produced by fission products or by recoil ions during actinide transmutation. This effect is the most important damage in fuels during irradiation in reactor. Some samples were broken after irradiation (inert matrices without actinide like $Y_3Al_5O_{12}$ and $MgAl_2O_4$, and composite $Y_3Al_5O_{12}$–UO_2) but the fabrication process seems to be a very sensitive parameter, particularly misleading for $MgAl_2O_4$. The addition of actinide oxides in inert matrices improves the behavior of these matrices under irradiation, but no significant difference has been observed between 'microdispersed' composites or 'macromass' composites. Among materials irradiated with ions, AnO_2–MgO composites have shown the best behavior.

6. Conclusion

Actinide oxide compounds with controlled heterogeneity compatible for transmutation in reactor can be easily prepared by dry process. However, the thermodynamics must be analyzed in detail before to determine the sintering conditions. The thermal properties of the solid solutions with actinide oxides cannot be estimated from specific heat calculated systematically with the proportional Kopp's law for mixtures and measurements are necessary. The fabrication process influences the behavior of materials under irradiation and addition of actinide oxide in inert matrices improves this property.

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