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Inert matrices for the transmutation of actinides: fabrication, thermal properties and radiation stability of ceramic materials

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Abstract

In this study, ceramic binary or ternary compounds were tested for their suitability to serve as inert matrices for transmutation of the minor actinides Np and Am, i.e. to achieve a reduction in their quantities by irradiation in nuclear reactors without formation of new actinides from the matrix. Five materials ($MgAl_2O_4$, $ZrSiO_4$, CeO_2, SiC and Si_3N_4) were selected and produced without and with ^{241}Am using the well known soaking method. Special emphasis was put on the characterization of the materials and the measurement of thermal properties like heat capacity and thermal diffusivity. Irradiation damage was investigated by ion implantation experiments. X-ray diffraction measurements of $MgAl_2O_4$, CeO_2 and $ZrSiO_4$ were performed on the as-produced specimens to provide the basis for evaluating expected lattice parameter changes during self-irradiation by α-decay in future experiments. In addition, ceramic samples containing 20 wt % UO_2 were produced to demonstrate that matrix materials can accept large amounts of an oxide similar to americium oxide. An assessment of thermodynamic data for the systems $SiC+UO_2$ and $Si_3N_4+UO_2$ was used to calculate pseudobinary phase diagrams. Structural, thermal and thermodynamic aspects of all selected matrices, and the reasons for their selection are discussed.

Inert matrices; Transmutation

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1. Introduction

Reprocessing of spent nuclear reactor fuels produces liquid high level waste (HLW) containing so-called minor actinides, mainly long-lived isotopes of Np and Am. These are essentially formed by multiple neutron capture starting with ^{238}U, the main isotope of the uranium used in today's nuclear fuel, i.e. UO_2. By reducing the radiotoxicity of the HLW, the public acceptance of peaceful nuclear energy can be increased. To this end, the minor actinides should be separated from the HLW with suitable chemical processes (partitioning) and their quantity should be significantly reduced by further irradiation in existing or new nuclear reactors (transmutation). To avoid the formation of new actinides, the partitioned Am or Np have to be incorporated into a matrix which is inert against formation of new actinides, thus replacing UO_2 with a material of low atomic number and with properties similar, or even better than those of UO_2.

The following criteria were adopted for a selection of inert materials to be studied in more detail:

- thermal neutron absorption cross section of the matrix elements <2.7 barns
- melting point or transition temperature of binary or ternary compounds >2173 K
- good behaviour against the reactor coolant (H_2O or Na) up to 773 K
- good compatibility with the cladding (zircaloy or steel) thermal conductivity of the compounds ≥ that of UO_2
- non-toxicity
- good radiation stability
- suitability for reprocessing methods currently in use or under development.

A further criterion used to select a limited number of suitable matrices was to include materials showing a high

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solubility for the actinides to be transmuted, thus leading to a single-phased material, in addition to other suggested matrices which do not dissolve actinides and thus lead to two-phased systems. Based on these considerations, five materials were selected: $MgAl_2O_4$ (spinel), $ZrSiO_4$ (zircon), CeO_2 (ceria), SiC and Si_3N_4.

2. Specimen fabrication, experimental procedures and thermodynamic calculations

The scope of the work was to obtain highly densified pellets of inert matrix materials, some of which being doped with ^{241}Am applying the soaking method described previously [1], in order to allow the subsequent characterization in terms of thermal properties and of radiation damage.

2.1. Fabrication of inert matrices (undoped samples)

Cylindrical pellets of $MgAl_2O_4$, CeO_2, $ZrSiO_4$, SiC and Si_3N_4 were produced by cold-pressing without binder addition (500 MPa pressure) and then sintered. The sintering conditions are shown in Table 1. The sintering programmes were optimized in order to achieve high densities. With zircon, the sintering temperature had to be selected in a way to avoid excessive dissociation which was observed to lead to loss of SiO_2 at high temperature.

In order to demonstrate that SiC, Si_3N_4 and $ZrSiO_4$ matrices can accept a large amount of an oxide similar to americium oxide, additional pellets of these three materials were prepared with 20 wt % UO_2, which corresponds to the amount suggested for Am-doped materials for transmutation in reactors. The sintering conditions shown in Table 1 were used also for these samples.

2.2. Fabrication of ^{241}Am-doped specimens applying the soaking method

In a first step, cylindrical pellets (diameter and height ~6 mm) with a green density of about 50% Theoretical Density (TD) were produced and characterized; subsequently, some of the samples were soaked with a defined $^{241}Am/HNO_3$-solution. The final concentration of ^{241}Am in the pellets used here was 2 wt %. Pellets containing 10 wt % were also prepared for future experiments. Pellets with densities of about 50% of the theoretical density are capable to absorb completely a certain amount of liquid because of the acting capillary forces (sponge-like behaviour). The applied soaking procedure was already shown to be working successfully in former investigations with waste matrices and actinides [1]. An approximate amount of liquid which can be absorbed by one pellet was determined in preliminary experiments using neodymium as inactive stand-in for americium.

Green pellets of all five materials ($MgAl_2O_4$, $ZrSiO_4$, CeO_2, SiC and Si_3N_4) were doped with ^{241}Am by dropping the liquid $^{241}Am/HNO_3$-solution with a micropipette onto the flat surface of the specimen. Approximately 120 μl of Am-solution were put into each sample (four steps, each of 30 μl; samples were turned upside down after each step). The doped pellets were sintered with the same conditions as the undoped samples.

2.3. Studies of irradiation damage

2.3.1. Self-irradiation of Am-doped matrices

The examination will be performed after extended storage time up to the time when saturation damage is reached. These results will therefore be reported later. In the present study, accelerated damage accumulation was reached as described in the next section.

2.3.2. Ion implantation on inert matrices

Techniques to study irradiation damage as applied to nuclear materials have been described before [2,3]. Most damage is due to fission products, heavy recoil atoms of the α-decay, and neutrons.

Heavy fission product ions (e.g. Xe, I) of fission energy (e.g. 72 MeV energy) were used to study damage effects by fission, and ion beams of heavy or light fission products (Kr, Xe) of about the recoil energy of α-decay (~100 keV) were employed to simulate the recoil atoms of the α-decay. Ion implantations were done in cooperation with a number of high energy accelerators from the labs mentioned in ref. [4]. The damage due to neutrons is being studied in the reactor irradiations performed in the frame of the EFTTRA-program [5].

Table 1
Sintering conditions for matrix material candidates

Sintering conditions	$MgAl_2O_4$, $MgAl_2O_4+Am$	CeO_2, CeO_2+Am	$ZrSiO_4$, $ZrSiO_4+Am$, $ZrSiO_4+UO_2$	Si_3N_4, Si_3N_4+Am, $Si_3N_4+UO_2$	SiC, SiC+Am, $SiC+UO_2$
Temperature:	2023 K	1623 K	1923 K	1923 K	1923 K
Atmosphere:	air	air	Ar/H_2 (5%)	Ar/H_2 (5%)	Ar/H_2 (5%)
Pressure:	0.1 MPa	0.1 MPa	0.1 MPa	0.1 MPa	0.1 MPa
Time:	8 h	8 h	8 h	8 h	8 h

2.4. Thermal properties

The heat capacity at constant pressure (for $MgAl_2O_4$, CeO_2 and $ZrSiO_4$) was measured with a high temperature calorimeter allowing temperatures up to 1300°C (Netzsch).

The thermal diffusivities of $MgAl_2O_4$, CeO_2, CeO_{2-x} and $ZrSiO_4$ were measured in vacuum with the well known laser-flash method.

2.5. Thermodynamic calculations

Thermodynamic calculations of the pseudobinary systems $SiC+UO_2$ and $Si_3N_4+UO_2$ were performed in order to supply a basis for further experimental investigations. The software used for these calculations is THERMO-CALC [6]; thermodynamic data for the binary phases (Gibbs energy, entropy, enthalpy, phase transition information) were taken from the databases integrated in THERMO-CALC (for SiC and Si_3N_4) and from a nuclear database created by AET-Technologies [7] (for UO_2).

3. Results

Some results about fabrication and technological properties of suitable ceramics for the transmutation of actinides were reported earlier [8]; structural and thermal properties are reported in this work.

3.1. X-ray diffraction (XRD) measurements

XRD measurements of $MgAl_2O_4$, CeO_2 and $ZrSiO_4$ were performed to determine the phases and their structures, and the lattice parameter values (see Table 2). This information is required to evaluate the lattice parameter change during self-irradiation by α-decay.

XRD of a sintered SiC+20 wt% UO_2 showed a two-phase structure of SiC and U(C,O). U(C,O) has a cubic structure and is a solid solution between UC and UO. The XRD results of $Si_3N_4+UO_2$ showed also a two-phase structure consisting of Si_3N_4 and UO_2, i.e. the phases did not react. Pellets of $ZrSiO_4$+20 wt% UO_2 showed a two-phase structure ($ZrSiO_4$ and UO_2) after sintering, i.e. 20% UO_2 is above the solubility limit of U in zircon. Previous work had indicated solubilities of up to 12%, but had not determined the solubility limit [9,10].

3.2. Thermal properties

The heat capacities, C_p, were measured at constant pressure between room temperature and 1300°C. Some results are shown in Table 2 (for $MgAl_2O_4$, CeO_2 and $ZrSiO_4$). The values at 600 K and 1000 K were used to calculate the thermal conductivity (see below).

The results for the thermal diffusivity, a, of $MgAl_2O_4$, CeO_2, and $ZrSiO_4$ obtained in this work are shown in Fig. 1. The values are very similar to those of high density $UO_{2.00}$ (from literature). The actual diffusivity of UO_2 used in LWR reactors is lower than the values shown in the figure, due to its lower density (~95–96% TD).

The thermal conductivity, λ, as a function of temperature, T, was calculated by the following equation:

$$\lambda(T) = \alpha(T).\,\rho(T).\,C_p(T)$$

$$\rho(T) = \rho_o(1 - \beta T)$$

where β is the thermal expansion coefficient (K^{-1}) and ρ_o is the density at 25°C ($kg\,m^{-3}$).

Table 2
Some results of the characterization of undoped samples

	$MgAl_2O_4$	CeO_2	$ZrSiO_4$
Phases (determined by X-ray diffraction):	$MgAl_2O_4$	CeO_2	$ZrSiO_4$
Crystal structure:	fcc	cubic (CaF_2)	tetragonal
Lattice parameter:	$a=b=c$ 8.0772±0.006 Å	$a=b=c$ 5.4104±0.0002 Å	$a=b=$ 4.7236±0.0003 Å $c=10.4110\pm0.004$ Å
Heat capacity ($W\,s\,kg^{-1}$)			
– at 600 K	1085	398	600
– at 1000 K	1295	400	797
Thermal diffusivity ($\times10^{-6}\ m^2\,s^{-1}$)			
– at 600 K	1.85	1.96	2.21
– at 1000 K	1.22	1.15	1.30
Thermal conductivity ($W\,m^{-1}\,K^{-1}$, calculated)			
– at 600 K	6.843	5.117	5.381
– at 1000 K	5.386	3.018	4.204
Density used for calculations ($g\,cm^{-3}$)	3.409	6.560	4.058

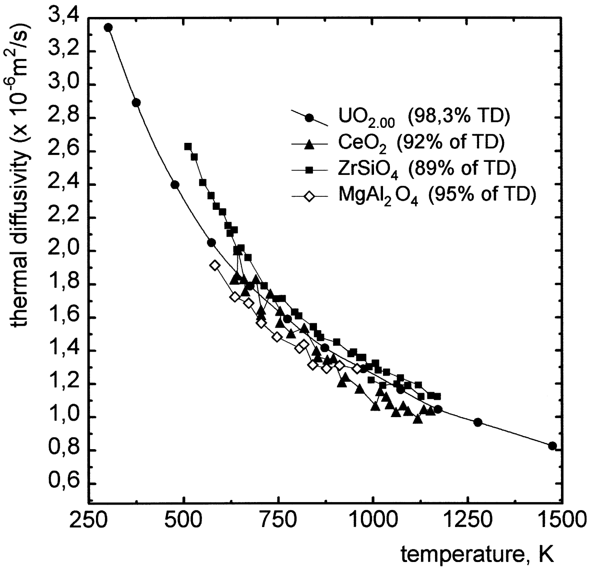

Fig. 1. Thermal diffusivity of ceramic matrix materials compared to $UO_{2.00}$.

The calculated conductivity values at 600 and 1000 K for spinel, zircon and CeO_2 are included in Table 2. The values for spinel are higher than those for UO_2, while the values for CeO_2 and zircon are lower than those of UO_2. The knowledge of this property is indispensable for the evaluation of materials which are foreseen for reactor irradiation. At a given power, a low conductivity causes higher central temperatures. Central melting must definitely be avoided during normal or transient reactor operation.

3.3. Phase diagram calculations

The calculations yielded a pseudobinary SiC–UO_2 system without any formation of ternary phases. However, since experimentally a ternary phase U(C,O) was detected, further investigation is required to prove if the sample had already reached the thermodynamic equilibrium. Calculations in the system Si_3N_4–UO_2 indicated that there is no ternary phase either, which is in good agreement with XRD data.

3.4. Irradiation damage

Ion implantation experiments were performed with energies in the range of those of α-decay for spinel (dose range 10^{14}–10^{17} Kr ions cm^{-2}, 190 keV) and of fission for spinel, for CeO_2, $ZrSiO_4$ and SiC (10^{17} I ions cm^{-2}, 72 MeV).

Spinel did not become amorphous at α-decay energies, though the Al_2O_3-sublattice lost long-range order at high doses [11]. At fission energy, swelling of $MgAl_2O_4$ was significant and polygonization occurred, i.e. a polycrystalline structure with very small grains was formed in single-crystalline spinel [12]. Amorphization was also observed at fission energy, but only along a fraction of the range of the iodine ions, the total range being ~7.5 μm.

The results for the remaining materials are being evaluated. SiC is being studied by our colleagues at Chalk River and these results will be published later.

3.5. Samples doped with ^{241}Am

XRD measurements to investigate the expected lattice parameter changes caused by self-irradiation of the matrices containing 2 and 10 wt % ^{241}Am are ongoing until the saturation of damage will be reached.

4. Conclusions and summary

New possible inert matrix materials which are foreseen to replace UO_2 for the transmutation of actinides have been selected and investigated. However, up to now there is no 'ideal' material which shows all the advantageous properties of UO_2. For example, CeO_2 is not compatible with Na and, if selected as inert matrix, can only be used in water cooled reactors. Similar arguments apply for compatibility with the cladding, e.g. for SiC and steel.

Spinel ($MgAl_2O_4$) and ceria (CeO_2) are favoured for future investigations because, besides other advantageous or acceptable properties, they are relatively stable against radiation. It has to be considered that the production of ceria samples (calcination, sintering) has to be performed in an oxidizing atmosphere to guarantee the desired stoichiometric composition [8]. $ZrSiO_4$ as matrix material will cause problems due to its relatively low dissociation temperature [8]. The irradiation behaviour of $ZrSiO_4$, SiC and Si_3N_4 is still being investigated.

Some of the results of this work led to the selection of $MgAl_2O_4$ as candidate material for reactor irradiation of specimens containing 10 wt % ^{241}Am within the frame of the EFTTRA [5] workgroup.

The investigation of the specimens fabricated in the present study will be continued with emphasis on α-decay damage.

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