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On the thermal conductivity of inert-matrix fuels containing americium oxide

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Abstract

Literature data on the thermal conductivity of americium oxides and americium-oxide containing compounds have been assessed. The influence of temperature and stoichiometry on the thermal conductivity of both solid solutions and heterogeneous composites of americium oxides and inert-matrix materials are discussed. The implications of the thermal conductivity on the choice of the inert-matrix material are examined. © 1998 Elsevier Science B.V.

1. Introduction

The interest in the transmutation of americium has raised the need for information on the thermal properties of americium containing fuels. Of the fuel concepts currently considered, homogeneous solid solutions of americium oxide and oxides such as UO_2, CeO_2 or Y_2O_3 or heterogeneous composites (dispersions) in an inert support material such as spinel ($MgAl_2O_4$) or magnesia (MgO) are being studied extensively [1]. Especially the thermal conductivity of such solid solutions or composites is an important property, since it determines the power that can be generated in an americium-containing fuel rod, but like many properties of these types of fuels, the thermal conductivity is poorly known and the obvious reason for this is the high radioactivity of americium as a result of which special facilities are required for its handling.

Thermal conductivity (λ) measurements at 333 K of freshly annealed AmO_2 ($\lambda = 0.69$ W/m K) and Am_2O_3 ($\lambda = 0.82$ W/m K) pellets have been reported by Schmidt [2]. The thermal conductivity of the AmO_2 pellet was found to be drastically lower than the thermal conductivity of other actinide dioxides with an identical crystal structure, i.e. ThO_2, UO_2 and PuO_2, which have a thermal conductivity at 333 K of 7-10 W/m K. Schmidt et al. [3] measured the thermal conductivity of $Am_{0.5}U_{0.5}O_{2-x}$ ($x = 0.08$ and $x = 0.19$) and $Am_{0.25}Np_{0.25}U_{0.5}O_{1.93}$ in the temperature range between 1000 K and 2500 K. The thermal conductivity of these compounds varies between 1 and 2 W/m K. An additional factor to be considered is the effect of self-irradiation on the thermal conductivity of AmO_2 and Am_2O_3, as described by Schmidt et al. [4]. It was observed that the conductivity decreases due to α-decay until saturation is reached after three days. Because of the experimental difficulties, we have used a different approach for establishing the thermal conductivity of americium-containing fuels, using semi-empirical estimations, analytical approaches and analyses by finite-element methods.

2. Discussion on the thermal conductivity of AmO_{2-x}

In this section the thermal conductivity of AmO_2, as measured by Schmidt [2], will be compared with theoretical predictions on the thermal conductivity of AmO_{2-x} in order to get a better insight in the thermal conductivity of AmO_{2-x}.

The temperature dependence of the thermal conductivity (λ) of AmO_2 and Am_2O_3 can be represented by Eq. (1) up to about 1800 K, since this equation also represents the thermal conductivity ($T \leq 1800$ K) of actinide oxides

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such as ThO_2, UO_2 and PuO_2 in pure form as well as containing substitutions or being non-stoichiometric:

$$\lambda = \frac{1}{A_0 + A_1(x) + BT}. \qquad (1)$$

T is the temperature, the parameter A_0 describes the temperature independent phonon scattering in the pure compound. The parameter $A_1(x)$ represents the influence of substitution or non-stoichiometry on the temperature independent phonon scattering. x represents the amount of non-stoichiometry or substitution. The parameter B, which represents the temperature dependent phonon–phonon scattering, is less sensitive to substitutions or other scattering centers. The systematics of the phonon–phonon interactions in the actinide oxides ThO_2, UO_2 and PuO_2 have been studied by Gibby [5] who compared experimental B-parameters taken from literature with the systematics obtained from Eq. (2), that has been derived from the Liebfried–Schlömann relationship [6]:

$$B_2 = B_1 \left(\frac{M_2}{M_1} \right)^{1/2} \left(\frac{a_2}{a_1} \right)^2 \left(\frac{T_{M1}}{T_{M2}} \right)^{3/2}. \qquad (2)$$

M is the molecular weight, a is the lattice parameter, T_M is the melting temperature and the subscripts 1 and 2 represent the oxides that are to be compared. The B-parameters obtained by Gibby [5] using Eq. (2) and $B = 2.29 \times 10^{-4}$ m/W for UO_2 are $B = 1.96 \times 10^{-4}$ m/W for ThO_2 and $B = 2.81 \times 10^{-4}$ m/W for PuO_2. Gibby observed good agreement between the B-values from literature and the above mentioned calculated B-values. Eq. (2) yields $B = 3.19 \times 10^{-4}$ m/W for AmO_2, using the UO_2-data of Gibby and $M = 273$, $a = 0.53772$ nm and $T_M = 2448$ K [7] for AmO_2.

No systematics can be observed between the A_0-values of ThO_2 ($A_0 = 0$ m K/W [8]), UO_2 ($A_0 = 3.0 \times 10^{-2}$ m K/W [9]), $U_{0.8}Pu_{0.2}O_2$ ($A_0 = 4.2 \times 10^{-2}$ m K/W [10]) and PuO_2 ($A_0 = 0.5 \times 10^{-2}$ m K/W [5]). Assuming that the A_0-value of AmO_2 lies in the same range as that of the above mentioned oxides (0 m K/W $\leq A_0 \leq 4.2 \times 10^{-2}$ m K/W) and B is 3.19×10^{-4} m/W, the calculated thermal conductivity of AmO_2 at 333 K lies in the range 6.7 W/m K-9.4 W/m K, which is approximately ten times larger than the thermal conductivity value measured by Schmidt.

In UO_{2-x} and (U, Pu)O_{2-x} fuel it has been shown that non-stoichiometry causes a strong decrease of the thermal conductivity [10]. Oxygen deficiencies create irregularities in the lattice which decrease the thermal conductivity by the following effects:

– The differences in effective atomic radius and atomic mass of an oxygen atom and a vacancy.

– Due to charge neutrality the oxidation state of some of the Pu^{4+}-atoms changes to a 3 + oxidation state. This induces a radius difference between the atoms with a 4 + and a 3 + oxidation state.

For (U, Pu)O_{2-x} it was found that the $A_1(x)$-term in Eq. (1) increases approximately parabolically with increasing x [10]:

$$A_1(x) = 1.528(x + 0.00931)^{1/2} - 0.1474. \qquad (3)$$

$A_1(x)$ (in m K/W) is derived for a plutonium content close to 20%, for x up to 0.1 and a density of 95% th.d. Since the atomic radius differences between Pu^{4+} and Pu^{3+} and that between Am^{4+} and Am^{3+} are approximately similar, the influence of non-stoichiometry on the thermal conductivity of (U, Pu)O_{2-x} and AmO_{2-x} will be comparable and consequently Eq. (3) can be used for AmO_{2-x}.

For example, the thermal conductivity at 333 K of $AmO_{1.62}$, which is the lower limit of the existence of the fcc AmO_{2-x} phase ($1.62 \leq 2 - x \leq 2.0$) [11], is approximated as 1.07 W/m K using $B = 3.19 \times 10^{-4}$ m/W, $A_0 = 2 \times 10^{-2}$ m K/W and $A_1(x = 0.38) = 0.81$ m K/W. The extrapolation of Eq. (3) to $x = 0.38$ ($AmO_{1.62}$) is drastic since the equation has only been determined in the range $0 \leq x \leq 0.1$. However, the shape of the extrapolated curve of Eq. (3) is in good agreement with the theory for the thermal conductivity of homogeneous mixtures (Section 3). The computed thermal conductivity of $AmO_{1.62}$ (λ(333 K) = 1.07 W/m K) and the measured value of Schmidt for AmO_2 (λ(333 K) = 0.69 W/m K) are rather similar taking into account the rough estimations that were made in the computations. Since Schmidt [3] did not report on the O/M-ratio of his samples and taking into account that the thermal conductivity values he obtained are very low, it cannot be excluded that his samples were non-stoichiometric.

3. The thermal conductivity of homogeneous mixtures

The thermal conductivity of (U, RE)O_2, (Pu, RE)O_2 and $(U_{0.8}Pu_{0.2})_{1-x}RE_xO_2$ (RE = rare earth) has been reviewed by Fukushima et al. [12]. Their work shows that the thermal conductivity of such systems can be described adequately by the theory developed by Ambegaokar [13] and Abeles [14]. In this paper this theory is used to estimate the thermal conductivity of $(Y, Am)_2O_3$ and (Ce, Am)O_2 for americium concentrations up to 30%.

The thermal conductivity of a homogeneous mixture of two elements can be analyzed with Eq. (1) in which the parameter $A_1(x)$ is represented by

$$A_1(x) = \frac{\pi^2 V \theta}{3 v^2 h} \Gamma, \qquad (4)$$

where V is the average atomic volume, θ is the Debye temperature, v is the average phonon velocity, h is Planck's

Table 1
Various properties of CeO_2 and Y_2O_3. Θ is the Debye temperature, v is the average phonon velocity, V is the average atomic volume and λ is the thermal conductivity

	CeO_2	Y_2O_3	Ref.
Θ (K)	530	550	[a]
v (m/s)	9.4×10^3	9.8×10^3	[b]
V (m^3)	1.33×10^{-29}	1.59×10^{-29}	
λ (W/m K)	12 (at 333 K)	15 (at 333 K)	[15,16]
Ionic radius of Ce^{4+} or Y^{3+} (nm)	0.0975	0.0900	[c]

[a] Obtained by fitting heat capacity data [17].
[b] Obtained by scaling the value of UO_2 [18].
[c] Obtained for coordination number 8 (Ce^{4+}) and coordination number 6 (Y^{3+}) [19].

constant. Γ is the scattering cross-section parameter of the phonon by the impurity type. Γ is given by

$$\Gamma = x(1-x)\left(\frac{M_1 - M_2}{(1-x)M_1 + xM_2}\right)^2 + \epsilon x(1-x) \times \left(\frac{r_1 - r_2}{(1-x)r_1 + xr_2}\right)^2, \tag{5}$$

where x is the mole fraction of impurity atoms, M_1 is the mass of the host atom, M_2 is the mass of the impurity atom, r_1 is the ionic radius of the host atom and r_2 is the ionic radius of the impurity atom. ε is a parameter that represents the strain generated in the lattice and is assumed to be about 100, which is obtained from an analysis of various solid solutions by Fukushima et al. [12]. Using the data in Table 1, the ratio in front of Γ in Eq. (4) is equal to 0.40 m K/W in the case of CeO_2 and 0.43 m K/W in the case of Y_2O_3. Using Eqs. (1), (4) and (5) and the ionic radii $r_{Am^{3+}} = 0.0975$ nm for coordination number 6 and $r_{Am^{4+}} = 0.095$ nm for coordination number 8 [20], the influence of AmO_2 and Am_2O_3 substitution in CeO_2 and Y_2O_3 respectively on the thermal conductivity has been estimated for $x < 0.3$ and is shown in Fig. 1. In both cases the contribution of the mass effect to Γ is larger than that induced by the strain effect. Hence, the uncertainties in the values of ε and the ionic radii do not induce a considerable error in the thermal conductivity.

The calculations performed in this section should only be treated as rough estimates that are probably an upper limit of the real conductivity, since americium oxide might introduce lattice defects or oxygen non-stoichiometry. These effects might induce an additional decrease of the thermal conductivity.

4. The thermal conductivity of heterogeneous composites

4.1. Spherical inclusions

The influence of spherical inclusions on the thermal conductivity can be represented by a special case of the equation of Schulz [20]:

$$1 - c_D = \frac{\lambda_D - \lambda_C}{\lambda_D - \lambda_M}\left(\frac{\lambda_M}{\lambda_C}\right)^{1/3}. \tag{6}$$

where λ_M, λ_D and λ_C represent the thermal conductivity of the matrix material, the dispersed phase and the composite, respectively. c_D $(0 \le c_D \le 1)$ represents the concentration of spherical inclusions. The influence of variation of the thermal conductivity of the spherical inclusions on the overall thermal conductivity is shown in Fig. 2 for $c_D = 0.2$ and $c_D = 0.4$.

Randomly ordered spherical inclusions have the smallest influence on the overall thermal conductivity compared with randomly ordered inclusions with other shapes [20].

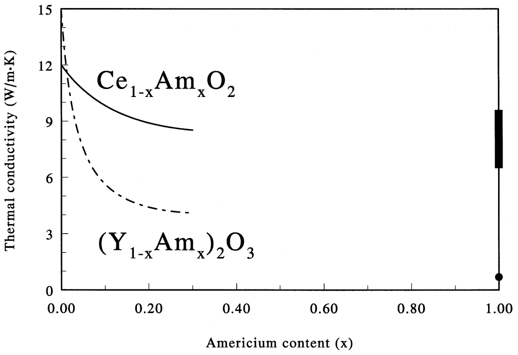

Fig. 1. The thermal conductivity of the homogeneous mixtures $Ce_{1-x}Am_xO_2$ and $(Y_{1-x}Am_x)_2O_3$ ($x < 0.3$) as calculated with Eqs. (1), (4) and (5) and the thermal conductivity of AmO_2 (●) as measured by Schmidt [2] and as estimated in Section 2 using the analogy with ThO_2, UO_2 and PuO_2 (solid bar).

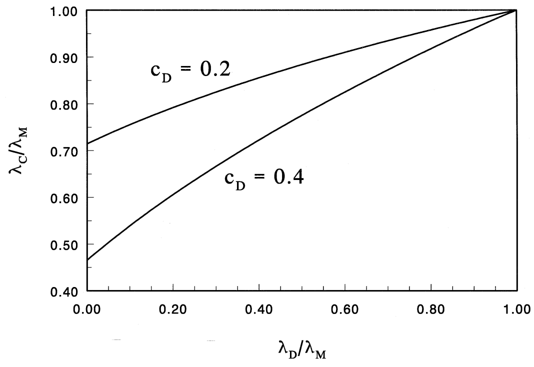

Fig. 2. The influence of variation of the normalized thermal conductivity of the spherical inclusions $0 \le \lambda_D/\lambda_M \le 1$ on the normalized thermal conductivity of the mixed material (λ_C/λ_M), computed for two concentrations ($c_D = 0.2$ and $c_D = 0.4$) of the spherical inclusions.

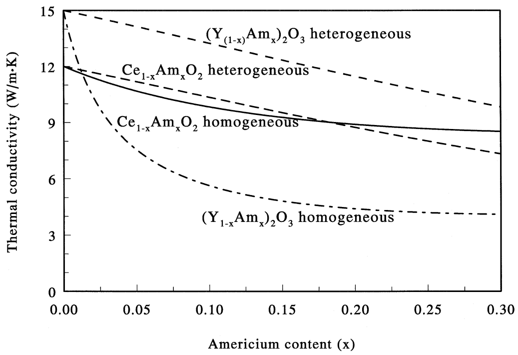

Fig. 3. The thermal conductivity of heterogeneous and homogeneous mixtures of $Ce_{1-x}Am_xO_2$ and $(Y_{1-x}Am_x)_2O_3$. The thermal conductivity of the homogeneous mixtures has been calculated with Eqs. (1), (4) and (5). The thermal conductivity of the heterogeneous composites have been calculated with Eq. (6).

Hence, the curves shown in Fig. 2 represent an upper limit of the thermal conductivity.

The overall thermal conductivity of a dispersion of spherical AmO_2 inclusions ($\lambda = 0.69$ W/m K) in a CeO_2 matrix and spherical Am_2O_3 inclusions ($\lambda = 0.82$ W/m K) in a Y_2O_3 matrix is shown in Fig. 3, together with the thermal conductivity of homogeneous mixtures. The americium content x has been computed using the CeO_2 and Y_2O_3 density derived from Table 1 and the AmO_2 (11.75 g/cm^3) and Am_2O_3 (10.31 g/cm^3) density derived from [21,22], respectively.

Heterogenous $(Y_{1-x}Am_x)_2O_3$ has a considerably larger thermal conductivity than homogeneous $(Y_{1-x}Am_x)_2O_3$. For $Ce_{1-x}Am_xO_2$ the difference of the thermal conductivity between both types of mixtures is much smaller, which makes it impossible to determine which type of mixture has the optimum thermal conductivity. However, due to diffusion during sintering of the pellets, in heterogeneous fuel there will exist homogeneous regions at the edges of the heterogeneous regions.

4.2. Randomly-shaped inclusions

Recently the finite element method (FEM) has been introduced as a technique to compute the thermal conductivity of heterogenous materials [23]. The FEM has the advantage that it takes the real shape and orientation of the second phase material into account. This technique is used to compute the thermal conductivity of a $MgO–AmO_x$ composite. A photograph of the microstructure of this material (Fig. 4) is entered in the commercially available FEM program 'ANSYS' [24]. With the FEM, the two-dimensional (2D) temperature distribution (Fig. 5) and the distribution of the y-component of the 2D thermal flux (Fig. 6) were obtained for a thermal gradient in the y-direction, assuming that $\lambda(AmO_x)/\lambda(MgO) = 0.1$. The FEM program calculates the 2D thermal conductivity, the porosity and the AmO_x-concentration of the material. The 2D thermal conductivity is the computed conductivity in the plane of the photograph divided by the conductivity of fully dense MgO. The 2D thermal conductivity is a lower limit of the real conductivity which makes it an important

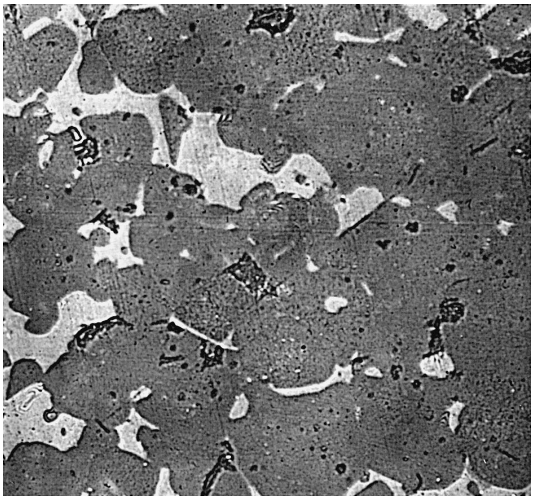

Fig. 4. Optical microscopy photograph of the microstructure of a heterogeneous composite of AmO_x and MgO (after Casalta [24]).

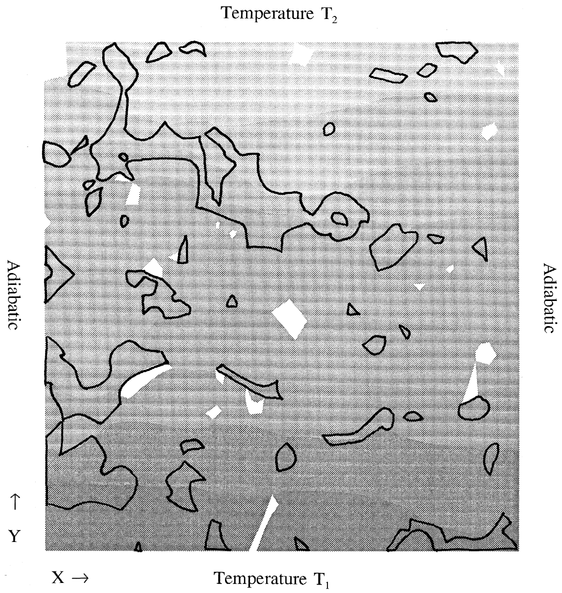

Fig. 5. The 2D temperature distribution obtained from FEM computations on the microstructure of the $MgO–AmO_x$ composite. The white regions mark the pores and the black lines mark the surface of the AmO_x-inclusions. The transitions from one greyscale to another mark isotherms. The thermal gradient is applied in the y-direction. The temperature difference between T_1 and T_2 is arbitrary since only the influence of the inclusions on the conductivity is calculated.

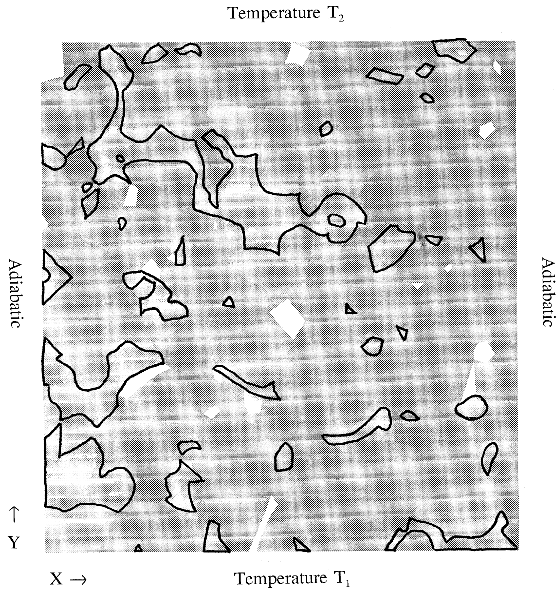

Fig. 6. The 2D distribution of the *y*-component of the thermal flux, as obtained from FEM computations on the microstructure of the MgO–AmO_x mixture. The white regions mark the pores and the black lines mark the surface of the AmO_x-inclusions. The thermal gradient is applied in the *y*-direction. The dark regions represent a larger flux in the *y*-direction than the light regions.

parameter for safety analysis. The combination of the 2D thermal conductivity and the AmO_x concentration is transferred into the 3D thermal conductivity, as described in Ref. [23]. The 3D thermal conductivity is the real conductivity of the two-phase material divided by the conductivity of fully dense MgO. The thermal conductivity of a heterogeneous composite of spherical (3D) AmO_x inclusions and spherical pores in a MgO-matrix (Eq. (6)) divided by the conductivity of fully dense MgO is shown as a comparison. The above mentioned thermal conductivity values have been computed for various ratios of the thermal conductivity of AmO_x and MgO (Fig. 7).

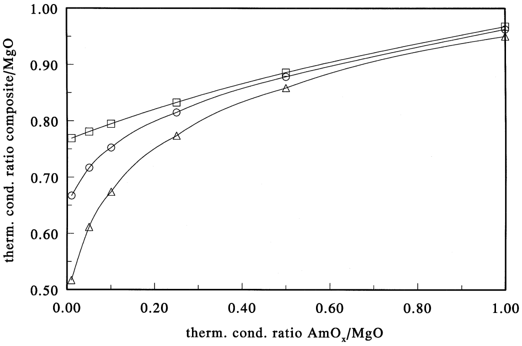

Fig. 7. The ratio of the thermal conductivity calculated with the 2D (△) and the 3D (○) technique, divided by the conductivity of fully dense MgO, for a heterogeneous mixture of AmO_x and MgO computed for various ratios of the thermal conductivity of AmO_x and MgO. The ratio of the thermal conductivity (□) of spherical AmO_x inclusions in a MgO-matrix, as computed with Eq. (6), is shown as a comparison. The AmO_x content (14.4 vol.%) and the porosity (2%) for all three curves are equal.

The porosity of the MgO–AmO_x composite is 2%, which causes the conductivity of the composites to be slightly smaller than that of fully dense MgO for a conductivity ratio AmO_x/MgO of 1.0. The 2D conductivity represents a lower limit of the conductivity, the conductivity as computed with Eq. (6) an upper limit and the 3D thermal conductivity as computed from the FEM data a 'best estimate'.

5. Discussion

The choice between homogeneous and heterogeneous fuels or targets for transmutation is influenced by various aspects and the thermal conductivity is only one of them. In the present discussion it has been suggested that the conductivity of stoichiometric AmO_2 is much higher than the value of Schmidt [2]. When the thermal conductivity of two pure compounds is higher than that of their homogeneous mixture, as is the case for most materials, the thermal conductivity of a heterogeneous composite is higher than that of a homogeneous mixture.

An additional advantage of a heterogenous composite is that the irradiation damage and the fission products are mainly localized in the americium oxide, while in a homogeneous mixture the irradiation damage and the fission products are homogeneously distributed. Irradiation damage and fission products induce a strong decrease of the thermal conductivity. The localized decrease of the thermal conductivity in a heterogeneous composite induces a smaller decrease of the overall conductivity than the homogeneously spread damage in a homogeneous mixture. However, the size of the americium oxide particles in the case of a heterogeneous composite should be considerably larger than the range of the fission products ($\simeq 10\ \mu m$) in order to take full advantage of this difference [25].

In the present paper the following aspects, that depend strongly on the AmO_x particle size, are not taken into account:

– The heat generation distribution in the heterogeneous composite. When most of the heat is generated in the fissile particles, this influences the temperature distribution. However, this has only a minor influence on the thermal conductivity of the material.

– The heat transport between the inclusions and the matrix. Due to a difference in thermal expansion or swelling of the two materials, cracks may form at the material interfaces. The influence of these cracks on the overall thermal conductivity depends amongst others on the particle size of the inclusions and the composition of the gas in the crack. When the heat transport between the inclusions and the matrix is very poor the overall thermal conductivity can be approximated by assuming that the conductivity of the inclusion is zero.

6. Conclusions

Comparison of the estimated data for the thermal conductivity of AmO_2 and $AmO_{1.62}$ with the experimental data of Schmidt [2] suggests that for the thermal conductivity measurements of AmO_2 and Am_2O_3 that were performed by Schmidt, insufficiently characterized samples were used which makes these data less useful. The thermal conductivity of heterogeneous mixtures of americium oxides and inert matrices is higher than that of a homogeneous mixture. This difference increases when the mass of the host atom decreases. Although the thermal conductivity of americium oxides is poorly known, that of fuels containing up to 30 at.% americium oxide can be estimated reasonably accurate.

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References

[1] J.F. Babelot, R. Conrad, W.M.P. Franken, J. van Geel, H. Gruppelaar, G. Mühling, C. Prunier, M. Rome, M. Salvatores, Proc. Global 95, Versailles, France, 1995, p. 524.
[2] H.E. Schmidt, Proc. 4ième Journées d'Actinides, Harwell, UK, 1974, Atomic Energy Research Establishment report AERE-R-7961, 1975.
[3] H.E. Schmidt, C. Sari, K. Richter, P. Gerontopoulos, J. Less-Common. Met. 121 (1986) 621.
[4] H.E. Schmidt, J. Richter, H. Matzke, J. van Geel, Proc. of the 22nd Int. Conf. Thermal Conductivity, Tempe, AZ, 1993, p. 920.
[5] R.L. Gibby, J. Nucl. Mater. 38 (1971) 163.
[6] G. Leibfried, E. Schlömann, Akad. Wiss. Göttingen, Math.-Physik. Kl IIA, 1954, p. 71.
[7] W.W. Schulz, The Chemistry of Americium, ERDA Technical Information Centre, Oak Ridge, TN, USA, 1976, p. 152.
[8] K. Bakker, E.H.P. Cordfunke, R.J.M. Konings, R.P.C. Schram, J. Nucl. Mater. 250 (1997) 1.
[9] C.G.S. Pillai, A.M. George, J. Nucl. Mater. 200 (1993) 78.
[10] Y. Philipponneau, J. Nucl. Mater. 188 (1992) 194.
[11] H. Zhang, M.E. Huntelaar, R.J.M. Konings, E.H.P. Cordfunke, ECN report ECN-I-96-051, 1996.
[12] S. Fukushima, T. Ohmichi, M. Handa, J. Less-Common. Met. 121 (1986) 631.
[13] V. Ambegaokar, Phys. Rev. 114 (1959) 488.
[14] B. Abeles, Phys. Rev. 131 (1963) 1906.
[15] K. Bakker et al., to be published.
[16] Y.S. Touloukian, R.W. Powell, C.Y. Ho, P.G. Klemens, Thermophysical Properties of Matter, vol. 2, IFI/Plenum, New York, 1970.
[17] Y.S. Touloukian, E.H. Buyco, Thermophysical Properties of Matter, vol. 5, IFI/Plenum, New York, 1970.
[18] S. Fukushima, T. Ohmichi, A. Maeda, M. Handa, J. Nucl. Mater. 116 (1983) 287.
[19] R.D. Shannon, Acta Crystallogr. A 32 (1976) 751.
[20] B. Schulz, High Temp.-High Press. 13 (1981) 649.
[21] W.H. Zachariasen, Acta Crystallogr. 2 (1949) 388.
[22] D.H. Templeton, C.H. Dauben, J. Am. Chem. Soc. 75 (1953) 4560.
[23] K. Bakker, Int. J. Heat Mass Transfer 40 (1997) 3503.
[24] S. Casalta, thèse de l'Université d'Aix-Marseille I, 1996.
[25] K. Bakker, R.J.M. Konings, The influence of americium oxide inclusions on the thermal conductivity of inert-matrix fuel, Proc. Actinides '97 conference, accepted for publication.