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An interdiffusional model for prediction of the interaction layer growth in the system uranium–molybdenum/aluminum

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Abstract

The codes PLACA and DPLACA, elaborated in this working group, simulate the behavior of a plate-type fuel containing in its core a foil of monolithic or dispersed fissile material, respectively, under normal operation conditions of a research reactor. Dispersion fuels usually consist of ceramic particles of a uranium compound in a high thermal conductivity matrix. The use of particles of a U–Mo alloy in a matrix of Al requires especially devoted subroutines able to simulate the growth of the interaction layer that develops between the particles and the matrix. A model is presented in this work that gives account of these particular phenomena. It is based on the assumption that diffusion of U and Al through the layer is the rate-determining step. Two moving interfaces separate the growing reaction layer from the original phases. The kinetics of these boundaries are solved as Stefan problems. In order to test the model and the associated code, some previous, simpler problems corresponding to similar systems for which analytical solutions or experimental data are known were simulated. Experiments performed with planar U–Mo/Al diffusion couples are reported in the literature, which purpose is to obtain information on the system parameters. These experiments were simulated with PLACA. Results of experiments performed with U–Mo particles disperse in Al either without or with irradiation, published in the open literature were simulated with DPLACA. A satisfactory prediction of the whole reaction layer thickness and of the individual fractions corresponding to alloy and matrix consumption was obtained.

1. Introduction

The need of converting research reactors fuel from highly enriched-uranium (HEU) to low-enriched-uranium (LEU – below 20% in the ^{235}U isotope) has forced the search for different uranium compounds with a uranium content higher than that of the traditional fuels. With the U_3Si_2/Al dispersion fuel a uranium density of 4.8 g cm^{-3} can be reached. The neutron flux achievable with this type of fuel satisfies the requirements of a large number of research reactors. However, the high flux reactors necessitate fuels with a higher uranium load. In the more recent years focus has been made on fuels based on U–Mo alloys, with a Mo content ranging from 6 to 10 wt%. Fuel plates constituted either by

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U–Mo particles dispersed in an aluminum matrix or by a monolithic foil of the alloy are being examined.

As for the dispersion fuel material, it has been found that when it is carried to a temperature of a few hundreds degrees, even without irradiation, a layer of U–Mo–Al compounds develops around the U–Mo particles. Its presence deteriorates the fuel behavior because its density is lower than that of the original alloy and hence the growth of the intermetallic layer causes a volume increase of the plate. Besides, the thermal conductivity of the intermetallic is poorer than that of the particles and the matrix. This provokes a gradual temperature increase in the plate during operation. It is generally accepted that the layer growth is a diffusion-controlled process, which explains that temperature elevation enhances layer development. Moreover, the experiments show that irradiation further increases the interaction layer growth and, therefore, accelerates plate deterioration. Due to the design characteristics of this type of fuel element, the plate thickness must remain within strict limits. In consequence, the plate swelling that would arise from the intermetallic layer growth would reduce significantly the life time of the fuel. The U–Mo particles to be used to fabricate the fuel plates may have different sizes and shapes depending on the manufacturing technique employed. However, for simplicity the particles will be assumed spherical for modellization purposes.

The generally accepted description of the dissolution or growth of a particle immersed in a medium involves a chemical reaction step occurring at the particle surface, followed by the long-range diffusion of the dissolved atoms in the surrounding matrix. As a consequence, the particle surface displaces in one or the opposite direction depending on the nature of the reaction. In a number of practical cases, the interface reaction proceeds at a speed sufficiently high as to guarantee that thermodynamic equilibrium at the interface is conserved. This implies, on the one hand, that the concentrations on both sides of the interface are those given by the corresponding equilibrium phase diagram. On the other hand, it implies that the rate-determining step is the long-range diffusion in the matrix.

A diffusion model is presented in this paper and its predictions are compared with the few existing experimental data. It simulates the intermetallic phase growth assuming that interdiffusion of Al and U through the layer is the rate-limiting step. The system contains three phases: the original U–Mo alloy, the Al matrix and the layer between both. Two moving interfaces separate the growing intermetallic layer from the two neighboring phases.

In order to gain knowledge of the system and to determine the physical parameters involved, some authors have carried out experiments in planar geometry, which are reported in the literature [1,2]. One of the laboratory techniques usually employed consists in pressing together a sample of U–Mo alloy and other of Al to form a diffusion couple. The couples are submitted to thermal treatments at different temperatures and time intervals. The reaction zone is then analyzed to determine its size and composition.

In the present work the interaction between U–Mo and Al is modelled in two geometries: planar, to represent the experiments with diffusion couples and spherical, to represent the conditions in the dispersion fuel foils, i.e., U–Mo particles immerse in a matrix of Al. Fig. 1 illustrates the two scenarios analyzed in this work.

The experimental observations indicate that the reaction zone is constituted by three sub-layers of different U–Mo–Al phases either in unirradiated [1–3] or irradiated [4] samples. The observations reported in Refs. [1,2,4] indicate that the weight proportions of U and Mo in the two larger sub-layers are the same as in the U–Mo alloy. The authors agree in identifying the sub-layer located next to the U–Mo alloy as $(U,Mo)Al_3$, which occupies the major fraction of the reacted zone. The following sub-layer has been identified as $(U,Mo)Al_{4.4}$ by [1,4] and as $(U,Mo)Al_4$ by [2]. Adjacent to the aluminum matrix a much thinner Al rich sub-layer is detected which composition is described by [2,3] as UMo_2Al_{20}.

Detailed modelling of this system leads to a multi-phase multi-component moving boundary problem. Its simulation would involve a number of physical parameters not available at the present time. However, the model can be conveniently simplified by introducing certain assumptions supported by the observations.

The code DPLACA has been elaborated to give account of the behavior of plate-type fuels containing a dispersion material, under normal operation conditions of a research reactor. (There exists another version of the code, PLACA, dedicated to monolithic plate-type fuels which has been previously employed to simulate the behavior of U–Mo

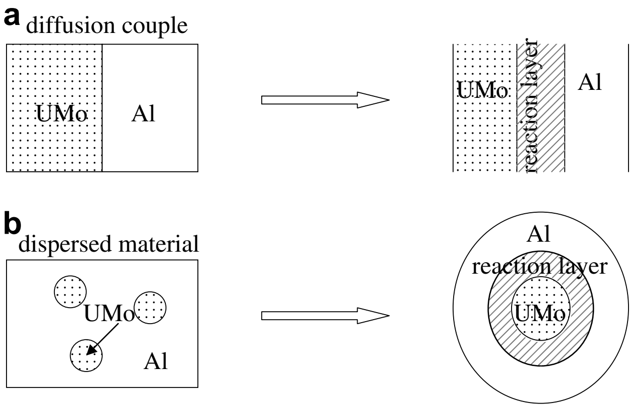

Fig. 1. Schemes of the systems simulated. (a) Diffusion couple before and after interaction at temperature. (b) Dispersed material before interaction (left scheme) and detail of a particle and the surrounding matrix with the reaction layer developed around the particle (right scheme).

and UAl_x fuel foils cladded in Zircaloy [5,6].) The use of particles of U–Mo alloy requires specific subroutines able to simulate the phenomena described above. The purpose of the present work is to develop a model to give account of these phenomena, to build and test the corresponding subroutines and to include them in the general code.

2. Hypothesis of the model

The model assumes that:

- The reaction layer growth is a diffusion-controlled process.
- The system is constituted by three phases: the U–Mo particle, the interaction layer and the Al matrix, either in planar or spherical geometry.
- U and Mo retain the initial relative proportions so that they can be treated for the simulation purposes as a single element which, for brevity, will be referred to in the following as U.
- Interdiffusion of U and Al takes place through the layer: U diffuses from the U–Mo particle towards the Al matrix and Al does in the opposite sense.
- U does not dissolve in the aluminum matrix as well as Al does not dissolve in the U–Mo alloy.
- U and Al exhibit a continuous composition variation through the interaction layer from $(U,Mo)Al_{4.4}$ at the layer–matrix boundary to $(U,Mo)Al_3$ at the layer–alloy boundary. The thinner Al rich sub-layer is ignored. The composition profiles of U and Al are illustrated in Fig. 2.

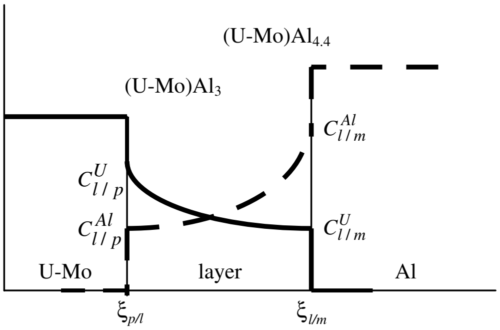

Fig. 2. Schemes of the concentration profiles of U (solid line) and Al (dotted line) assumed for the modellization.

- The chemical reaction at the alloy–layer interface, $\xi_{p/l}$, proceeds instantaneously. The rate-limiting step is diffusion of Al through the interaction layer. The alloy provides all the U (and Mo) necessary to form the new phase.
- Similarly, the reaction at the layer–matrix interface, $\xi_{l/m}$, is governed by the diffusion rate of uranium through the layer, being the reaction itself instantaneous.

3. Description of the code

DPLACA solves the most significant processes that the fuel plate undergoes during irradiation in a research reactor. Temperature, stress and strain distribution, thermal expansion, elastic and plastic strains, mechanical interaction between core and cladding, fission gas release, swelling and densification are modelled. The stress–strain and heat conduction problems are non-linear due to plasticity and to the temperature dependence of the thermal conductivity. The code is bidimensional and uses the finite element method to integrate the differential equations. The analysis of a transversal and a longitudinal section of the plate yields a quasi-three-dimensional description of the system.

The subroutine devoted to simulation of the interaction layer kinetics solves the diffusion equation for each diffusing element (U and Al) in each phase. The problem is assumed one-dimensional either in the planar or spherical geometry. If the diffusion coefficient D is assumed constant the equation can be expressed as

$$\frac{\partial C}{\partial t} = \frac{D}{r^n}\frac{\partial}{\partial r}\left(r^n \frac{\partial C}{\partial r}\right), \tag{1}$$

where C is the concentration of the diffusing substance. According to the type of coordinates employed, n is equal to 0 for cartesian and 2 for spherical coordinates, respectively. (With $n = 1$ Eq. (1) also holds for cylindrical symmetry.) The solution $C(r,t)$ is subjected to the initial and boundary conditions in each phase.

The moving boundary problem, also known as Stefan problem, basically consists in determining the kinetics of the boundary separating the two neighboring phases. As a result of the interface movement, one of the phases grows in detriment of the other. If $\xi(t)$ indicates the interface position, $C_1(r,t)$ and $C_2(r,t)$ the content of a given species in each phase, D_1 and D_2 the respective diffusion coefficients of that element, then the mass balance at the boundary yields the interface velocity

$$\left(C_1^{\xi} - C_2^{\xi}\right)\frac{\mathrm{d}\xi}{\mathrm{d}t} = -D_1 \frac{\partial C_1}{\partial r}\bigg|_{r=\xi} + D_2 \frac{\partial C_2}{\partial r}\bigg|_{r=\xi}. \tag{2}$$

C_1^{ξ} and C_2^{ξ} represent the concentration of the given element at each side of the interface. The assumption of thermodynamic equilibrium at the interface implies that the boundary concentrations are given by the corresponding equilibrium phase diagram, and are functions of temperature only.

The model to be applied to the system U–Mo/Al must include two species diffusing in opposite senses and reacting to form the intermediate layer. Aluminum flows from the matrix to the alloy and uranium (together with Mo), from the alloy to the matrix, both traversing the intermetallic growing layer. In principle both species contribute to the movement of both interfaces so that an equation like (2) has to be formulated for each element, U and Al, for each boundary. But, when the simplifying assumptions listed in Section 2 and illustrated in Fig. 2 are adopted, the following expressions are obtained for the velocities of the alloy–layer ($\xi_{\mathrm{p/l}}$) and layer–matrix ($\xi_{\mathrm{l/m}}$) interfaces:

$$\frac{\mathrm{d}\xi_{\mathrm{p/l}}}{\mathrm{d}t}\left(-C_{\mathrm{l/p}}^{\mathrm{Al}}\right) = D_{\mathrm{l}}^{\mathrm{Al}} \frac{\partial C_{\mathrm{l}}^{\mathrm{Al}}}{\partial r}\bigg|_{\xi_{\mathrm{p/l}}}, \tag{3}$$

$$\frac{\mathrm{d}\xi_{\mathrm{l/m}}}{\mathrm{d}t} C_{\mathrm{l/m}}^{\mathrm{U}} = -D_{\mathrm{l}}^{\mathrm{U}} \frac{\partial C_{\mathrm{l}}^{\mathrm{U}}}{\partial r}\bigg|_{\xi_{\mathrm{l/m}}}. \tag{4}$$

In these expressions $C_{\mathrm{l}}^{\mathrm{U}}(r,t)$ and $C_{\mathrm{l}}^{\mathrm{Al}}(r,t)$ are the concentrations of both elements in the layer. At the phase boundaries they adopt the values given by the stoichiometry of the compounds at the limits of the layer: $C_{\mathrm{l/m}}^{\mathrm{U}}$ is the concentration of U at the layer boundary next to the matrix and corresponds to the compound (U–Mo)$Al_{4.4}$; $C_{\mathrm{l/p}}^{\mathrm{Al}}$ is the concentration of Al at the layer boundary next to the alloy and corresponds to the compound (U–Mo)Al_3; $D_{\mathrm{l}}^{\mathrm{U}}$ and $D_{\mathrm{l}}^{\mathrm{Al}}$ indicate the respective diffusion coefficients in the layer. The coefficients of interdiffusion of U and Al in the growing layer are necessary for the simulation and should be empirically determined. $C_{\mathrm{l}}^{\mathrm{U}}(r,t)$ and $C_{\mathrm{l}}^{\mathrm{Al}}(r,t)$ are obtained as solutions of equations like (1).

Various numerical methods have been devised to solve one-dimensional Stefan problems [7]. In the present work the diffusion equation (1) is discretized employing the finite difference method, with a forward scheme to approximate the time derivatives and a centered scheme for the space derivatives. This yields an explicit expression for the concentration in the ith spatial node at the $(j+1)$th time step in terms of the concentrations at the previous time step in three neighboring nodes

$$\begin{aligned} C_i^{j+1} &= C_i^j + \frac{nD\Delta t}{r_0 + i\Delta r}\frac{C_{i+1}^j - C_{i-1}^j}{2\Delta r} \\ &\quad + \frac{D\Delta t}{\Delta r^2}\left(C_{i-1}^j - 2C_i^j + C_{i+1}^j\right). \end{aligned} \tag{5}$$

The *moving grid method* is used in this work. A uniform grid is defined in each phase and the number of nodes in each one is maintained constant along the process. Due to the movement of the interfaces, the grid has to be computed at every time step.

Then, the solution is obtained by interpolation between the old and the new grids.

4. Numerical calculations. Code testing

The calculation routine developed in the present work was tested in several moving boundary problems. For some of them analytical solutions are known; for others, the code predictions were compared with experimental data. The next sections describe the steps followed.

4.1. A single diffusing species and two moving interfaces

The high temperature interaction between O and Zr gives rise to the formation of a superficial oxide layer followed by a α-Zr(O) layer and finally a β-Zr(O) region. In planar geometry and with a sufficiently thick sample an analytical solution can be found for this problem [8,9]. The expressions for the solute concentration in each phase contain the space and time variables related in the form $r/\sqrt{Dt}$ and the velocities of the interfaces are proportional to $1/\sqrt{t}$. This dependence is generally described as parabolic kinetics.

The numerical and analytical results obtained for the interfaces positions are compared in Fig. 3. The lower curve represents the interface between the sample and the atmosphere. The initial concentration profile required by the numerical procedure to start the calculation was generated with the analytical equations for a short initial time. It is seen that a good agreement exists between both families of solutions. The small departure observed for long times is due to the condition of semi-infinite medium which is maintained in the analytical solution but not in the numerical simulation.

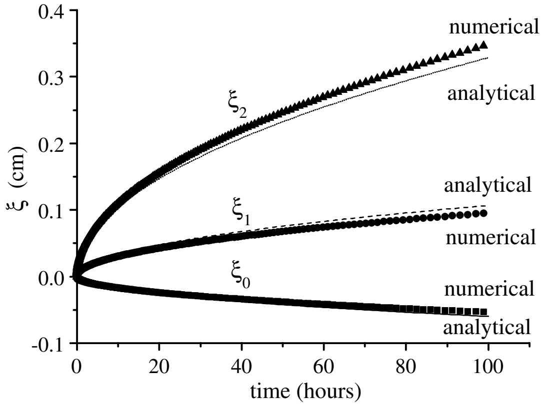

Fig. 3. Comparison between the analytical and numerical results obtained for the position of the interfaces: ξ_0 boundary of the stoichiometric oxide in contact with the oxidizing atmosphere; ξ_1, oxide-α phase boundary; ξ_2, boundary between the α and β phases.

4.2. Diffusion of two elements in a multi-phase system

In Ref. [10] experimental results corresponding to the system Mo/Si in planar geometry are reported. Two phases are formed due to interaction: a thin layer of Mo_5Si_3 next to the pure Mo phase and other of $MoSi_2$ that occupies most of the interaction thickness. The similarities between this system and the U–Mo/Al system make this example useful for code testing. The comparison between the experimental results and the numerical simulation with DPLACA for the layer thickness are shown in Fig. 4. For simplicity the layer of Mo_5Si_3, which represents less than 10% of the whole thickness, is ignored. The excellent agreement between both sets of data is evident.

The interaction between U and Al has been investigated in works as ancient as those by De Luca and Sumsion [11], Castleman [12], Harlow and Gamba [13], LeClaire and Bear [14], among others. The development of an interaction layer mainly constituted by UAl_3 was observed in U–Al diffusion couples, obeying a parabolic growth rate law which indicates that volume diffusion is the rate-determining step. The interdiffusion coefficients

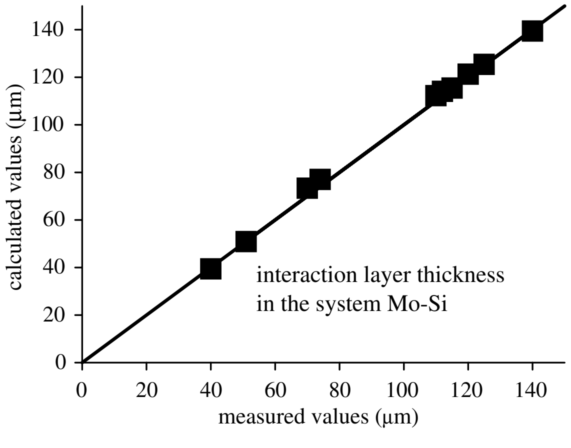

Fig. 4. Comparison between the calculated interaction layer thickness in the system Mo–Si and the experimental values reported in [9].

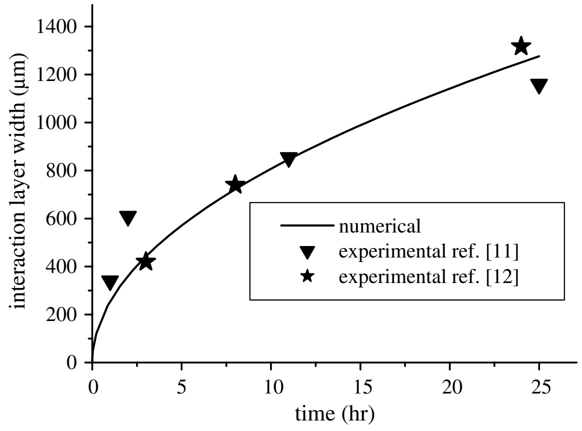

Fig. 5. Comparison between the simulated interaction layer growth in U–Al diffusion couples at 550 °C and experimental values reported in [11,12].

of U and Al were more recently obtained by Ryu et al. [1] in a similar system (see Section 5.1) at 550 °C. Among the above mentioned experiments, those performed at that temperature were selected and compared with the results of the numerical simulation obtained with PLACA. In some instances the pressure had to be previously normalized. Fig. 5 reveals a reasonably good fitting between the experimental and numerical values.

5. Simulation with DPLACA of the interaction U–Mo/Al. Comparison with experiments

Vermolen and Vuik [15] developed a model to describe dissolution or growth of a particle in a multicomponent alloy. Diffusion of the various chemical elements present in the system is assumed to govern the process; cross-diffusion is taken into account. The concentration profile of each element in the medium surrounding the particle (assumed stoichiometric) is obtained from

$$\frac{\partial c_i}{\partial t} = \sum_{j=1}^{N} D_{ij} \nabla^2 c_j \quad \text{with } i = 1, \ldots, N, \tag{6}$$

where N is the number of chemical elements and D_{ij} represents the diffusion coefficient of element i in presence of a concentration gradient of element j; those with $i \neq j$ are referred to as the cross-diffusion coefficients; those with $i = j$ represent the normal diffusion coefficients; all of them are assumed independent of concentration. The interface ξ separating the particle from the medium moves obeying equations like

$$\left(c_i^{\mathrm{part}} - c_i^{\mathrm{sol}}\right) \frac{\mathrm{d}\xi}{\mathrm{d}t} = \sum_{j=1}^{N} D_{ij} \frac{\partial c_i}{\partial n}, \tag{7}$$

where n indicates the direction normal to the interface. This type of problem is designed as ‘vector-valued Stefan problem’.

The authors apply this model to the dissolution of Al_2CuMg particles in aluminum, a system for which the normal and cross-diffusion coefficients are known. Although the hypothesis contained in this approach are consistent with the characteristics of the system U–Mo/Al, the difficulty arises from the number of physical parameters required, which are not available in this case.

With a different approach, multicomponent diffusion has been extensively studied by Dayananda et al. [10,16,17]. The method consists in evaluating the interdiffusion fluxes of all the components present in a solid–solid diffusion couple at any time and any section of the concentration profiles. These are designated $C_i(x)$ with $i = 1, \ldots, n$, where n is the number of components. The interdiffusion flux is calculated from

$$\tilde{J}_i(x) = \frac{1}{2t} \int_{C_i^{+/-}}^{C_i(x)} (x - x_{\mathrm{M}})\, \mathrm{d}C_i, \tag{8}$$

where x_{M} is the location of the Matano plane and $C_i^{+/-}$ is an abbreviate notation to indicate the concentrations at the phase boundary (C_i^{+} or C_i^{-}), i. e. the concentrations of component i of both terminal alloys employed in the couple assembly. This expression is valid for single-phase and multi-phase couples. In its derivation the functions C_i are assumed to depend on the Boltzmann parameter $(x - x_{\mathrm{M}})/\sqrt{t}$ and the variation of the molar volume is assumed negligible within the diffusion region. Then, the integrated interdiffusion coefficient is evaluated from

$$D_i = \int_{x_1}^{x_2} \tilde{J}_i\, \mathrm{d}x, \tag{9}$$

over a concentration range from $C_i(x_1)$ to $C_i(x_2)$. For binary systems, the integrated interdiffusion coefficients for both components are equal. In this case, the interdiffusion coefficient to be inserted in the Fick’s law has an average value in the composition range $C_i(x_1)$ to $C_i(x_2)$ given by

$$\overline{\overline{D}}_i = D_i / [C_i(x_1) - C_i(x_2)]. \tag{10}$$

If the interdiffusion flux $\tilde{J}$ is measured in mol/(m^2 s), the units of D are mol/(m s); the concentration C

has to be expressed in mol/m^3 in order that $\overline{\tilde{D}}$ is expressed in m^2/s. These are also the units of $\tilde{D}$ if the values of D are multiplied by the molar volume v (the units of $D \cdot v$ are m^2/s) and C is expressed in at.%.

5.1. Simulation of experiments in planar geometry

In the experiments carried out by Ryu et al. with U–Mo/Al diffusion couples annealed at 550 °C during 5 and 40 h [1] the Matano plane was localised. (This plane coincides with the original U–Mo/Al surface: $x_M = \xi_0$.) The authors then evaluated the integrated interdiffusion coefficients D_U and D_{Al} (according to Eq. (9)) for the concentration profiles of U and Al in the interaction layer, following the method outlined above. From the data of Ref. [1] the mean interdiffusion coefficients $\overline{\tilde{D}}_U$ and $\overline{\tilde{D}}_{Al}$ were obtained by means of Eq. (10). With these values and using the calculation tool already tested for the Mo/Si system, the U–Mo/Al interaction was simulated. The distances X_1 and X_2 travelled by the U–Mo/layer and layer/Al interfaces with respect to the Matano plane during the experiments were also determined. The comparison between the calculated and the (few) measured values shown in Table 1 reveals a good agreement.

Fig. 6 shows the simulated kinetics of the interfaces movement. The calculations were performed with the data corresponding to the annealing of 40 h. The experimental points are superimposed for comparison. A small departure is observed between the points measured after 5 h and the calculated curve. This can be explained considering that the initial stages of layer formation most probably follow a kinetics governed by the reaction rate rather than by the long-range diffusion. This means that the kinetics is slower than that predicted by a parabolic-rate law. The effect of this initial period is less important for the longer annealing.

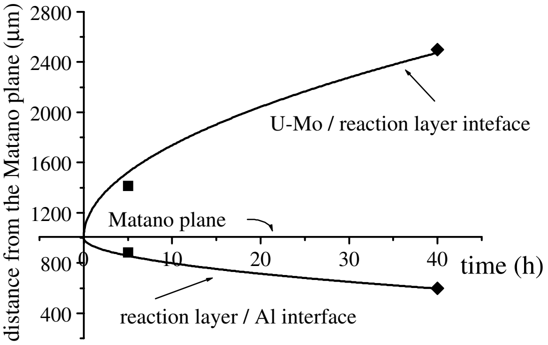

Fig. 6. Evolution of the interfaces for the U–Mo/Al diffusion couple annealed at 550 °C during 40 h. The symbols represent the experimental points reported in [1].

The code was then applied to simulate the experiments reported by Mirandou et al. [2]. The value measured for the whole layer thickness was 175 μm. This set of experiments was simulated with DPLACA according to the hypothesis listed in Section 2. The calculated concentration profiles of U and Al are shown in Fig. 7. The calculated layer thickness is 162.47 μm, which agrees quite well with the experimental value.

5.2. Simulation of experiments in spherical geometry

In Ref. [1] experiments performed with U–Mo particles dispersed in a Al matrix are also reported. Thermal treatments produce reduction of the particles size along with the formation of a shell of reaction product around each particle. This layer forms partly in the prior-particle and partly in the prior-matrix regions.

Analytical resolution of this problem is not a simple task. In fact, an analytical solution can be found for the growth of a spherical particle in an initially homogeneous medium, starting from a negligible radius, assuming that equilibrium conditions are maintained at the growing surface. As in the planar case, also in this one the variables r and t appear in the expression for concentration in the form $r/\sqrt{Dt}$ [18]. But the problem of surface reaction of a particle in a medium, with the radius of the

Table 1
Comparison between the experimental and numerical values of the interaction layer thickness for thermal treatments of 5 and 40 h at 550 °C

Anneal. time (h)	$D_U \cdot v$ (μm^2/s)	$D_{Al} \cdot v$ (μm^2/s)	$\overline{\tilde{D}}_U$ (μm^2/s)	$\overline{\tilde{D}}_{Al}$ (μm^2/s)	X_1 (μm)		X_2 (μm)		Layer thickness (μm)	
					Exp.	Num.	Exp.	Num.	Exp.	Num.
5	0.71	0.91	14.1731	14.0432	115	98.13	415	354.6	530	452.73
40	1.5	1.9	29.9431	29.3210	400	403.38	1500	1472.6	1900	1876

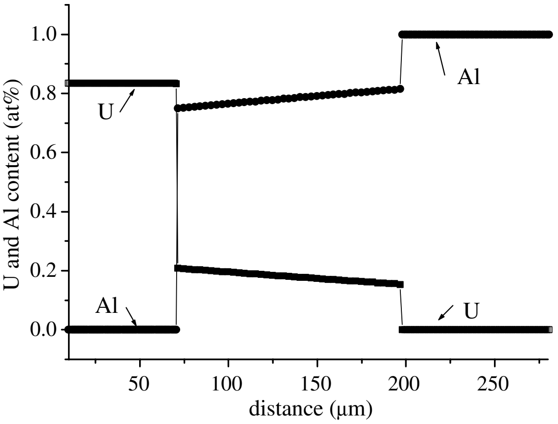

Fig. 7. Calculated concentration profiles of U and Al in the interaction layer according to the experimental conditions of Ref. [2].

Table 2
Comparison between the analytical and numerical values of the reaction layer thickness in spherical particles

Temperature (°C)	Time (h)	k ($\mu m^2/s$)	Layer thickness (μm)	
			Analytical	Numerical
500	40	9.1667×10^{-4}	11.4000	11.9400
525	25	0.0026	15.7000	16.6202
550	4	0.0133	14.6000	14.8612

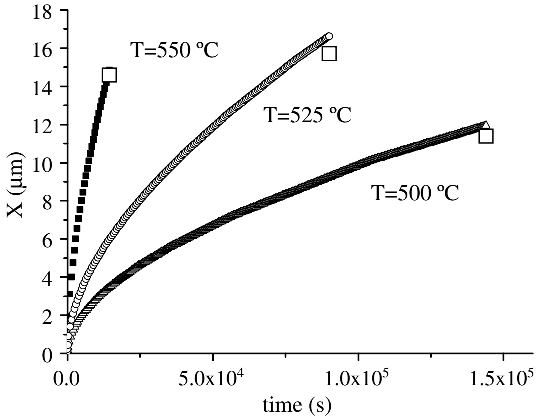

Fig. 8. Evolution of the reaction layer thickness in spherical particles without irradiation at three different temperatures. The open symbols represent the results obtained with the analytical approach reported in [1].

particle decreasing from an initial value, cannot be given an analytical expression. Vermolen et al. [19] give an expression for the interface velocity, in the derivation of which a number of assumptions are made. However, it is not accurate when the particle radius is small.

The model developed by Ginstling–Brounshtein reported in Ref. [1] was adopted. It assumes a three-dimensional diffusion process through the reacted shell of thickness x around a particle of initial radius r_0 and gives the kinetic relation

$$x^2\left(1-\frac{2x}{3r_0}\right)=kt, \tag{11}$$

where k is a temperature dependent parameter that obeys an Arrhenius type law. Its values were obtained in [1] making a regression of the experimental values of the layer thickness. For small values of x, this expression predicts an almost parabolic dependence of thickness with time. The problem of simultaneous diffusion of U and Al was solved in spherical coordinates and the kinetics of both layer boundaries was obtained with Eqs. (3) and (4). The comparison between the experimental and calculated results for the interaction layer thickness at the end of the thermal treatment is shown in Table 2. The analytical and numerical predictions of the layer thickness are superimposed in Fig. 8. An excellent agreement is observed.

5.3. Simulation of experiments under irradiation

The experiments reported above are oriented to analyzing the influence of time and temperature only. They were carried out at relatively high temperatures in order to accelerate the processes and to achieve the results in experiments of short extent. During normal reactor operation the temperatures are significantly lower and the periods significantly longer but conversely irradiation enhances the processes. Hofman et al. [20–22] performed post-irradiation examinations on U–Mo/Al samples and elaborated an empirical relation for the interaction layer thickness (x) as a function of absolute temperature (T), fission rate density ($\dot{f}$), time (t) and weight fraction of molybdenum (w_{Mo})

$$x=\sqrt{2.2443\times10^{-19}(1.625-6.25w_{\mathrm{Mo}})\dot{f}^{0.75}t\exp\left(-\frac{10000}{1.987T}\right)}, \tag{12}$$

where x is measured in cm, t in seconds and $\dot{f}$ in fissions/(cm^3 s). This formula expresses a parabolic dependence of x with t, i.e. $x=\sqrt{Kt}$ where K is the parabolic rate coefficient given by

$$K = 2.2443 \times 10^{-19}(1.625 - 6.25w_{\mathrm{Mo}})\dot{f}^{0.75} \times \exp\left(-\frac{10\,000}{1.987T}\right) \quad \left[\frac{\mathrm{cm}^2}{\mathrm{s}}\right]. \tag{13}$$

No conclusive argument is given in the literature relative to the evaluation of the individual fractions corresponding to the prior-particle and prior-matrix fractions of the reaction layer. The model developed in this work is able to determine the time dependence of each interface position provided that the correct diffusion coefficients of uranium and aluminum are given as input data.

In the experiment FUTURE two plates of U–7 wt%Mo fuel particles dispersed in aluminum were irradiated during 40 days at full power. Leenaers et al. [4] performed detailed post-irradiation examinations on these plates. They measured the interaction layer thickness and found that, in the higher flux regions, it reaches 11 μm at the end of life. In one of the samples the mean diameter of the particles before irradiation, that of the remaining particle and the layer thickness at the end of the irradiation period were measured. According to these results it can be estimated that the prior-particle fraction of the reacted layer represents about 37% of the whole layer thickness. These authors also present a simulation performed with the MAIA code that assumes the layer as constituted by a single chemical compound. In spite of this restriction the estimation of the plate parameters is acceptable.

These experiments were simulated with the version of the DPLACA code developed in this work. Diffusion of U and Al through the reaction layer is solved in spherical geometry with the assumptions listed in Section 2. The main difficulty stems from the incomplete knowledge of the physical parameters required by the model. As for the diffusion coefficients of U and Al in the reaction layer, the chemical diffusion coefficients presented in Section 5.1 have proved to be adequate to represent the out-of-pile experiments. However, under irradiation these coefficients do not seem to be the more appropriate. Assuming that layer growth is also in these conditions a diffusion-controlled process and in order to include the effects of irradiation, modified diffusion coefficients are proposed. Considering that in diffusion-controlled processes a proportionality relation holds between the parabolic rate and diffusion coefficients, we propose that the chemical diffusion coefficients of U and Al be proportional to the empirical relation (13). Taking into account that in the experiments reported in [1] these coefficients verify an approximately constant relation $\widetilde{D}_{\mathrm{Al}}/\widetilde{D}_{\mathrm{U}} \cong 1.2$ in the sub-layers identified by these authors as L1 and L2, the parameters $\widetilde{D}_{\mathrm{U}} = K$, $\widetilde{D}_{\mathrm{Al}} = 1.2K$ were adopted for the simulation purpose. This choice has to be inscribed in the category of a numerical experiment.

The growth of the interaction layer causes a gradual deterioration of the thermal conductivity and consequently temperature in the fuel plate increases as burn-up progresses, even under constant irradiation conditions. This induces acceleration of the diffusion processes which enhance layer growth. Inclusion of these effects in the model converts heat and mass diffusion into non-linear problems.

With the considerations mentioned above the code DPLACA was used to simulate the conditions of the experiment FUTURE [4]. An initial particle radius of 20 μm was assumed; this is a standard value for the powders fabricated by KAERI, used for constructing the plates. The calculations reveal that the temperature at the mid-plane of the plate grows almost linearly from 130 °C at the beginning of life to 245 °C at the end of irradiation [5]. In Fig. 9 the locations of both interaction layer boundaries are shown as functions of time; the layer thickness is also plotted for which a value of 10.73 μm is predicted at the end of life. This has to be compared with the 11 μm reported in [4] from the experiment. The corresponding point is superimposed in the plot.

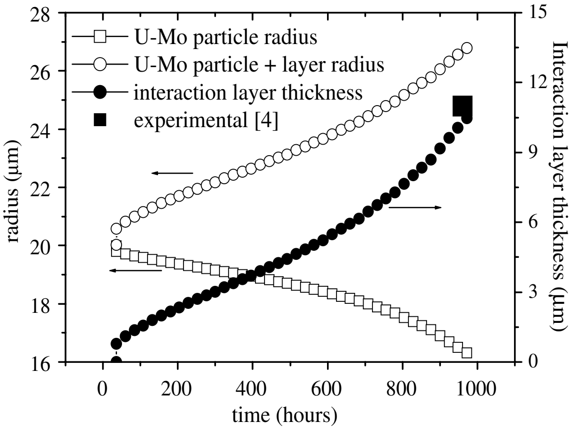

Fig. 9. Time dependence of the particle/layer and layer/matrix interfaces position and of the interaction layer thickness around spherical particles under irradiation.

6. Summary and discussion

The model and code we present in this work have been designed to give account of the phenomena taking place in the system U–Mo/Al where the interaction between both materials gives origin to a new intermediate layer separated from the original phases by definite surfaces. The model proposes that the growth of this layer is a diffusion-controlled process either under the exclusive effect of temperature or under the combined effect of irradiation. Strictly speaking the situation can be described as a multiphase multi-component vector Stefan problem with cross-diffusion. The difficulties implied in this description forces the introduction of a number of simplifying assumptions. Basically, the model considers that the rate-determining step is diffusion of uranium and aluminum through the layer. The chemical reactions at both interfaces are assumed to proceed instantaneously, the velocity of reaction at the U–Mo particle surface being limited by the arrival of Al atoms there and, conversely, the velocity of reaction at the matrix boundary by the arrival of U atoms. The experiments show that the interaction layer is not uniform in composition but formed by three distinct sub-layers. However, there is not full agreement among the different authors about the exact composition of sub-layers. The model assumes that at the boundaries the layer composition is given by $(U\text{–}Mo)Al_3$, at the U–Mo alloy side, and $(U\text{–}Mo)Al_{4.4}$, at the matrix side. It further assumes that a continuous composition gradient exists through the layer between both limiting compositions. Although this consideration represents a clear departure from reality, it yields a significant simplification of the calculations together with a reasonable accuracy.

The experiments with planar diffusion couples of U–Mo/Al performed by Ryu et al. [1] and Mirandou et al. [2] as well as those with spherical U–Mo particles disperse in aluminum reported in [1] are numerically simulated with the code DPLACA. These tests were conducted with the purpose of exploring the effect of temperature and time on the development of the interaction layer. The calculated results are in satisfactory agreement with the measured values.

With reference to the experiments with diffusion couples it has to be mentioned that those reported in [1] were performed with the alloy U–10 wt%Mo while those in Ref. [2] with U–7 wt%Mo. It is likely that this difference in Mo content has an influence on the stability of the alloy and hence on the reaction rate with aluminum. This aspect is not included in the modellization since no quantification of this effect is available. The difference in Mo content is made present through the values of the weight percents of U and Al at both layer boundaries that enter in the diffusion equations and determine the respective concentration gradients.

Simulation of experiments with irradiated plates of dispersed fuel, as those reported in [4], also gave satisfactory numerical results as compared with the post-irradiation data. In this respect it is worth mentioning that DPLACA is able to predict not only the whole layer thickness but also the individual fractions corresponding to particle and matrix consumption. In contrast, other similar codes require the introduction of additional hypothesis to perform an equivalent evaluation.

The model adopted, although simple gives a good representation of the system. It can be improved by introducing two (or three) distinct interaction sub-layers but this would demand more precise experimental information not available at the present time.

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