Modelling of liquid phase segregation in the Uranium–Oxygen binary system

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A B S T R A C T

In the uranium–oxygen (U–O) binary system, the existence of a miscibility gap induces the segregation between two immiscible liquid phases at thermodynamic equilibrium: an oxidic phase and a metallic one. Within the framework of severe accidents in a Light Water Reactor (LWR), the knowledge of in-vessel corium (U–O–Zr-steel system) behaviour and the associated vessel failure risk are of prime interest. The corium pool configuration plays a key role on the heat flux distribution and therefore on the vessel integrity. A coupled thermochemistry-thermalhydraulics model is needed for investigating the stratification kinetics of a corium pool. The work presented here is a first step in the development of such a model, and is focused on the modelling of the kinetics of liquid phase segregation in the U–O binary system. With this aim, we have developed a Cahn–Hilliard model, derived from a free energy functional, for investigating the liquid phase segregation. The present paper discusses the coupling of the transient Cahn–Hilliard solver with a U–O CALPHAD thermodynamic database and the parameterization of such a kinetic model.

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1. Introduction

The liquid phase segregation in the uranium–oxygen system is of prime interest for applications in the nuclear industry. Indeed, a severe accident can occur in a nuclear reactor if, subsequent to the loss of the primary coolant (*i.e.* the water), the reactor core is no longer cooled. During such a hypothetical severe accident, the core could melt down and form a hot molten material mixture called corium (U–O–Zr-steel system) that consists of molten nuclear fuel (UO_2), the partially oxidized fuel cladding (Zr, ZrO_2) and the vessel steel (Fe, Cr, Ni). Corium can be transferred to the reactor vessel lower head and reactor pit in case of vessel failure. The "in-vessel retention" (IVR) is a severe accident management strategy [1,2], whose purpose is to keep the integrity of the second containment barrier (*i.e.* the reactor vessel). It consists in reflooding the reactor pit ("External Reactor Vessel Cooling" ERVC).

The success of such a strategy is determined by the heat flux from the corium pool to the vessel wall. It is well known that corium exhibits a liquid phase separation between an oxide-rich and a metallic phase. The distribution of the two phases in space can dramatically influence the heat flux. The main risk of vessel failure is related to the possible existence of a thin metallic layer at the top of the corium melt and the associated focusing effect in terms of lateral heat flux. Fig. 1 shows a possible corium pool stratification with a steel layer above a two phase corium pool stratification.

The distribution of different phases in the corium pool depends on time, since the density of the phases depends both on temperature and composition. The latter can change with time due to the progressive vessel ablation, the relocation of corium from the core, etc. Therefore, a detailed description requires to follow the evolution of the pool stratification. Our final goal is to model finely the behaviour of an oxidic–metallic corium pool in the reactor vessel lower head. The complete 3D modelling of corium pool kinetics would require to couple the description of phase separation with thermal hydrodynamics model based on a Computational Fluid Dynamics (CFD) approach, which is out of the scope of the work presented here. In this context, a mesoscopic modelling regarding the species transfer at the interface between two liquid immiscible phases is needed. Phase-field methods have emerged as an efficient tool for mesoscopic modelling of complex microstructures. Moreover, such a modelling approach can be made consistent with thermodynamic data based on CALPHAD approach [3,4]. A general introduction to the phase-field method is given in [5] and this kind of method finds application, for example, in solidification dynamics [6], solid-state transformations [7], spinodal decomposition [8] and liquid phase separation [3,9]. Phase-field

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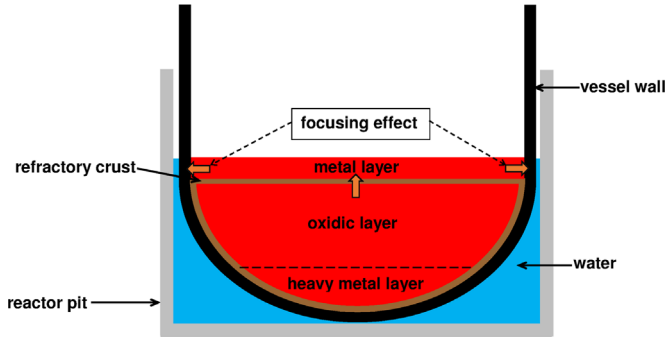*E-mail address:* clement.cardon@cea.fr (C. Cardon).

Fig. 1. A possible corium pool stratification in the LWR vessel lower head.

models derived from a thermodynamic functional are based on a diffuse-interface description in which order parameters, functions of space and time completely describing the state of the system, vary continuously across the interface and take constant values in bulk phases: diffuse-interface models do not require to follow explicitly the moving interface.

As a first step towards such a detailed modelling, we present here a 1D Cahn–Hilliard model for the kinetics of liquid phase segregation in the U–O binary system. We have chosen this system because it exhibits, like in-vessel corium, a miscibility gap in the liquid phase. We achieve a good thermodynamic description of the system by using a U–O CALPHAD database, that is coupled with a transient Cahn–Hilliard solver through the Open Calphad software [10]. In [11], this software has already been used for a phase-field model with finite interface dissipation.

It is well known that the length scales that can be treated with a phase-field model are set by the thickness of the diffuse interfaces. The "natural" thickness of liquid–liquid interfaces is of the order of nanometers. A Cahn–Hilliard model with physically realistic parameters would therefore not be suitable for modelling of macroscopic scales. Indeed, during severe accident, the corium pool size in the nuclear reactor is of the order of magnitude of meter and it would be impossible to capture the interface length scale for 3D meshes. We present a method that allows us to upscale the interface thickness, that is, to work with thicker interfaces without changing the kinetics of the model on spatial scales that are larger than the thickness of the diffuse interfaces. This thickness thus becomes a numerical parameter of our model that can be chosen according to the desired spatial mesh size, while keeping bulk thermodynamics, the interface free energy and the time scale for diffusion constant. Similarly to previous works on other phase-field models [12], this method involves an appropriate change in the parameterization of the model. We validate this method by numerical simulations in one dimension.

2. The U–O binary system and the associated CALPHAD database

The U–O binary system presents a miscibility gap at liquid state for a large range of temperature and composition. Two liquid phases coexist: an "oxidic" phase enriched in oxygen and a "metallic" one with a low fraction of oxygen.

We have used a U–O CALPHAD database in terms of a compound-energy formalism (CEF) model with one sublattice and associates (a full description of the different models describing the Gibbs energy is given in [13]). A description of the Gibbs energy associated with different phases in the U–O binary system is given in [14]. The model of Gibbs energy for the liquid phase is written for constituent molar fractions y. In the U–O system, there are 3 constituents: U (uranium), O (oxygen) and UO_2 (uranium

dioxide) and the sum over constituent molar fractions is unity:

$$y_U + y_O + y_{UO_2} = 1 \tag{1}$$

In the following, G_M and G_m denote the Gibbs energy per mole of formula unit and the Gibbs energy per mole of components for the liquid phase, respectively, and linked in the following way:

$$G_m = \frac{G_M}{N} \tag{2}$$

where $N = y_O + y_U + 3y_{UO_2}$ is the total amount of components per mole of formula unit in the liquid phase.

The formula unit is defined as the sum of all sites in all sublattices of the phase and the molar Gibbs energy per mole of formula unit for the liquid phase is expressed as

$$G_M = y_O G_O^0 + y_U G_U^0 + y_{UO_2} G_{UO_2}^0$$
$$+ RT [y_O \ln(y_O) + y_U \ln(y_U) + y_{UO_2} \ln(y_{UO_2})] + G_M^{Ex} \tag{3}$$

with G_i^0 the Gibbs energy of formation for constituent i, $R = 8.314 \, \text{J mol}^{-1} \text{K}^{-1}$ the ideal gas constant and T the temperature.

The excess contribution G_M^{Ex} is

$$G_M^{Ex} = y_O y_{UO_2} L_{O,UO_2} + y_O y_U L_{O,U} + y_U y_{UO_2} L_{U,UO_2} \tag{4}$$

$L_{i,j}$ is the binary interaction parameter between constituents i and j and described by Redlich–Kister polynomial functions:

$$L_{i,j} = \sum_\nu L_{i,j}^\nu \left(y_i - y_j \right)^\nu \tag{5}$$

$L_{i,j}^\nu$ may be dependent on temperature T. These interaction parameters are available in the NUCLEA thermodynamic database [15] used for the corium system.

For convenience, the following notations are introduced:

$$\tilde{G}_M(y_O, y_{UO_2}) = G_M(y_O, y_{UO_2}, 1 - y_O - y_{UO_2}) \tag{6}$$

$$\tilde{G}_m(y_O, y_{UO_2}) = G_m(y_O, y_{UO_2}, 1 - y_O - y_{UO_2}) \tag{7}$$

The Gibbs molar energy $\tilde{G}_m(y_O, y_{UO_2})$ of the U–O CALPHAD database for the liquid phase is plotted in Fig. 2.

This graph shows that $\tilde{G}_m$ is minimum when the maximum number of moles of uranium is oxidized and the system only contains uranium dioxide UO_2. An equilibrium calculation performed with the Open Calphad software at 3200 K yields the phase composition listed in Table 1. This equilibrium calculation confirms that there is no "free" oxygen (in the sense of constituent: $y_O = 0$) at thermodynamic equilibrium. In our modelling, we will make the assumption that the system never contains "free" oxygen in its initial state. As a consequence, there will be no "free" oxygen in the system during the transient state.

x_O and x_U respectively denote the molar fraction of oxygen and uranium components depending on the constituent molar fractions y_O and y_{UO_2}:

$$x_O = \frac{y_O + 2y_{UO_2}}{1 + 2y_{UO_2}}, \quad x_U = \frac{1 - y_O}{1 + 2y_{UO_2}} \tag{8}$$

With the assumption $y_O = 0$, the molar fraction of oxygen x_O is given by Eq. (9) and x_O is in the range $[0, \frac{2}{3}]$:

$$x_O = \frac{2y_{UO_2}}{1 + 2y_{UO_2}} \tag{9}$$

The state of the system is completely determined by x_O:

$$y_{UO_2} = \frac{x_O}{2 - 2x_O}, \quad y_U = 1 - y_{UO_2}, \quad y_O = 0 \tag{10}$$