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Abstract

This work provides a computational model that will help to predict the life-span of SiC based refractories used in waste to energy plant (WTE) linings. For this particular application, gas present in the atmosphere diffuse through the porosity and react with the refractory producing SiO_2 and $CaSiO_3$ solids. These new phases clog gradually the pores and cause swelling of the material and as a result irreversible deformation of the lining. The proposed thermo-chemo-mechanical model that simulates these phenomena is briefly summarized and some of the parameters are identified. Then, first results obtained with the model implemented in a F.E.M code are shown. They prove the ability of the model to reproduce qualitatively the swelling of post-mortem bricks taken from WTE linings.

Keywords: SiC based refractories, Coupling, Thermo-chemo-mechanics

Introduction

Refractories are often subjected to extreme solicitations: high temperature gradient, aggressive chemical environment and mechanical constraint. Consequently, refractory degradations result from these combined solicitations. The goal of this study is to furnish a first step to the development of a fully coupled thermo-chemo-mechanical computational model that will help to predict the refractory lining life-span and optimize the design of such linings. This model falls within the scope of previous works on steel ladle's refractory[1,2]. It is written in the framework of continuum thermodynamics of irreversible processes[3,4], and focuses on modelling of the couplings between thermochemistry and thermomechanics. The observed degradations of silicon-carbide-based refractories used in waste-to-energy plants (WTE) are the support of this work. This study realised in the context of the French research program ANR DRuIDe, deals with four different SiC based refractories, two of them containing calcium aluminate binders provided by the manufacturer Calderys and two other containing nitrogen binders provided by the manufacturer Saint-Gobain.

Figure 1: New (top) and old (bottom) SiC based refractory tiles (oxides binders) in a WTE facility (tile height: 245mm)

In WTE, the thickness of the lining is small (approximately 60 mm) to facilitate the heat transfer. The refractories are in contact with smoke and ashes on the hot face and with a metallic water wall -temperature approximately 250°C - on the cold face. The temperature in the combustion chamber at the bottom level in the hot flame is close to 1200°C. About 17 m higher, at the top of the chamber, it falls down to around 500°C. At the intermediate level (i.e. 7 m) SiC based refractories containing oxides binders slowly swell during service and, sometimes, fall down. Figure 1 illustrates the deformations of typical tile after a long period of use.

Herein, the refractory swelling is explained by the reactive transport of species (i.e. O_2 and gas species containing Ca) by diffusion in the gas present in the porosity space. Observations of microstructures of worn refractories have revealed the appearance of new phases (silica and wollastonite) mainly in the matrix binder and in the porosity[5]. So, it is assumed that a part of the SiO_2 produced by the oxidation of SiC and that a part of the $CaSiO_3$ produced by the reaction between Ca precursor and SiO_2 clog gradually the pores[5]. Firstly, it induces a decrease of the diffusion rate; secondly, the induced chemical strain causes the swelling of the structure. In the model currently developed, due to a lack of experimental data, only the SiC oxidation parameters have been identified. Then, even if the wollastonite formation is

implemented, only the SiC oxidation model will be developed herein.

The computation of the coupled thermo-chemo-mechanical model is made in three steps. The classical resolution of energy balance is made in the first step. Then, the reactive transport of species under thermal gradient is solved. Lastly, the mechanical problem is solved accounting for some effects induced by the formation of new phases. Herein, the equations of the model are shortly summarised and first qualitative results are presented.

Energy balance

The temperature field in the lining is obtained through the classical energy balance applied to the whole lining

$$\rho C_p \frac{\partial T}{\partial t} = div(\lambda \boldsymbol{grad}(T)) \qquad (1)$$

where T is the temperature, ρ the bulk density, C_p the specific heat and λ the thermal conductivity of the refractory which depends only on the temperature. Moreover, in the rest of the text, bold type will refer to vector while normal type will refer to scalar. The effects induced by the thermo-chemical phenomena like the heat source (or well) linked to the enthalpy of reaction and the change of thermal characteristics are neglected. The convective energy transported by the gases is neglected too. These assumptions are mainly justified by the fact that the heat flux due to the thermal gradient is much higher than the other heat flux transfer or production involved previously. As a result, the computation of the thermal field can be made separately.
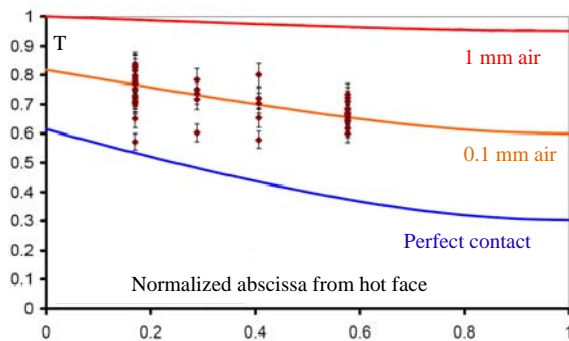
Figure 2: Normalized temperature versus localisation from hot face (x=0) to cold face (x=1) for different contact conditions at the cold face. Dot represent experimental measures on an industrial plant.

The computed temperature fields in the thickness of the lining under service condition considering a quasistatic regime are presented on figure 2 considering different boundary conditions on the cold face, from perfect contact between the refractory part and the water wall to strongly insulate layer made by a one millimetre film of static air. The temperatures obtained from several thermocouples placed into the tiles of existing WTE are also reported. A satisfactory agreement is obtained considering a 0.1 mm-thick air film.

Mass balance

The mass balance is written for the two reactive gaseous species considered in the model (i.e., O_2, Ca precursor) in term of the local fluctuation of their mass ratio x_i

$$\rho \dot{x}_i = -div\boldsymbol{J}_i + \sum_r v_{ir} M_i \dot{\xi}_r \qquad (2)$$

where i denotes the species, $\boldsymbol{J}_i$ the mass flux of component i, v_{ir} the stoechiometric coefficient for specie i in reaction r, M_i the molar mass for i, ξ_r the extent of reaction r and the dot denotes the time derivative of the quantity.

The extent is defined regard to the considering reaction. For example, in the case of SiC active oxidation, the extent rate $\dot{\xi}_S$ is defined as[6]

$$\dot{\xi}_S = k_a \left(\frac{\rho x_{SiC}}{M_{SiC}} \frac{\rho x_{O2}}{M_{O2}} \right) \left(1 - \frac{Q_a}{K_a} \right) \qquad (3)$$

where k_a is the rate constant which follows an Arrhenius law, Q_a is the mass action value at the considered time and K_a the equilibrium constant. Let us underline that the equilibrium constant is equal to the mass action value at the equilibrium. To account for the local formation of a silica layer, and so to passive oxidation, equation (3) is modified as

$$\dot{\xi}_S = \frac{1}{2} \sqrt{\frac{k_p}{t}} \left(\frac{\rho x_{O2}}{M_{O2}} \right) \left(1 - \frac{Q_p}{K_p} \right) \qquad (4)$$

For little fluctuation of the oxygen partial pressure this expression permits to obtain the classical dependance of the extent to the square root of time. The transition between active (index a) and passive (index p) oxydation under constant temperature and atmosphere is assumed to be linear in time. This point is debatable, but as the main goal is long term prediction, the effect of the transistion regime is negligible. However, the active oxydation could cover a large duration because of a possible combination of SiO(g) with other gaseous species than oxygen, preventing the formation of a passivation layer. So, the model may take into account this possibility.

The flux of each species is assumed to result from diffusion into the gas in the porosity, which leads to

$$\boldsymbol{J}_i = -D_i \boldsymbol{grad}(\rho x_i) \qquad (5)$$

where D_i is the diffusivity of species i. Due to lack of information, to account for progressive clogging up of the porosity by the product of reactions, it is assumed that the diffusivity changes linearly with porosity

$$D_i = D \frac{\phi}{\phi_O} \qquad (6)$$

where ϕ is the porosity (i.e., index 0 denotes initial value) and D is the initial diffusivity estimated with the Chapman-Enskog theory[7]. The porosity is assumed to be a linear function of the sum of the extent of the two reactions

$$\phi = \phi_0 - \alpha_S \xi_S - \alpha_w \xi_w \qquad (7)$$

where s and w refer to the SiC oxidation which produce silica and to the reaction which produces wollastonite respectively. Then, the mass balance for each species is coupled by the expression of the extent of each reaction which influences the source term and the diffusivity.

Chemical swelling

In the framework of small deformation, strain partition is considered[3]. The total strain is the sum of the thermal strain, the mechanical strain and a chemical strain. Moreover, a linear dependence between chemical strain $\boldsymbol{\varepsilon_c}$ and the extent of each reaction is assumed:

$$\boldsymbol{\varepsilon_c} = \beta_S \xi_S \boldsymbol{I} + \beta_w \xi_w \boldsymbol{I} \qquad (8)$$

Where I is the second rank identity tensor.

Identification

The identification of all the parameters of the model is an ongoing work. Only the method and results for the SiC oxidation part is summarized hereafter. Moreover, for sake of proceeding length, only results for the SiC based concrete commercially denotes SF60 (60% wt. of SiC) produced by Calderys are presented.

The identification for the oxidation kinetics was done thanks to thermogravimetric analyses (TGA) made by Bahloul[8]. Two assumptions are made to proceed to the identification: first, transport phenomena of gases inside the specimen are neglected during TGA; second, the kinetic on little dense specimen is assumed to be representative of the local kinetic in a concrete. While the first assumption is roughly acceptable, the second is more questionable. It is important to underline that, for the "macroscopic" model, the necessary data concern the oxidation kinetic locally at each point

in the castable, not on the global oxidation rate of a "large" dense specimen.

The identification of the parameters of the chemical strain requires to correlate the strain to the oxidation extent. Assuming a homogeneous oxidation in the dense samples during dilatometry, after the same duration, the extent should be the same that in TGA specimen. Thanks to the small size of dilatometry samples (9x9x15 mm[3]) combined with a porosity of 17% this assumption may be acceptable. The simulation of the isothermal expansion test with the directly identified parameters proposed later (see figure 5) confirms the relevance of this hypothesis.
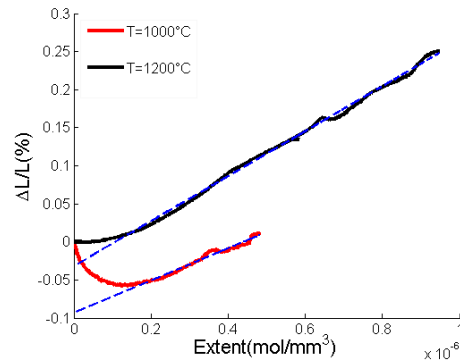

Figure 4: Chemical strain versus extent

Figure 4 shows the evolution of the chemical strain with the oxidation extent. After a delay which depends on temperature a linear relationship takes place between the oxidation strain and the oxidation extent. The slope does not seem to be temperature dependent. The apparent delay may correspond to the shrinkage induced by last stage of sintering of the matrix binder. Then, figure 4 confirms that it is reasonable to model in a first approximation the chemical expansion by a simple linear law function of the extent.

F.E.M. implementation and first results

The reactive transport equation (2), including the oxidation extent evolutions (3-4), is implemented in the software ABAQUS thanks to a UMATHT subroutine. To do this, equations have been re-written in function of partial pressure of gases in the pores. The chemical strain (8) is implemented in ABAQUS via the UEXPAN subroutine. As often for such unidirectional coupling, first, the uncoupled heat transfer is solved. Then, the calculated temperature field is prescribed for the reactive transport computation. Finally, the temperature and oxidation extent fields are prescribed as loading in the mechanical computation.

Before applying this model to the case of a WTE refractory lining, the isothermal expansion test on SF60 castable under air has been computed.

Figure 5 shows the comparison between numerical and experimental results, confirming the good agreement between the model and the experience.

First F.E.M computations with the proposed thermo-chemo-mechanical model, assuming an elastic behavior for the mechanical part, have been done considering the geometry of a tile with the SF60 castable material properties. Even if this simulation is not fully representative of the reality (currently tiles are not made with this refractory) results are qualitatively meaningful as the material of the tile is a SiC based refractory subjected to a similar corrosion mechanism. Furthermore, it is easier to compare the shape of a worn tile laid down in the furnace than to extract worn castable parts from the lining without creating irrelevant damages.
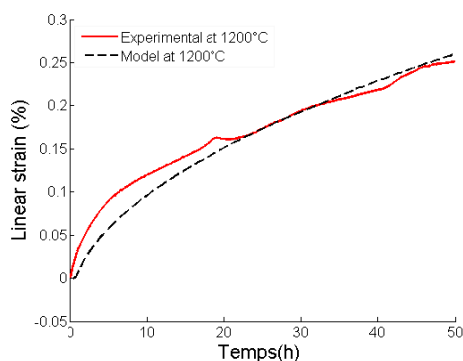

Figure 5: isothermal expansion test under air at 1200°C

Figure 6 shows the initial and worn shapes at room temperature of a real tile and the worn one predicted by the model at room temperature after one year of use with a steady fume temperature of 1050°C. The whole curvature of the worn tile is well reproduced by the model but it must be underlined that the model shape is here multiplied by 10. Indeed, the predicted displacement of the circular area on figure 6 is 0.6 mm, while on the real worn tile it has been measured at around 5 mm. This large discrepancy may be due to three main reasons: first, tiles are SiC based refractory with oxides binders, then the oxidation kinetics may be different than for castable, moreover the porosity (i.e. specific surface) are different; second, the real time spent by the worn tiles in the WTE is not currently known (and is probably more than one year); third, the swelling induced by the wollastonite growth is not taken into account in this computation and its contribution could be dominant.

Despite of the current shortcoming of the model, the analysis of the first results give interesting qualitative information. For example, it helps to better understand the combined effect of the thermal gradient (i.e. design effect) and the chemical reaction. This coupling induces a higher swelling at the bottom left (in red on computation) of the fume face than on the bottom right (in blue on computation) of the fume face. Indeed, the

thermal heterogeneity, combined with the oxygen activity gradient, induces a heterogeneous swelling.
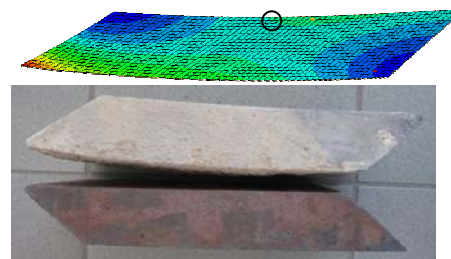
Figure 6: from bottom to top, new tile, old tile and first qualitative numerical results in term of displacement (multiplied by 10) after one year.

Conclusions

One of the goals of the French research program ANR DRuIDe was to build methods and tools to better understand the thermo-chemo-mechanical wear of SiC based refractory linings in Waste To Energy facilities (WTE). The proposed model, built in the framework of the thermodynamics of irreversible processes, gives a partial answer. Indeed, the first results are encouraging as the worn tile shape is qualitatively well reproduced. But, to tend towards a really predictive model, a huge experimental work still being under investigation in order to identify all the physical parameters introduced in the model. However, this work constitutes one step more to reinforce the method to study thermo-chemo-mechanical coupling in the field of refractory.

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