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CONSTITUTIVE LAWS OF CARBONEOUS MATERIALS OF ALUMINIUM ELECTROLYSIS CELL: CURRENT KNOWLEDGE AND FUTURE DEVELOPMENT

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Abstract

The Hall-Héroult cell behaviour at different stages of the electrolysis process is an important point to take into consideration in the design and the optimization the cell. Nowadays, numerical simulation has become a powerful and essential tool since *in situ* measurements are difficult to perform and cost expensive. For those numerical simulations, constitutive laws and their parameters' identification in laboratory are required for all the relevant physics of the cell materials. For the mechanical behaviour of the cell, many efforts have been done to characterize, to understand and to develop constitutive laws for the carboneous materials. Plasticity, viscosity, visco-elasticity, baking, etc., are examples of phenomena which have been addressed up to date, on both transient and steady state situations. This paper presents an overview on various level of modeling of the mechanical behaviour of the carbon cell lining material, from elastic to more complex like a thermo-(chemo)-visco-elasto-plactic one.

Introduction

Aluminium producers invest time and money in research and development to reach the theoretical minimum energy requirement for the actual Hall-Héroult electrolysis cells [1], i.e. cells based on prebaked anodes. To reach this goal, all the aspects of the aluminium production must be optimized, including the cell materials. Therefore, knowledge of all the relevant physical behaviour of the cell materials is essential over the entire life of the reduction cell.

It is now well known that the start-up phase is crucial and could determine the performance and the life expectancy of the cell. Thus, in the last decade, efforts have been made to optimize it through the use of numerical modeling. Moreover, once the electrolysis process has began in the reduction cell, the prevailing high temperature, molten phases and the overall corrosive environment make *in situ* measurements very difficult to achieve. Therefore, numerical modeling has become an essential tool to evaluate all the phenomena taking place in the cell, from simple ones to the more complexes ones. To be relevant, actual models require the development of three-dimensional multi-physical constitutive laws.

Overview of the numerical models

The problematic of the Hall-Héroult electrolysis cell being a multi-physical one, a wide range of numerical models have been proposed to assess those physics at different stages of the cell operation. However, most of the available models are developed to solve thermal, electrical, chemical and MHD problems, coupled or not and only few mechanical related models have been proposed. Briefly, Arkhipov *et al.* [2] have proposed a stationary thermo-mechanical and thermo-electrical (uncoupled) behaviour of a Soderberg cell. Sun *et al.* [3] have developed a thermo-chemo-mechanical three-dimensional model where all the material mechanical behaviour were considered linear elastic. Hiltmann *et al.* [4] have proposed a 3D thermo-mechanical model, where thermal load comes from a transient thermal model adjusted with their experimental data. None of those models have coupled all the important physics prevailing in the Hall-Héroult reduction cell at various stages of operation. Therefore, in previous studies of cell design (START-Cuve project), an integrated approach was adopted for the finite element simulation of cell preheating by developing the FE toolbox **FESh**$^{++}$ where all of the important phenomena are coupled. The models developed in this FE toolbox required the integration of all the relevant materials constitutive laws, such as those related to the carboneous materials.

During the last decade, some works, mostly based on the finite element toolbox **FESh**$^{++}$, have been carried out to assess the start-up of the Hall-Héroult cell. While Richard *et al.* [5] have assessed the three-dimensional thermo-chemo-mechanical behaviour of the refractory concrete, Picard *et al.* [6], D'Amours *et al.* [7], and Zolochevsky *et al.* [8] (see also the related references) have oriented their work on the long term mechanical behaviour of the carboneous materials located in the cell lining, namely the carbon cathode blocks and the ramming paste, which ones are the main subjects of the review presented in this paper.

Constitutive laws of carboneous materials

During the preheating phase, the confined carbon cathode blocks and the ramming paste are subjected to high temperatures inducing stresses, through the thermal expansion phenomenon of the materials. If the tensile or compressive stresses reach critical levels, a mechanical failure, mainly cracking, could occurs and ultimately provoking the end of the cell life prematurely. Therefore, the constitutive laws of the carbon materials must take into account all the relevant mechanical phenomena.

Ramming paste

The baked ramming paste has an elastoplastic behaviour similar to the carbon cathode blocks since both materials are made of carbon aggregates and a coal tar pitch binder. D'Amours *et al.* [7] have already detailed the elastoplastic model developed for the carbon cathode blocks. Basically, a failure envelope function of the shear stress and of the hydrostatic pressure was defined as :

$$F(\sigma_m, \rho, r(e,\theta)) = a_f \left[\frac{\rho\, r}{f_c}\right]^{\alpha_f} + \frac{m_f}{f_c}\left[\sigma_m + \frac{\rho\, r}{b_f}\right] - 1 = 0 \tag{1}$$

where σ_m is the hydrostatic pressure, ρ is deviatoric stress, m_f is the friction parameter, $r(e,\theta)$ is the polar coordinate, f_c is the absolute uniaxial compressive strength and a_f, b_f and α_f are constants to be identified.

To compute both the elastic and the plastic strains during the hardening of the carbon cathode, a strength parameter k controlling the evolution of the loading surface up to the failure envelope is introduced and expressed in function of the equivalent plastic strain ϵ_p and of a ductility parameter d_h. The following relation for the strength parameter k is extracted from Etse and Willam [9] :

$$k(\epsilon_p, \sigma_m) = k_0 + (1-k_0)\sqrt{\frac{\epsilon_p}{d_h}\left(2 - \frac{\epsilon_p}{d_h}\right)} \tag{2}$$

where ϵ_p is the accumulated equivalent plastic strain in the material and d_h is the ductility parameter, which one is used to take into account the hydrostatic pressure effect on the ductility and the on plastic strain of the material. The ductility parameter is then itself function of the hydrostatic pressure; $d_h = f(\sigma_m)$.

Unlike the carbon cathode blocks, the ramming paste is green at the beginning of the start-up of an aluminium reduction cell. In its current state, the previous model developed for the cathode blocks can't be used for the ramming paste because it doesn't take into account the baking effect of this green material. During the manufacturing of the reduction cell, the ramming paste is compacted to form the peripheral seam of the lining. This compaction allows to the ramming paste to get some mechanical strength. During the preheating of the cell, the ramming paste is baked and several irreversible microstructural changes occur. Weight loss, swelling followed by a shrinkage and increase of the mechanical strength are some macrostructural changes that are observed during the ramming paste baking.

The irreversible baking effects on the evolution of the macrostructural mechanical properties of the ramming paste during the preheating phase have been taken into account through a baking index [10]. This index allows to take into account the irreversible effects, related to the temperature increase, on the mechanical properties. Thus, any decrease of the temperature during a finite element simulation doesn't allow to decrease the mechanical properties introduced in the constitutive model. The concept of baking index has already been summarized by Richard *et al.* [10]. Briefly, the baking index evolves proportionally with the uniaxial compressive strength, which one is function of the temperature, and is normalized to 1 at the maximum value of the compressive strength. The evolution of the baking index is shown in Fig. 1 for a specific ramming paste. In the context of cell preheating, some thermal and mechanical parameters are now function of the temperature, such as the thermal expansion of the ramming paste, while other ones are also function of the baking index ξ, such as the mechanical strength. Thus, the constitutive law is now a thermo-chemo-elasto-plastic one. In that case and by assuming small additive strains, the total stain rate can be decomposed as :

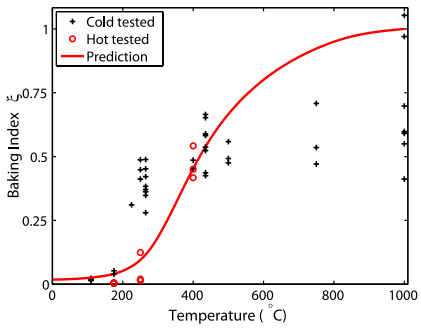

Figure 1: Evolution of the baking index.

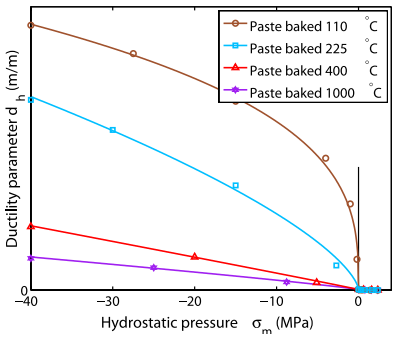

Figure 3: Evolution of the ductility curves.

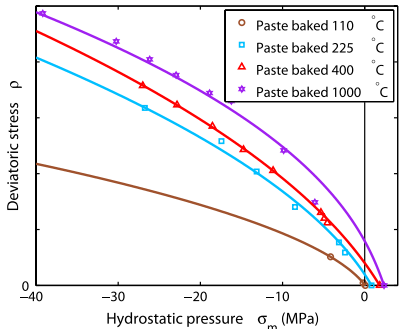

Figure 2: Evolution of the failure envelopes.

$$\dot{\boldsymbol{\epsilon}} = \dot{\boldsymbol{\epsilon}}_e + \dot{\boldsymbol{\epsilon}}_p + \dot{\boldsymbol{\epsilon}}_{th} + \dot{\boldsymbol{\epsilon}}_{ch} \tag{3}$$

For the chemo-elasto-plastic component of the constitutive model, confined compression tests have been repeated for four different groups of ramming paste samples previously baked at different index levels corresponding to the temperatures of 110, 225, 400 and $1000°C$. The measured and the approximated compressive meridians of the four different failure envelopes are shown in Fig. 2. To model the increase of the mechanical strength of the ramming paste in function of its baking index with the use of Eq. 1, it is necessary to express the majority of the parameters as a function of the baking index ξ. The new equation of the failure envelope thus becomes :

$$F(\sigma_m, \rho, r, k, c, \xi) = \left\{ (1-k)\left[\frac{\sigma_m}{f_c(\xi)} + \frac{\rho\, r(\theta)}{b_f(\xi)\, f_c(\xi)}\right]^2 + a_f(\xi)^{\frac{1}{\alpha_f(\xi)}} \frac{\rho\, r(\theta)}{f_c(\xi)} \right\}^{\alpha_f(\xi)} + \frac{k^{\beta_f(\xi)} m_f(\xi)}{f_c(\xi)}\left[\sigma_m + \frac{\rho\, r(\theta)}{b_f(\xi)}\right] - k^{\beta_f(\xi)} c = 0 \tag{4}$$

Each one of the six different parameters in the previous equation, which are function of the baking index ξ, is expressed mathematically by a linear or quadratic function allowing the model to approximate the measured envelopes shown in Fig. 2.

A similar dependency of the ductility parameter d_h towards both the hydrostatic pressure σ_m and the baking index ξ has to be defined to allow the elastoplastic model to reproduce adequately both the strains and the stresses of the ramming paste during a preheating. From the same uniaxial and confined compression tests performed on the ramming pastes previously baked at four different baking indexes, different curves representing the relationship between the ductility parameter d_h and the hydrostatic pressure σ_m have been measured and approximated. These four curves are shown in Fig 3. This figure firstly shows that the ramming paste is highly ductile when it is still green and when there is a compressive load applied. The figure also shows that the baking level has almost no influence when a tensile load is applied on a ramming paste sample; this one will always break in a brittle manner. Figure 3 finally shows that there is a decrease of the ductility when the ramming paste is baked.

Cathode

The elastoplastic constitutive law developed for the baked ramming paste by D'Amours *et al.* [7] can assess the hardening, softening and plastic strain of carbon materials. However, the long-term visco-elastic (creep/relaxation) behaviour was not taken into account. Therefore, Picard *et al.* [6] have proposed a consistent three-dimensional visco-elastic model, based on a thermodynamic framework to identify the model parameters previously determined with a phenomenogical approach, i.e. a rheological model that has been extended to the 3D case shown in Fig. 4. Instead of being defined by scalars, the parameters of the model are fourth order tensors and both the strains and the stress are second order tensors. Moreover, the number of Kelvin-Voigt elements constituting the proposed rheological model is, *a priori*, undetermined. The model has been developed with the

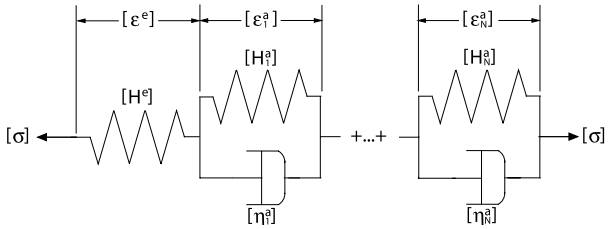

Figure 4: Three-dimensional Kelvin-Voigt rheological model. From [6].

hypothesis that the mechanical strains/stresses have no influence on the thermal, chemical, etc. variables. Thus, the mechanical problem can be uncoupled from the thermal and the chemical ones. The dependencies of external parameters (e.g. temperature) will then be taken into account in the finite element model throughout algebraic functions, as discussed later. Moreover, the carbon cathode has been assumed to be an isotropic material. Thus, the topology of all the positive semi-definite stiffness fourth order tensors of the rheological model can be assumed to be similar to the elastic one

$$\begin{aligned} [H^e] &= [H^e(E,\nu)] \\ [H^a_\alpha] &= \left[H^a_\alpha(E_{H^a_\alpha},\mu_\alpha)\right] \\ [\eta^a_\alpha] &= \left[\eta^a_\alpha(E_{\eta^a_\alpha},\varsigma_\alpha)\right] \end{aligned} \tag{5}$$

where α is the corresponding Kelvin-Voigt element, E is the Young's modulus and ν is the Poisson's ratio. The parameters $E_{H^a_\alpha}$ and $E_{\eta^a_\alpha}$ are similar to a Young modulus and μ_α and ς_α to a Poisson's ratio. Considering a sustained uniaxial compressive load with free lateral stress, the stress-strain relations proposed by Picard *et al.* [6] are

$$\begin{aligned} \epsilon_1 &= -\frac{\sigma_1}{E_{H^e}} - \frac{\sigma_1}{9}\sum_{\alpha=1}^{N} K_\alpha^{a^{-1}} \frac{1-e^{-\lambda_{\alpha_1} t}}{\lambda_{\alpha_1}} \\ &- \frac{\sigma_1}{3}\sum_{\alpha=1}^{N} G_\alpha^{a^{-1}} \frac{1-e^{-\lambda_{\alpha_2} t}}{\lambda_{\alpha_2}} \end{aligned} \tag{6}$$

$$\begin{aligned} \epsilon_r &= \frac{\nu\sigma_1}{E_{H^e}} - \frac{\sigma_1}{9}\sum_{\alpha=1}^{N} K_\alpha^{a^{-1}} \frac{1-e^{-\lambda_{\alpha_1} t}}{\lambda_{\alpha_1}} \\ &+ \frac{\sigma_1}{6}\sum_{\alpha=1}^{N} G_\alpha^{a^{-1}} \frac{1-e^{-\lambda_{\alpha_2} t}}{\lambda_{\alpha_2}} \end{aligned} \tag{7}$$

where

$$K_\alpha^{a^{-1}} = \frac{3(1-2\varsigma_\alpha)}{E_{\eta^a_\alpha}} \quad ; \quad G_\alpha^{a^{-1}} = \frac{2(1+\varsigma_\alpha)}{E_{\eta^a_\alpha}} \tag{8}$$

and

$$\lambda_{\alpha_1} = \frac{E_{H^a_\alpha}(1-2\varsigma_\alpha)}{E_{\eta^a_\alpha}(1-2\mu_\alpha)} \quad ; \quad \lambda_{\alpha_2} = \frac{E_{H^a_\alpha}(1+\varsigma_\alpha)}{E_{\eta^a_\alpha}(1+\mu_\alpha)} \tag{9}$$

where $-\sigma_1$ is the constant compressive axial stress, ϵ_1 the corresponding strain and ϵ_r the hoop strain. All other strain components are null. The positive coefficients $K_\alpha^{a^{-1}}$ and $G_\alpha^{a^{-1}}$, defined in Eq. 7, are related to the hydrostatic and deviatoric creep mechanisms respectively. The coefficients λ_α, defined in Eq. 8, are also positive and are related to a relaxation time. Combined with experimental data [6], Eq. 6 and 7 are used to identify the parameters of all the fourth order tensors of Eq. 5 by the means of a least squares method through the use of a genetic algorithm available in Matlab. Both the axial and radial data must be used to identify the parameters [6]. Figure 5 shows an example of parameter identification results, based on a rheological model with 2 Kelvin-Voigt elements (Fig. 4). The experimental creep strains data are those of a virgin (non contaminated by the electrolysis process) semi-graphitic carbon cathode samples at room temperature. In the presented case, the model with two Kelvin-Voigt elements well represents the global creep behaviour of the material in both directions and the values

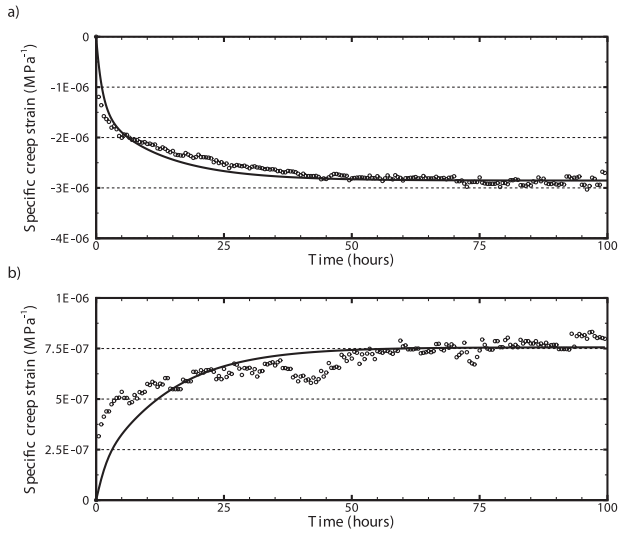

Figure 5: Parameter's identification results for the semi-graphitic carbon cathode material. a) Axial strain, b) Radial strain. ∘ Experimental, — Model. From [6].

of all the corresponding parameters are listed in Table I. The number of elements can be increased or lowered, if necessary, for other materials.

Table I: Semi-graphitic carbon cathode material parameters of a 3D rheological model with 2 Kelvin-Voigt elements

	$E_{\eta_\alpha^a}$	ς_α	$E_{\eta_\alpha^a}$	μ_α
First element	840306	0.07	712153	0.13
Second element	7562665	0.20	689502	0.39

The constitutive laws proposed in this paper for the ramming paste and for the carbon cathode have been combined together in the finite element toolbox **FESh**$^{++}$ to create a quasi-brittle thermo-visco-elasto-plastic constitutive law for the baked carbon cathode material. As mentioned earlier, the visco-elastic constitutive law [6] has been developed on the basis that the mechanical problem can be uncoupled from the thermal and the chemical ones. Therefore, the proposed visco-elastic constitutive law can be used to identify the parameters of experimental creep tests at various temperatures. Thereafter, with the help of an interpolation method (polynomial, exponential, etc.), the visco-elastic parameters can be redefined with algebraic equations which are function of temperature. A similar procedure can be done to take into account the dependencies towards other parameters, such as the baking index [10], the chemical contamination level of carbon material, etc.

However, experimental data are still lacking to determine all the parameter dependencies for the proposed models. Also, most experimental data related to the mechanical behaviour of the carbon cathode blocks available so far under different conditions [8] are mostly uniaxial, which is insufficient for the three-dimensional visco-elastic parameters identification [6].

Future development

The lining materials of the Hall-Héroult cell are at room temperature and then heated up before the bath pouring. Also, the carbon materials will be contaminated by different chemical species during the electrolysis process. The parameters of the constitutive laws proposed for the ramming paste and for the carbon cathode materials have been identified at room temperature. In fact, to characterize the ramming paste, the material was first baked at the desire baking index then cooled at room temperature before being tested. In both cases (paste and cathode), the lacking of high temperature experimental data is due to apparatus restrictions. Moreover, preliminary numerical results obtained within the START-Cuve project have shown the importance of taking into account the visco-elastic behaviour of the ramming paste during the pre-heating phase.

Therefore, in the upcoming months, new equipments developed in collaboration with manufacturers will be acquired. Those equipments will allow the characterization of the long term creep/relaxation behaviour of the carbon cathode materials and of the ramming paste (previously baked at various level), at room temperature up to 1000°C. The high temperature elastoplastic behaviour of baked carbon materials will also be studied. Moreover, the new equipments have been designed to test 101.4 mm diameter carbon material cylinder under a maximum compressive load of 35 MPa at 1000°C. Other equipments will also be developed to perform long term creep test under electrolysis on those relatively large samples.

The experimental data that will be gathered with the upcoming equipments will allow the establishment of a thermo-chemo-visco-elasto-plastic constitutive law for the carbon cell lining materials able to take into account all the relevant mechanical behaviours under the wide range of cell operation conditions. The laws are also planned to be adapted to the carbon anode.

Conclusion

Understanding the mechanical behaviour of the carbon materials located in the cell lining is critical in order to avoid early mechanical failure, mainly during the pot start-up. Thus, experimental works were required to assess the behaviour of those materials, namely the ramming paste and the carbon cathode blocks, and for the development of three-dimensional constitutive laws. The 3D visco-elastic constitutive law recently developed by Picard *et al.* [6] has been combined, in the finite element toolbox **FESh**$^{++}$, with the thermo-chemo-elasto-plastic one previously proposed by D'Amours *et al.* [7] for the baked ramming paste. The new law is ready to use to run transient non linear thermo-chemo-mechanical numerical simulations.

Future experimental works are needed to identify the model parameters under various conditions such as at high temperature under electrolysis and at low baking index (ramming paste). Finally, upcoming works should also assess the carbon anode by using similar thermo-chemo-mechanical constitutive laws.

Acknowledgments

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