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## APPLICATION OF MECHANOCHEMISTRY MODEL TO OXIDATION OF PURE NICKEL SPHERES

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**Summary** In this work, we study the two-phase chemical reactions on the example of the oxidation of nickel. We have carried out an experiment of high-temperature oxidation of nickel balls, and obtained the experimental data for the growth of the oxide layer over time. To select the best analytical solution we consider three different rheology for the oxide of nickel: elastic, elastoplastic and viscoelastic. We compare the solution for each rheological model with experimental data.

### INTRODUCTION

In this contribution we discuss an extension of a microscopic model of oxidation to macro scale. In particular, we sketch a protocol of experimental validation of it based on measurements for (approximately) spherically-symmetric samples.

Stress-assisted chemical reactions are relevant in various industrial and medical applications and in modern technologies. It is enough to mention for instance batteries charging/discharging cycles: along with the introduction of silicon instead of carbon the issue of the dramatic change of volume in the active material is observed, which results in massive cracking when inappropriately handled [2]. In MEMS the oxidation process is responsible for rapid fatigue effects [3]. For composite material meant for high temperature resistance, the metallic inclusions being heated up and oxidized, expand and induce internal strain to the matrix [4, 5]. All these and a lot of other processes can be described using the two-phase reaction model, it is thus important to be able to handle it efficiently. The model however relies heavily on the rheological properties of the involved materials, which are in general to be defined. Here we present a procedure of identification of a proper model, based on few experimental data.

First we recall the general theoretical model, and some steps to reduce it to analytically tractable problem. Then we describe the available experimental data and some features to be taken into account during its acquisition. We conclude by some preliminary analysis of the experiment, the details of which will be described in [1].

### TWO-PHASE REACTION MODEL

To describe the two-phase chemical reactions such as oxidation processes or charging/discharging of batteries, we consider the following model. We have some initial solid, we can set the geometrical parameters, boundary conditions and the mechanical properties of the body. There is a diffusion of some chemical, for example, it can be oxygen in the case of the oxidation or lithium in the case of the lithiation of silicon (charging of batteries), etc. A chemical reaction between the initial solid body and some diffusive constituent is of the following type: it begins from the outer surface of the initial solid, localized on the interface between initial and transformed material and maintained by the diffusion of the diffusive constituent through the transformed material.

To obtain the equation for the chemical reaction front propagation, taking into account the effect of the stress-strain state in the body, we use the classical kinetic equation ([8]) from the chemical thermodynamics. We substitute the normal component of the chemical affinity tensor  $A_{NN}$  ([9]) instead of scalar chemical affinity  $A$  in the equation for the reaction rate, hence we obtain the kinetic equation for the surface element of reaction front with the normal  $\mathbf{N}$ :

$$\omega_N = \frac{\nu_- M_-}{\rho_-} k_* c \left( 1 - \exp \left( -\frac{A_{NN}}{RT} \right) \right) = 0 \quad (1)$$

where  $\nu_-$  is the stoichiometric coefficient,  $M_-$  is the molar mass and  $\rho_-$  is the mass density of the initial solid;  $k_*$  is the reaction constant;  $c$  is the molar concentration of the diffusive constituent;  $A$  is the chemical affinity;  $R$  is the universal gas constant;  $T$  is the temperature. And the normal component of the chemical affinity tensor in the case of the small deformations is defined ([9]) as follows :

$$A_{NN} = \frac{n_- M_-}{\rho_-} \left\{ \gamma(T) + \frac{1}{2} \boldsymbol{\sigma}_- : (\boldsymbol{\varepsilon}_- - \boldsymbol{\varepsilon}_-^{ch}) - \frac{1}{2} \boldsymbol{\sigma}_+ : (\boldsymbol{\varepsilon}_+ - \boldsymbol{\varepsilon}_+^{ch}) + \boldsymbol{\sigma}_- : \llbracket \boldsymbol{\varepsilon} \rrbracket \right\} + \nu_* RT \ln \frac{c}{c_*} \quad (2)$$

where  $\gamma$  is the temperature-dependent parameter of the reaction;  $\boldsymbol{\sigma}_\pm$  and  $\boldsymbol{\varepsilon}_\pm$  are the stress and strain tensors for the transformed and initial material, respectively;  $\boldsymbol{\varepsilon}_\pm^{ch}$  are the strain tensors which define the volumetric change due to the chemical transformation;  $\nu_*$  is the stoichiometric coefficient of the diffusive constituent;  $c_*$  is the solubility of the diffusive constituent in the transformed material.

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## EXPERIMENTAL SETUP

In the current work we consider the oxidation of nickel balls. Nickel oxide nano-particles and nickel are widely used in heavy industries [6, 7]. To obtain the kinetic equation we have to choose the rheological model for the transformed material (initial material is elastic) and solve the mechanical problem in the spherical coordinates. To get the best analytical solution for this experiment we will consider three different rheology for the transformed material: elastic, viscoelastic and elastoplastic. For each rheological model we obtain the specific solution and the kinetic equation. This permits to spell-out the solutions to be compared with experimental data.

Several balls were oxidized in the air at temperature 800°C for up to 500h: each ball was oxidized for a different amount of time: the first one for 100h, the second for 200h, ... and the fifth for 500h. After that, each ball was cut in halves, polished, and the outer layer was captured in the electronic microscope.

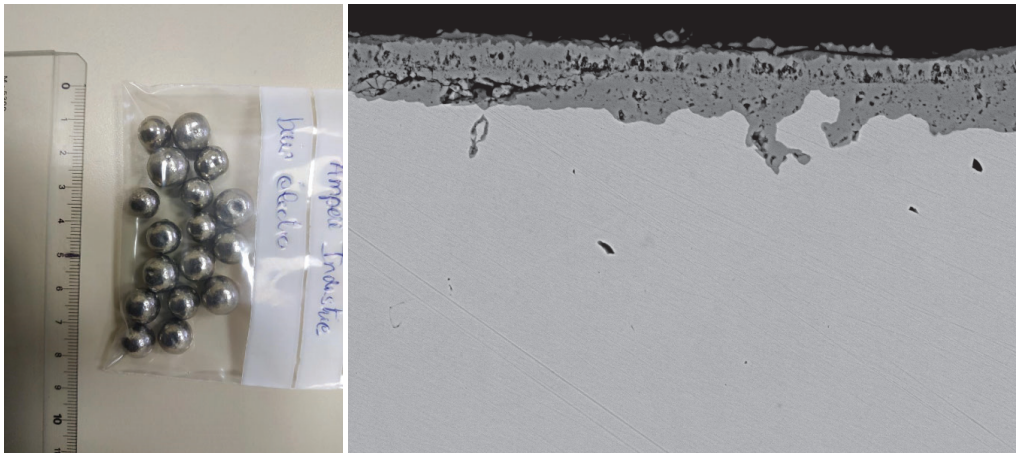


Figure 1: Experiments. Available samples (left) to be chosen for oxidation. Measurement results (right) – TEM imaging.

## PRELIMINARY CONCLUSIONS AND PERSPECTIVES

Several remarks about the experiment are in place here. First, nickel oxide has a very fragile structure, however NiO is much stiffer than pure nickel. That makes the process of polishing hard: debris of NiO tend to scratch the pure metallic surface. It is thus very complicated to obtain precise mechanical properties of the oxide layer close to the interface. Second, with transmission electron microscopy we make the chemical analysis, study the morphology of the oxide, get the grain boundaries and measure the oxide thickness. However the balls used for different times of oxidation are slightly different in size and are not of perfectly spherical shape. Hence, measuring of the thickness of the oxide layer for each ball has to be relative to the initial radius of the ball. Here it is important to note, that the experiment confirms the validity of small deformations hypothesis. It means that the linearized model 2 is valid, and the time-dependence of the averaged renormalised thickness of the oxide layer is relevant.

Having analysed the dependence of the thickness of the oxide layer on time, we can say the best guess for the rheological properties would be elastoplastic. We will give proper details about this conclusion in a longer article ([1]). In the same paper we will also comment on the processing of images obtained by microscopy: renormalisation, reassembling and segmentation.

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