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General approach on the growth strain versus viscoplastic relaxation during oxidation of metals

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Abstract

High temperature oxidation of metals induces residual stresses in metals and growing oxides. In this work, the evolution of the residual stresses in those oxides layers, during isothermal oxidation of metals is studied. A new justification is proposed in order to explain the origin of those stresses leading to a proportional dependence between the growth strain and the oxide layer thickness. Moreover, we emphasize the relation between viscoplastic strain and growth strain. Using the mechanics of thin layers, as well as the analysis proposed to describe the growth strain, a system of equations is deduced that predicts the stresses evolution with oxidation time. Comparison with previous experimental results is also made.

Keywords: High temperature oxidation; Growth strain; Viscoplasticity; Multiscale approach; Residual stresses; Modelling; Asymptotic solutions

1. Introduction

When metals or alloys are oxidised at high temperature an oxide film generally develops. The existence of a stress accompanying the oxide growth has been known for many years [1]. In particular, the role of stresses during the isothermal oxidation process may influence the structure and the protective properties of the oxide scales. Classical models (elasticity and/or viscoplasticity) are able to predict the stress relaxation [1]. But, the origin of those stresses must, therefore, be sought-after in a growth strain related to the formation of the oxide above the substrate.

1.1. Growth strain origins

Huntz et al. [2] indicate several main possible origins for the growth strain during isothermal oxidation:

- the oxygen dissolution in the metal or alloy (incompatibility of the atomic volumes);
- the epitaxy (lack of compatibility of the crystalline lattices);
- the Pilling and Bedworth approach (incompatibility of the molar volumes);
- the possibility that the oxide grows in the oxide grain boundaries.

These hypotheses are based on incompatibilities of some parameters leading to a stress state in the oxide layer. For static films on substrates, residual stresses result only from bidimensionnal mismatch, such as epitaxy [1,3–5]. In this study, we are interested in phenomenon linked to the growing films, such as oxide films. In that case, "tridimensionnal" mismatch can also occur at the interface due to the

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substitution of metal by the oxide. The oldest explanation justifying this growth strain has been proposed by Pilling and Bedworth [6]. The oxidation reaction product (i.e. the oxide) has a molar volume (V_M) different from the metal. This difference of volume is assumed to induce an isotropic growth strain $\varepsilon^\mathrm{growth}$ given by the ratio:

$$\begin{aligned} &\mathrm{PBR} \equiv \frac{V_{\mathrm{M\ in\ oxide}}}{V_{\mathrm{M\ in\ metal}}} \\ &\varepsilon^\mathrm{growth} = \sqrt[3]{\mathrm{PBR}} - 1 = \varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz} \\ &\quad \text{(isotropic strain model)} \end{aligned} \tag{1}$$

This simple analysis provides good qualitative results. In particular, the sign of the PBR indicates if stresses in the oxide layer are tensile or compressive. However, the magnitude of the associated stresses is often over estimated, typically several tens of GPa compared with less than 1 GPa from experiments.

In a different analysis, Tolpygo et al. [7] propose a new approach to take into account the evolution of the grain size as well as the width of the grain boundaries where the growth strain takes place. These authors define the growth strain as the ratio of the oxide volume growing along a grain boundary on the oxide grain volume. It means, by hypothesis, that both an inward and outward fluxes exist in grain boundaries, in order to form the oxide. The oxide grain size is submitted to an evolution caused by its growth [7,8]. This model is based on strains localised along the grain boundaries perpendicular to the interfaces, in agreement with the analysis of Rhines and Wolf [9]. Tolpygo et al. have proposed a microstructural approach based on a volume ratio, similar to the Pilling and Bedworth analysis, but this new ratio depends on parameters evolving with oxidation time.

The model proposed lately by Clarke [10] is also based on a microstructural approach. A mixed flux (inward and outward diffusion) is again assumed in the short circuits of diffusion, i.e. the grain boundaries. This hypothesis allows an oxidation reaction in the layer along the grain boundaries. The part of the oxide growing at the grain boundaries (in the volume of the layer) is assumed to be weak in comparison to the one that forms at the internal or external interfaces. The kinetic remains classically controlled by the diffusion in volume and/or in the short circuits, and the oxide forms mainly at the interfaces. In this case, the weak oxide proportion that develops in the grain boundaries is sufficient to explain the appearance of a lateral strain rate $\mathrm{d}\varepsilon^\mathrm{growth}/\mathrm{d}t$ related to the oxide growth.

This model leads to the analytical expression for the growth strain:

$$\frac{\mathrm{d}\varepsilon^\mathrm{growth}}{\mathrm{d}t} = D_\mathrm{ox}\frac{\mathrm{d}h_\mathrm{ox}(t)}{\mathrm{d}t}. \tag{2}$$

The D_ox parameter depends on microstructural features. If the D_ox parameter is constant, the direct integration of Eq. (2) shows that the growth strain follows the kinetic evolution of the oxide layer thickness. Therefore, the growth kinetic influences the stress via the growth strain, in both outward cationic and inward anionic oxidation.

2. Mechanical behaviour of thermal oxides

In the present work, a different approach is considered, based on a model which is not directly linked to microstructural incompatibilities, but on general thermodynamical explanation, on a multiscale approach and on symmetrical properties. To find a mechanical constitutive behaviour for thermal oxides under high temperature oxidation, a relation between the strain rate tensor $\dot{\bar{\bar{\varepsilon}}}$ and the particles diffusion flux $\vec{J}$ is assumed. Indeed, as a definition of the strain rate, we have [8]:

$$\dot{\bar{\bar{\varepsilon}}} = \frac{1}{2}\left(\bar{\bar{\nabla}}\vec{v} + \left(\bar{\bar{\nabla}}\vec{v}\right)^\mathrm{T}\right), \tag{3}$$

where $\vec{v}$ is the velocity field of the crystalline lattice of the material. "T" means the transposed matrix. $\bar{\bar{\nabla}}$ is the spatial derivative operator. Moreover, we can consider as a first approximation a direct relation, following Suo et al. [11], between the velocity and the diffusion phenomenon:

$$\vec{v} = -\Omega_\mathrm{a}\vec{J}, \tag{4}$$

where Ω_a represents the atomic volume (per unit of mole). Besides, using symmetrical considerations on our geometry (with // and $\perp$ representing the coordinates according to the Fig. 1), the strain tensor can be written:

$$\begin{aligned} \bar{\bar{\varepsilon}} &= \begin{pmatrix} \varepsilon_{//} & 0 & 0 \\ 0 & \varepsilon_{//} & 0 \\ 0 & 0 & \varepsilon_{\perp} \end{pmatrix} \text{ corresponding to the in-plane stress } \bar{\bar{\sigma}} \\ &= \begin{pmatrix} \sigma_{//} & 0 & 0 \\ 0 & \sigma_{//} & 0 \\ 0 & 0 & 0 \end{pmatrix} \end{aligned}$$

Such a tensor is justified at a macroscopic scale and can be verified experimentally, what we have shown in a previous paper [12]. But at a microscopic scale, $\sigma_\perp \neq 0$, as demonstrated for viscoplasticity in the following.

Finally, the oxide behaviour is based on the simplified equation:

$$\dot{\bar{\bar{\varepsilon}}} = -\Omega_\mathrm{a}\bar{\bar{\nabla}}\vec{J} \tag{5}$$

The diffusion flux $\vec{J}$ of the "i" species can be expressed by using the general non-equilibrium thermodynamics formalism [13,14]:

$$\vec{J}_i = -\sum_{j=1}^{N-1}\left\{\bar{\bar{D}}_{ij}(T,\bar{\bar{\sigma}},\rho_j)\cdot\vec{\nabla}\rho_j\Big|_{T,\bar{\bar{\sigma}}}\right\} + \bar{\bar{\beta}}_i(T,\bar{\bar{\sigma}},\rho_j)\cdot\left(\vec{\nabla}\cdot\bar{\bar{\sigma}}\right)\Big|_{T,\rho_j}, \tag{6}$$