Modelling of the effect of grain boundary diffusion on the oxidation of Ni-Cr alloys at high temperature

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ABSTRACT

Grain boundaries in oxide scales have a strong effect on oxidation kinetics when they act as diffusion short circuits. This study proposes a quantitative evaluation of the phenomenon by modelling. Various cases of oxide microstructure evolution are treated using both analytical and numerical resolutions. Results showed that the effect of oxide grain growth on the oxidation kinetics can be analysed considering a transitory stage for which the oxidation kinetics is not purely parabolic. Some guidelines for choosing the appropriate post-treatment method for the analysis and extrapolation of experimental oxidation kinetics are given.

1. Introduction

Parabolic constants values reported in literature for chromia forming alloys [1–13] are distributed on several orders of magnitude, these values are gathered on Fig. 1. It has been shown that under O_2 atmospheres, chromia grow by diffusion of spieces across the oxide scale [13,15,16] and that diffusion short-circuits, such as grain boundaries in oxide scales, have a major effect on oxidation kinetics [10,17,18].

In his review on the influence of grain boundary diffusion on high temperature oxidation, Atkinson [1] showed that the values of the experimental parabolic constant (k_p) published for chromia are distributed over a range of about three orders of magnitude for the same temperature. Atkinson calculated theoretical k_p values for polycristalline chromia using tracer diffusion coefficient from Hagel *et al.* [14], and k_p value for single cristal chromia using single cristal tracer diffusion coefficient for chromia that he determined experimentally [1]. He showed that experimental reported k_p values were closer to theoretical values corresponding to polycrystalline chromia than to theoretical value corresponding to single crystal chromia. These experimental and theoretical k_p values are plotted on Fig. 1. Knowing that the calculated k_p for polycrystalline chromia can be up to six orders of magnitude higher than the one of single crystal chromia, it was concluded that chromia growth was quantitatively affected by grain boundary diffusion [1]. Notice that such a dispersion of reported k_p values can also be

explained by other phenomena such as a transitory regime caused by formation of NiO [19] or the presence of reactive elements that can slow down diffusion [10,20].

Concerning the influence of grain boundaries, several authors proposed oxidation models taking into account accelerated diffusion by short-circuit diffusion paths. Perrow et al. [18] proposed an analytical solution for oxidation kinetics taking into account grain boundary diffusion in nickel oxide scales. They used the effective diffusion coefficient proposed by Hart [21], which is a weighted average between lattice and short-circuit diffusion coefficients. Hart's law was initially established for the modelling of accelerated diffusion by dislocation. However, it can be adapted to diffusion through grain boundaries. Besides the use of Hart's law, Perrow et al. [18] added the influence of grain size evolution via a parabolic growth law. Hussey et al. [22], who worked on iron oxides growth kinetics, followed the same hypotheses as Perrow et al. [18] and determined an instantaneous parabolic rate constant in the case of a parabolic oxide grain growth. Rhines et al. [23,24] observed cubic oxidation kinetics on NiO scales associated with a cubic grain size growth. Davies and Smeltzer [25,26] proposed an analytical treatment by means of an exponential law for the decay of short-circuit proportion over time. More recently, Hallström et al. [27] proposed a numerical approach based on thermodynamics calculations applied to chromia growth. Nevertheless, this model does not take oxide microstructure evolution into account. Other authors have considered the diffusion through grain boundaries in oxide scales [28–30]
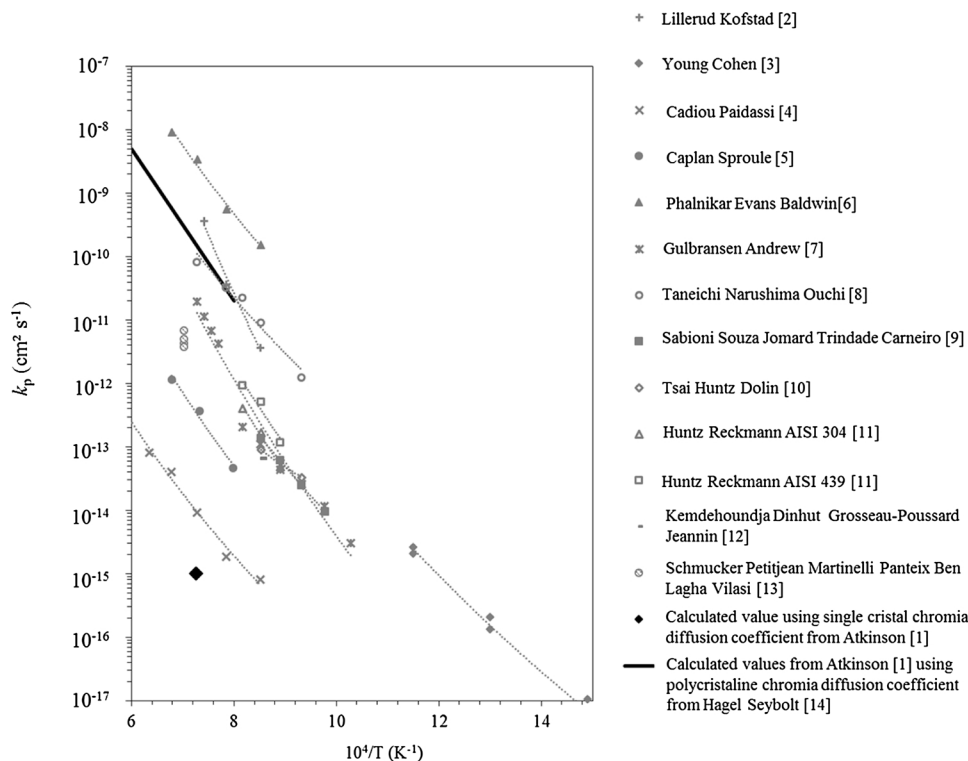
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Fig. 1. Arrhenius plot of experimental parabolic rate constant for Cr_2O_3 reported in literature [2–13], and calculated by Atkinson [1] using single crystal or polycrystalline chromia diffusion coefficient from Hagel *et al.* [14].

and even the influence of oxide microstructure on oxidation kinetics [31,32], with an experimental approach.

Some different approaches have been developed concerning oxidation kinetics modelling by taking into account formation and growth of several phases which are also steps forward the description of complex oxide microstructure. Larsson et al. [33] performed a numerical simulation of multiphasic iron oxide growth. Nijdam et al. [34,35] developed coupled thermodynamic-kinetics oxidation model, which is able to predict the phases formed and their impact on oxidation kinetics.

In this framework, this study proposes a new quantitative estimation of the influence of grain boundary diffusion on oxidation kinetics. Oxidation models proposed are applied on chromia-forming alloys. The studied cases consider (1) the evolution of grain size over time, (2) a grain size gradient across the oxide scale, and (3) a combination of both. For the simplest cases (1) and (2), some new analytical solutions were found. However, for the complex cases (3), which combine grain size evolution in time and space, a numerical approach is required. The numerical EKINOX model [36–38] has been used and modified for this study in order to take into account grain boundary diffusion and microstructural evolutions in the oxide scale. Chromia growth kinetics were then modelled using input data based on literature experimental data [10].

The first part of this paper presents the existing oxidation kinetics models available in the literature. These models take into account both lattice and grain boundary diffusion in the oxide scale according to A-type diffusion [39] and consider homogeneous oxide grain size or simple grain size growth law. The second part is dedicated to new analytical models proposed, and to the numerical modelling using the EKINOX code. These new models are able to take into account the oxide grain size growth according to a cubic law and a grain size gradient across the oxide scale. Moreover, a numerical model is adapted in order to treat the complex case of grain size growth and grain size gradient combination.

In results section kinetics obtained using the various analytical and numerical models are presented. Firstly, these oxidation kinetics are

discussed, and then, a parametric study is carried out on the effects of the oxide grain size growth kinetics. In the discussion part, the two methods, which are usually performed for the analysis and the extrapolation of experimental oxidation kinetics, are used on calculated kinetics and they are compared. These are referred in this work as the "parabolic law" method and the "log-log" method. Finally, the two methods are compared for long term extrapolation.

2. Literature models for oxidation kinetics and extrapolation methods

2.1. Wagner's theory simplified

In the case of continuous oxide scale formation, Wagner proposes a model for oxide scale growth that looks at diffusion across the oxide scale as the rate-limiting step [40]. A simplified expression for the parabolic rate constant can be given assuming that the species concentrations at metal/oxide and oxide/gas interfaces are time invariant. This assumption supposes that diffusion occurs through lattice only, that the diffusion coefficient is constant and that usual hypotheses of stationarity, electroneutrality and fluxes conservation are assumed [40]:

$$e^2 = k_{p,L}(t - t_0) + e_0^2 \qquad (1)$$

$$k_{p,L} = 2\Omega \widetilde{D}_L \Delta C \qquad (2)$$

2.2. Diffusion models taking into account bulk and short-circuit diffusion

When the influence of diffusion along short circuits is taken into account within the global diffusion phenomenon, several limiting cases can be described. These different cases depend on the space distribution of grain size and on the values of diffusion coefficients in lattice and in short circuits [41,42]. Hence three different regimes involving grain boundary diffusion are classically considered and called A-type, B-type