Corrosion Science 73 (2013) 89–98

Contents lists available at SciVerse ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Analytical models for the internal oxidation of a binary alloy that forms oxide precipitates of high stability

Amitesh Madeshia *

Department of Materials Science and Engineering, Ohio State University, Columbus, OH 43210, USA

ARTICLE INFO

Article history:
Received 5 July 2012
Accepted 29 March 2013
Available online 10 April 2013

Keywords:
A. Alloy
B. Modelling studies
C. Atmospheric corrosion
C. High temperature corrosion
C. Internal oxidation
C. Kinetic parameters

ABSTRACT

Since the experimental work of Smith on internal oxidation many attempts have been made to quantify the observations. This paper outlines the mathematical development of the extended model starting from the pioneering work of Rhines et al.

A proper definition of the mass balance of individual components at the reaction interface predicts the transition behaviour. A proper definition of the convective velocity due to precipitation of oxide of larger molar volume compare to matrix phase in the differential mass balance introduces a volumetric flow towards the exposed surface that explains the outward extrusion of the matrix reported by many researchers.

1. Introduction

Internal oxidation is a process in which the species of low atomic radius (H, C, N, O, P, S) diffuse into an alloy and form oxide(s)/compound(s) with the less noble alloying elements [1]. This is predominantly a diffusion-controlled process since most of the oxides are highly stable. Such diffusion-controlled processes follow a parabolic growth law. Hence the rate constant becomes the most important parameter in order to predict degradation [2] or enhancement [3] in materials properties. The internally oxidized region is also called subscale zone in the literature irrespective of the presence of an outer scale [4,5]. The experimental observation of subscale formation was first reported by Smith [6–8]. Expressions for the rate constant were given by Rhines et al. [9], Darken [10], Meijerling and Druyvesteyn [11], as well as Wagner [12] for the internal oxidation of a binary alloy that forms only one type of oxide precipitate of negligible solubility-product.

This paper reviews the analytical works from Rhines et al., Darken, Meijerling and Druyvesteyn, Wagner, Hagan et al. [13] and Leblond [14] along with the extended model [15]. The Hagan et al. model used an improved version of the Wagner equation derived in the extended classical model [15] and predict the limit to internal oxidation independent of the Wagner hypothesis. The extended model also addresses a modified version of Hagan et al. model which is practical to many experimental observations [16–18]. The focus will be on the oxide-precipitate phase of high stability whose solubility-product in the base metal can be approximated to zero.

The content of this paper is organized in seven sections that include introduction, discussion and conclusions. The second section starts with the definition of fluxes and diffusion equations in multiphase region, which is reduced by many approximations in the third section. In the fourth section solution to these diffusion equations are given based on the local-equilibrium assumptions and assumptions on the boundary conditions. The fifth section addresses the various existing analytical models in the literature based on the mass balance at the reaction interface that apply concentration profiles from the previous section. Finally, all the existing models are compared along with the extended model followed by conclusions. All the symbols used in this paper are collectively defined in the Appendix. The bra of curly bracket next to some of the equations are used to express many of the key terms used in the equation.

2. Fluxes and the diffusion equation

The fluxes and the diffusion equation for components in the multiphase region are written similar to a single-phase region provided all notations are expressed in terms of the average or cumulative of all the phases present.

$$\bar{J}_i = -\bar{D}_{ij}\nabla\bar{C}_j \tag{1}$$

$$\dot{\bar{C}}_i = -\nabla\cdot\bar{J}_i - \nabla\cdot v\bar{C}_i \tag{2}$$

---

[*] Present address: 2 West Jubliganj, Nanpara, UP 271 865, India. Tel.: +91 953 250 4576.

E-mail address: ami.osu@gmail.com

0010-938X/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.corsci.2013.03.028

where $\bar{C}_i$, $\bar{J}_i$, $\bar{D}_{ij}$ and v are the average concentration, the average flux, the effective diffusion coefficients that relates the average flux to the gradients of average composition, and the convective velocity respectively. Unless otherwise stated the initial outer/exposed surface of the sample is taken as the origin of the reference frame for differential mass balance in the internally oxidized sample. The sample-end/laboratory reference frame will coincide to this initial reference frame for a constant and same molar volume for all phases in the system irrespective of their composition. The fluxes are defined in the volume reference frame in this paper. Consequently, the convective velocity is the velocity of the volume reference frame in the initial reference frame.

Compare to the average concentrations, the fluxes and the diffusion equation for components in each individual phase of the multiphase region cannot be taken identical to the respective single-phase region [19]. This limitation originates because of the restriction imposed on the compositions, for each individual phase in the multiphase region, to vary along the tie feature under local-equilibrium assumption. Strictly speaking, these constraints are applicable to the phase junctions. However, such constraints are conveniently applied to any point along the line of diffusion whenever the diffusion equation is solved for one dimension particularly in the direction normal to the exposed surface.

A relation between the fluxes for components in each phase of multiphase region can be derived by use of the equilibrium Lever rule, where compositions are tied and constrained to vary only along the tie feature.

$$\bar{C}_i = f^k C_i^k \tag{3}$$

where $\bar{C}_i$, C_i^k and f^k are the average concentration, the concentration along the tie feature, and the volume fraction of the k^{th} precipitate. Similarly, the average fluxes can also be approximated and expressed in terms of individual fluxes shown below.

$$\bar{J}_i = f^k J_i^k \tag{4}$$

where J_i^k are constrained to vary along the respective tie feature. The above expression is an approximation since fluxes, $\bar{J}_i$ and J_i^k, are vectors and hence it is good for the precipitates such as needles, rods or plates oriented in the direction of the diffusion in one-dimensional treatment. Moreover, the interface between the matrix and the precipitate phases do not affect the overall diffusion.

Eqs. (3) and (4) are reduced to Eqs. (5) and (6) for the internal oxidation of a binary alloy, AB denoted as α, that forms only one type of precipitate phase, BO_v denoted as β.

$$\bar{C}_i = (1 - f^\beta) C_i^{\alpha\backslash\beta} + f^\beta C_i^{\beta\backslash\alpha} \tag{5}$$

$$\bar{J}_i = (1 - f^\beta) J_i^{\alpha\backslash\beta} + f^\beta J_i^{\beta\backslash\alpha} \tag{6}$$

where $\bar{C}_i$, $C_i^{\alpha\backslash\beta}$, $C_i^{\beta\backslash\alpha}$ and f^β are the average concentration, the concentration along the $\alpha\backslash\beta$ solvus, the concentration along the $\beta\backslash\alpha$ solvus and the volume fraction of the β precipitates respectively. In general, the fluxes in the multiphase region, $J_i^{\beta\backslash\alpha}$ and $J_i^{\alpha\backslash\beta}$, are not defined in the same way as in the single-phase region [19].

3. Internal oxidation, classification and basic assumptions

The process of internal oxidation has been studied under two categories: in the absence of any external scale also called the exclusive internal oxidation and in the presence of external scale. The analytical treatment to internal oxidation beneath the stationary or growing external scale becomes similar to exclusive internal oxidation under the local-equilibrium assumption i.e. a local equilibrium exists at the scale/subscale interface. The analytical treatments for internal oxidation included in this paper are based upon the mass balance of individual species at the inter-region boundary, the boundary between a two-phase region and a single-phase region. These mass balance equations employ the fluxes where concentration gradients are obtained from the concentration profiles derived from the differential mass balance. But the differential mass balance, Eq. (2), is nontrivial to solve for a concentration profile after substitution from Eqs. (5) and (6). However, this diffusion equation reduces to a convenient form under following six approximations:

(1) The oxide i.e. the precipitate phase is of a stoichiometric composition.
(2) The solubility-product of the precipitate phase can be approximated to zero.
(3) Diffusion of oxygen in the precipitate phase is negligible compare to the matrix phase.
(4) Local equilibrium exists at the phase-interface boundary as well as at the inter-region boundary. This inter-region boundary is addressed as the reaction interface in this paper, which is only valid for a sharp reaction interface. Analytical treatments that assume zero solubility-product for the precipitate phase in the base metal generate a sharp reaction interface.
(5) Bulk flow due to volume increase associated with the precipitation occurs in the direction towards the exposed surface only.
(6) And the above all, the time and the width of the initial transient of internal oxidation are negligible compared to those of the parabolic growth rate. Alternatively, the resolution of the time and the length scale of measurements are much greater than the reaction time in the diffused reaction zone and the width of the diffused reaction zone respectively.

The first approximation reduces the average fluxes by approximating $J_i^{\beta\backslash\alpha}$ equal to zero for a stoichiometric phase since $C_i^{\beta\backslash\alpha}$ is constant and equal to C_i^β.

$$\bar{J}_i = (1 - f^\beta) J_i^{\alpha\backslash\beta} \tag{7}$$

The second approximation reduces the concentration of the solute phase, $C_B^{\alpha\backslash\beta}$, in the subscale zone to zero. The second and third approximations impose a constant average concentration of the component B, $\bar{C}_B = \bar{C}_B^{\alpha\|\alpha+\beta}$, throughout the subscale zone for an invariant interface composition (the fourth approximation). The first–fourth approximations give a constant volume fraction of the precipitate phase, $f^\beta = (\bar{C}_B - C_B^{\alpha\backslash\beta})/(C_B^\beta - C_B^{\alpha\backslash\beta}) = \bar{C}_B/C_B^\beta$, throughout the subscale zone.

Since there is no solute in the matrix phase of the two-phase region due to zero solubility-product, the flux and the diffusion equation for oxygen in the matrix phase of two-phase region are conveniently written as if they are moving in the single-phase region α. This also implies that the phase diagram will not impose any constraint on the concentration profile of oxygen in the matrix phase of the two-phase region.

$$J_O^{\alpha\backslash\beta} = -D_O^\alpha \nabla C_O^{\alpha\backslash\beta} \Rightarrow J_O^\alpha = -D_O^\alpha \nabla C_O^\alpha \tag{8}$$

$$\dot{C}_O^{\alpha\backslash\beta} = \nabla D_O^\alpha \nabla C_O^{\alpha\backslash\beta} - v \nabla C_i^{\alpha\backslash\beta} \Rightarrow \dot{C}_O^\alpha = \nabla D_O^\alpha \nabla C_O^\alpha - v \nabla C_i^\alpha \tag{9}$$

The flux and the diffusion equation for solute in the single-phase region is given as

$$J_B^\alpha = -D_B^\alpha \nabla C_B^\alpha \tag{10}$$

$$\dot{C}_B^\alpha = \nabla D_B^\alpha \nabla C_B^\alpha \tag{11}$$