

## Accepted Manuscript

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PII: S0010-938X(17)30245-7  
DOI: <http://dx.doi.org/doi:10.1016/j.corsci.2017.07.005>  
Reference: CS 7136

To appear in:

Received date: 10-2-2017  
Revised date: 3-7-2017  
Accepted date: 11-7-2017

Please cite this article as: L.Latu-Romain, Y.Parsa, S.Mathieu, M.Vilasi, A.Galerie, Y.Wouters, Towards the growth of stoichiometric chromia on pure chromium by the control of temperature and oxygen partial pressure, Corrosion Science <http://dx.doi.org/10.1016/j.corsci.2017.07.005>

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# Towards the growth of stoichiometric chromia on pure chromium by the control of temperature and oxygen partial pressure

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## Highlights

*“Towards the growth of stoichiometric chromia on pure chromium by the control of temperature and oxygen partial pressure”*

- The identification of the nature of point defects in chromia has been demonstrated thanks to TEM and photoelectrochemical characterization.
- The duplex morphology (equiaxial and columnar) does not depend on the nature of the point defect but on the growth direction (either inward or outward).
- A stoichiometric chromia has been grown by adjusting the oxygen partial pressure.

## Abstract

The possibility to tune the semiconducting properties of chromia scales thermally grown on pure chromium as a function of temperature and oxygen partial pressure  $p(\text{O}_2)$  has been demonstrated in the present paper. While at 800 °C and a  $p(\text{O}_2)$  of  $10^{-14}$  atm, a single n-chromia is observed, at 900 °C and a  $p(\text{O}_2)$  of  $10^{-12}$  atm, a duplex n- and p-chromia is obtained. Between these two situations, a stoichiometric chromia exhibiting insulating properties could be identified at 850 °C and a  $p(\text{O}_2)$  of  $10^{-13}$  atm. In every case, the morphology of the oxide scale is duplex and seems to depend only on the growth direction: equiaxial grains for an inward (anionic) growth and columnar grains for an outward (cationic) growth. The nature of point defects, linked to the n or p semiconducting character, governs the oxide growth but surprisingly, does not seem to have any influence on the oxide scale morphology. Finally, the control of the growth of an insulating stoichiometric chromia layer should permit to optimize its protective character.

Keywords: B. TEM; C. High temperature corrosion

## 1. Introduction

Chromia forms protective scales and ensures the chemical durability of high-temperature alloys, denominated as chromia formers -like stainless steels and Fe-Cr-Ni alloys- [1]. Even if studied for many decades [2] the growth mechanisms of chromia scales are still not clearly established. This oxide presents indeed a complex defect structure and can exhibit two types of semiconductivity (either n or p) depending on oxidation conditions [3]. It is a well-known fact that the thermal oxide growth is generally limited by point defects diffusion; and these phenomena have been very well described in 1977 by Wagner [4]. However, the identification of point defects that govern the oxide growth remains very difficult. Works using atomic simulations have been conducted in order to predict the stability of different disorders in chromia [5-7]. It has been for instance concluded that anion Frenkel

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