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ELECTRIC PROPERTIES OF Al₂O₃ SCALES DEVELOPED BY OXIDATION, IN RELATION WITH THE DOPANT NATURE AND DISTRIBUTION IN THE SCALE

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EXTENDED ABSTRACT (for more informations, see references /1/ to /3/).

The understanding of oxidation mechanisms of alloys requires the knowledge of the oxide transport properties. In most cases, up to now, these properties were determined from conductivity and diffusion measurements on "pure" and doped single crystalline or polycrystalline oxides whose behaviour can be different from thermally grown oxide behaviour.

Consequently, a laboratory apparatus /1/ was developed in order to determine the transport properties of thermally grown oxides. It consists:

- either in measuring the residual potential difference \( V_o \) between the outer and inner oxide interfaces, which gives the ionic transport number \( t_i \),
- or in plotting the electrical characteristic curves \( V = f(i) \) of the thermally grown oxide scale, which leads to the average conductivity \( \sigma \), then the ionic average conductivity \( \sigma_1 \) and the electronic average conductivity \( \sigma_e \),
- or in accelerating the oxide growth while oxidizing under an applied electric fields. Now, the effective charge \( z^e \) of the moving species in the oxide scale is obtained.

The formalism used is developed in ref. /1/. This procedure was applied to the determination of the transport properties of alumina scales developed on synthetic FeCr₂₃Al₅.

Such alumina scale growth depends on the incorporated impurities which are detected and analyzed by SCAN+EDAX, electron microprobe and XPS. Most of the results are detailed in ref. /2/ and /3/.

It appears that:

- The alumina scale is characterized by a residual potential \( V_o \) (without an applied electric field, i.e. for \( i = 0 \)). The \( V_o \) value is directly related to the oxygen chemical potential gradient \( \Delta \mu \) in the oxide and to the ionic transport number:

\[
V_o = \frac{t_i \Delta \mu}{4F}
\]

Fig. 1, relative to characteristic curves \( V = f(i) \) indicates that \( V_o(1=0) \) decreases with the outer \( P_{O_2} \). Moreover, for low outer equilibrium \( P_{O_2} \), the diode effect of the alumina scale, as reported by others works /4/ for high applied voltages, is no longer observed.

- Whatever the outer \( P_{O_2} \), the alumina scale behaves as a mixed conductor, with \( t_i \) varying from 0.45 to 0.24 when the outer \( P_{O_2} \) decreases from 1 to \(-10^{-24}\) atm. This result indicates that thermally grown alumina can differ from synthetic alumina /5,6/.

- All the transport parameters: \( V_o, \sigma, \sigma_1, \sigma_e, t_i \) depend on the oxidation temperature and time. Particularly, increasing the oxidation time induces impurity incorporation in the scale, as shown for example by Fig. 2 and 3, and a slight increase of the transport parameters (i.e. \( \sigma, \sigma_e, \sigma_1 \) and \( t_i \)).
Fig. 1: Characteristic $V = f(i)$ curves of alumina developed on a FeCrAl alloy at 1080°C.

Fig. 2 and 3: XPS analyses for chemical state of chromium (2) and carbon (3) in alumina scales developed on a not very pure FeCrAl alloy by oxidation for various times under 1 atm $O_2$.

- Applying an electric field modifies the alumina growth rate and indicates that moving species is an ionic one. Assuming that alumina growth preferentially occurs by oxygen diffusion, the effective charge of this moving species is found equal to $-2$. Thus, it appears that alumina growth mainly occurs by ionic oxygen diffusion: neutral or molecular oxygen diffusion is negligible. Nevertheless the nature of the defect responsible for this diffusion, $V_0^+$ or $O_1^-$ cannot be pointed out. More experiments are needed.
The migration activation energy of the main atomic point defect (V̅₀ or O̅́₁) is equal to 366KJ mol⁻¹ (3.8eV).

A breakdown is observed in the curves σ₁ and σ₀ versus temperature (for ~950°C), due to either the influence of oxide grain boundaries or precipitation phenomena.

REFERENCES


