Ionic Partial Conductivity in Cr₂O₃ Scales

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Knowledge of electrical conductivity and defect structure, as well as corresponding ionic transport process in growing Cr_2O_3 scales are of importance for both fundamental studies and application of chromia forming alloys. However, previous studies on Cr_2O_3 are mainly based on oxide behaviour sintered chromia pellets ¹⁻⁴. Considering the difference between thermally grown scales and the sintered oxide in structure, stochiometry and purity, it is more significant to investigate the ionic transport process directly in thermally grown Cr_2O_3 scales.

The objective of this work is to study ionic conductivity and temperature dependence in Cr_2O_3 scales. An asymmetry polarisation technique was used to separate the ionic conductivity from electronic conductivity. Cr_2O_3 scales were selectively grown on Ni-20%Cr alloy in H₂/H₂O vapour at 900°C for 24 hours.

A typical polarisation curve is shown in Fig1, from which the ionic transport number t_i can be extracted. Fig.2 gives the distribution map of ionic transport number with temperature and applied voltage in Cr₂O₃ scales. The map reveals that Cr₂O₃ is an insulator at room temperature and becomes a mixed ionic and electronic semiconductor when the temperature is increased. The ionic transport number t_i decreases with increasing temperature. Three regions in terms of the high ($t_i > 0.5$), medium (0.5> $t_i > 0.2$) and low regions were identified in order to evaluate the variation in ionic transport numbers with temperature and applied voltage. Activation energies of 0.6eV for electronic conductivity, and of 0.3eV for ionic conductivity were obtained below 700°C, as indicated in Fig.3. Above 700°C, the chromia scale became an intrinsic electronic conductor, with a corresponding activation energy of 1.7eV. This value is consistent with previous data obtained from sintered chromia pellets¹. However, this critical temperature is much lower than that for chromia oxide(1000-1200°C).

Based on the asymmetry polarisation curves, the concentration and mobility of ionic carriers and their temperature and potential dependence have been obtained. As can be seen in Table.1, the concentration of the ionic carriers is about $3x10^{18}$ cm⁻³ below 500 °C. Above 500 °C, it increases with increasing temperature. The mobility of ionic carriers is independent of temperature, and has a value of $1 \sim 3x10^{-12}$ V⁻¹sec⁻¹.

This appears to be the first time such data have been in the literature.

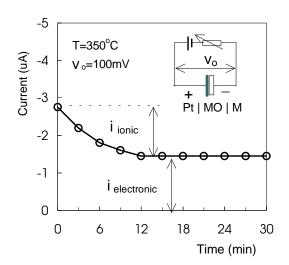


Fig.1 Asymmetry polarisation curve of Cr₂O₃ scale

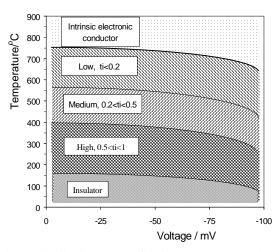


Fig.2 Distribution map of ionic transport numbers with temperature(T) and voltage(V_o) in Cr_2O_3 scale.

Table.1 The concentrations of ionic carrier under different temperatures and potentials (unit: 10^{18} cm⁻³)

different temperatures and potentials (unit:10 cm)						
$T(^{o}C)$	300	350	400	500	600	700
50mV	2.63	2.60	2.25	2.10	7.50	8.76
75mV		2.68	2.80	2.63	7.62	15.00
100mV	2.82	3.03	3.30	3.85	8.45	
150mV				4.60	8.72	
200mV				5.89	12.5	

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