Effect of oxygen partial pressure on the semiconducting properties of thermally grown chromia on pure chromium

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ABSTRACT

Oxidation of chromium at 800 °C for 30 min at oxygen activity from 5.10^{-14} atm to 5.10^{-13} atm have been conducted to grow an insulating chromia. Microstructural and semiconducting properties have been investigated using electron microscopy and photoelectrochemistry. The scales always exhibit a duplex microstructure with equiaxed and columnar grains, as well as a both n-type and insulating semiconduction type. Successive oxidation tests have demonstrated the higher protective nature of this chromia scale compared to the air grown one. Chromia semiconducting properties are finally described vs. oxygen activity in a large range of variation.

1. Introduction

Chromia forming alloys, such as stainless steels, are exposed to severe environments. Their chemical durability at high temperature is generally ensured by the formation of a thin, adherent and dense chromia layer on their surface [1]. Most of the time, the matter transport (provided by the point defect diffusion) controls the thermal oxide growth rate [2,3]. Despite being studied for a long time [4–15], Cr_2O_3 presents a complicated defect structure and its structural and electronic properties remain unclear. From Crawford and Vest [16] in 1964, and during the 90's from Kofstad studies [8], it has been suggested that in a wide range of oxygen partial pressure, and for temperature above 1000 °C, chromia exhibits an intrinsic electronic conductor behavior. Furthermore, it is well established that chromium oxide is a dual semiconductor, either n or p depending on oxidation temperature and oxygen partial pressure [5,17,18]. Su and Simkovich [19] suggest that Cr_2O_3 behaves as a p-type semiconductor at high $p(O_2)$ ($> 10^{-5}$ atm) whereas it's more likely to be an n-type semiconductor for low $p(O_2)$. Recent works in our research group [20,21] has shown that, under specific conditions, it is possible to grow an insulating stoichiometric chromia. While the internal layer of the oxide always exhibits an n-type conduction, the external layer shifts from n-type ($p(O_2) = 10^{-14}$ atm, 800 °C) to p-type ($p(O_2) = 10^{-12}$ atm, 900 °C), including insulating stoichiometric chromia when $p(O_2) = 10^{-13}$ atm (850 °C). Even if these experimental previous studies allowed us to control the conduction type with the oxidation parameters, we were not able to dissociate the effects of temperature and oxygen partial pressure. Nowadays some theoretical work allows to calculate defect formation energy and

diffusion coefficients in chromia [22]. It should be moreover added that recently the role of point defects in chromia failure has been theoretically evaluated [23], and shows that the presence of Cr vacancies may play a role on susceptibility to cracking.

In this new work, we would like to dissociate the effect of pressure and temperature, by performing isothermal oxidations for oxygen partial pressure from 5.10^{-14} atm to 5.10^{-13} atm, in order to grow an insulating chromia. In such layer, the chromia should be very close to stoichiometry with a minimum point defect density which should enhance the chemical durability of the underneath metal. SEM and STEM are used to determine chromia morphology and TEM-ASTAR for its crystallographic orientation. Cr_2O_3 semiconducting properties are assessed by photoelectrochemistry (PEC).

2. Experimental section

Pure chromium (99.99% purity, from Goodfellow SARL, France) was cut into square samples ($10 \times 10 \times 1$ mm) and prepared by SiC grinding up to grade 320 (in order to avoid further oxide spallation). Samples were positioned in a silica tube with a buffering powder mixture. After being primary vacuumed, the tube was sealed and placed in a muffle furnace for the oxidation step. This procedure, so-called Rhines pack method [24], permits to control the oxygen activity during the oxidation step. In order to tune oxygen activity, oxidation temperature can be varied with the same buffer or the buffer nature can be changed keeping the oxidation temperature constant. Because the choice of different buffering metal/oxide (or oxide 1/oxide 2) couple is limited, the second possibility may seem difficult to implement to scan
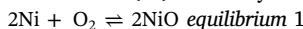
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a narrow oxygen partial pressure range, such as from 5.10^{-14} atm to 5.10^{-13} atm. However, it is possible to finely control $p(O_2)$ at a fixed temperature, by customizing the buffer (Ni/NiO in this case) in order to lower the metal (Ni) thermodynamic activity:

$$2Ni + O_2 \rightleftharpoons 2NiO \quad equilibrium\ 1$$

$$p(O_2) = \frac{a_{NiO}^2}{a_{Ni}^2 \exp\left(\frac{-\Delta_r G_T}{RT}\right)} \tag{1}$$

where $p(O_2)$ is the oxygen partial pressure, a_{NiO} is the bunsenite thermodynamic activity, a_{Ni} the nickel thermodynamic activity, $\Delta_r G_T$ the Gibbs free energy at the given temperature, R the ideal gas constant and T the temperature. Oxygen partial pressure was controlled in the intended study range (from 5.10^{-14} atm to 5.10^{-13} atm) by adjusting a_{Ni}. For this purpose, small amount of copper (Cu) was added to nickel (Ni) during the buffer production. Thermodynamic calculations, carried out with Thermo-Calc using SSOL4 database, showed that Cu does not oxidize under this study oxidation parameters, and can therefore be considered as inert. Thus, three different buffers have been synthesized by producing $Ni_{1-x}Cu_x$ alloys with x varying from 0.05 to 0.3. After being reduced to powder and mixed with NiO, buffers have been oxidized in sealed tube during 72 h at 1000 °C under secondary vacuum to bring them to thermodynamic equilibrium. Buffers structures were determined by X-ray diffraction (Fig. 1a). For each of the three buffers, two phases are found: nickel oxide (NiO) and nickel copper solid solution ($Ni_{1-x}Cu_x$). Splitting of the peaks at high angle is explained by $K\alpha_1$ and $K\alpha_2$. The absence of copper oxide confirms the inert nature of Cu. Using Vegard's law and assuming that Ni and Cu behave as a total solid solution, the composition (x) of $Ni_{1-x}Cu_x$ can be determined by a linear regression between the mesh parameters of the two pure phases: $a_{Ni} = 352.4$ pm and $a_{Cu} = 361.5$ pm. By measuring the peak displacement at a high angle (Fig. 1b), we were able to define the exact composition of the Ni/Cu solid solution for each of the three buffers: buffers 1 (resp. 2 and 3) composition is $Ni_{0.27}Cu_{0.73}$, (resp. $Ni_{0.18}Cu_{0.82}$ and $Ni_{0.07}Cu_{0.93}$). For each of these buffers, nickel thermodynamic activity (a_{Ni}) is determined as a function of Ni composition (SSOL4 database) by using Fig. 2. Thereby, nickel activity of $Ni_{0.27}Cu_{0.73}$ (resp. $Ni_{0.18}Cu_{0.82}$ and $Ni_{0.07}Cu_{0.93}$) is approximately equal to 0.54 (resp. 0.41 and 0.15). By using (Eq. (1)) and running thermodynamic calculations, it was possible to calculate the oxygen partial pressure, depending on the oxidation parameters and the buffer nature. These results, as well as those from our previous study [20] are presented in Table 1. By controlling buffers composition, it is possible to finely control $p(O_2)$, without varying the oxidation temperature. It is therefore possible to independently control these two major oxidation parameters (Fig. 3). Finally, Cr samples were oxidized at 800 °C during 30 min in a sealed
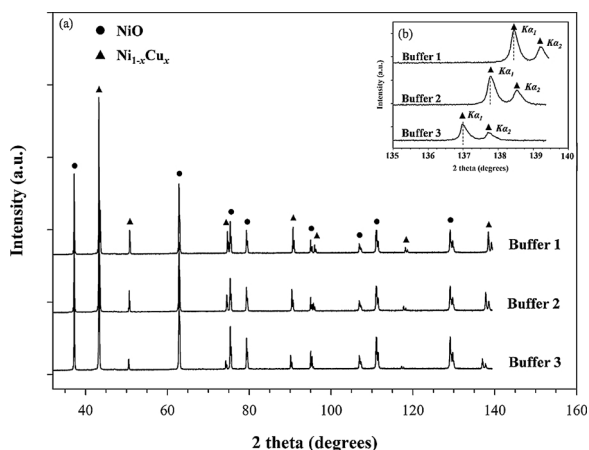

Fig. 2. Nickel activity (a_{Ni}) versus nickel mass fraction (x_{Ni}) for Ni/Cu solid solution at 800 °C from ThermoCalc SSOL4 database calculations.

silica tube containing one of the three $Ni_{1-x}Cu_x$/NiO buffering powder mixture. The grown oxide thickness is expected to be around 1 µm, which is the adequate value to carry out PEC analysis.

Photoelectrochemistry is an ex-situ nondestructive method which uses the light-matter interaction and has been extensively described elsewhere [20,25,26]. After oxidation and cooling, the sample is used as the working electrode (area exposed to the electrolyte is ~ 0.2 cm²) in a classical three-electrodes electrochemical cell. The oxide behaves like a semi-conductor; if it is illuminated by a monochromatic light whose energy $E = h\nu$ is higher than its bandgap E_g, electron-hole pairs are photo-generated. Thanks to an adequate polarization, it is possible to separate charge carriers. For an n-type (resp. p-type) semiconductor, electrons (resp. holes) are collected through the scale to the metal/oxide internal interface whereas holes (resp. electrons) are transferred to the electrolyte by

Table 1

Oxide semiconducting properties as a function of oxidation parameters. Equilibrium oxygen partial pressures $p(O_2)$ depending on oxidation parameters have been calculated from Thermo-Calc SSOL4 database.

	Buffer	$T/$(°C)	$p(O_2)/$atm	Oxide semiconduction	
				Internal	External
Previous study [19]	Ni/NiO	900	1.10^{-12}	n-type	p-type
		850	1.10^{-13}		Insulating
		800	1.10^{-14}		n-type
This study	$Ni_{0.07}Cu_{0.93}$/NiO	800	5.10^{-13}	n-type	Insulating
	$Ni_{0.18}Cu_{0.82}$/NiO		1.10^{-13}		
	$Ni_{0.27}Cu_{0.73}$/NiO		5.10^{-14}		

Fig. 1. XRD pattern of $Ni_{1-x}Cu_x$/NiO buffering powder for 3 different compositions (in inset: high magnification of the XRD pattern from $2\theta = 136$ to $140°$).
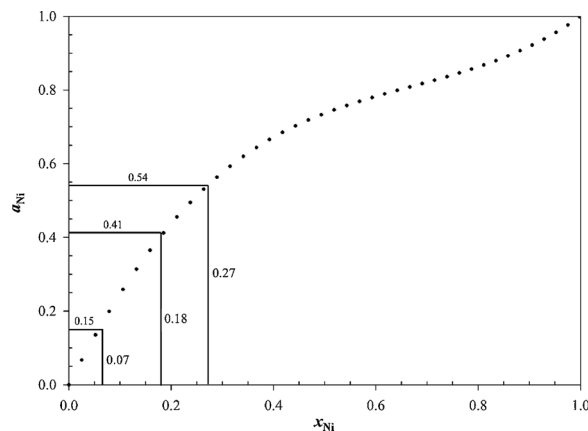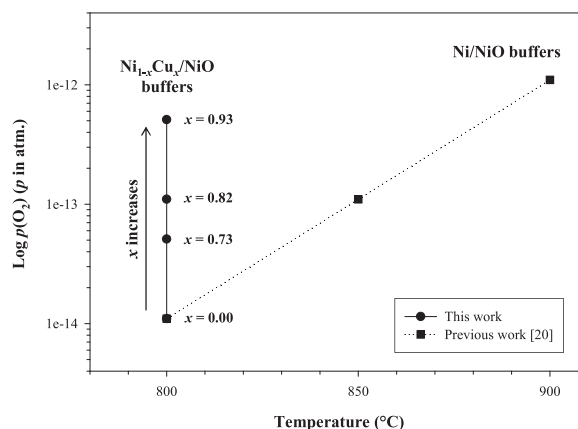

Fig. 3. Oxygen partial pressure versus oxidation temperature for Ni/NiO and $Ni_{1-x}Cu_x$/NiO buffers.